ISC'25
5th International Symposium on Characterization

PROCEEDINGS BOOK

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Symposium Theme

INTERNATIONAL YEAR OF Quantum Science and Technology

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PREFACE

It is with great pleasure that we welcome you to the **5th International Symposium on Characterization (ISC'25)**, held in the breathtaking region of **Cappadocia, Türkiye**. This premier international event continues the proud tradition of bringing together leading researchers, industry experts, and scholars from around the world to share their latest findings, foster collaboration, and explore emerging frontiers in the field of characterization.

In an era defined by rapid scientific and technological advancements, characterization science plays an indispensable role in understanding and optimizing the properties, performance, and applications of materials across disciplines. **ISC'25** continues to build upon the success of its predecessors (ISC'21–ISC'24), providing a vibrant platform for discussing state-of-the-art experimental, analytical, and theoretical approaches in materials science, nanotechnology, functional coatings, energy systems, biomaterials, and quantum-enabled technologies.

This year's symposium coincides with the **Year of Quantum Science and Technology**, reflecting our commitment to highlighting groundbreaking developments that bridge fundamental research with practical innovation. The sessions, keynote addresses, and poster presentations featured in this program exemplify the symposium's interdisciplinary spirit and dedication to advancing global scientific dialogue.

We extend our deepest appreciation to our **distinguished keynote and invited speakers**, whose insights enrich the symposium's scientific depth; to all **authors and presenters** for their invaluable contributions; and to the **reviewers** whose expertise ensured the quality and integrity of the program. Our heartfelt thanks also go to the **organizing committee members, supporting institutions, and sponsors** whose dedication and generosity have made ISC'25 possible.

Cappadocia, with its extraordinary landscape, cultural heritage, and inspiring atmosphere, provides a unique backdrop for this gathering. We hope that this symposium will not only facilitate the exchange of knowledge but also foster new collaborations, friendships, and scientific visions that extend well beyond these days together.

Thank you for being part of **ISC'25**, and we wish you a memorable and intellectually stimulating experience in Cappadocia.

Prof. Dr. Atilla Evcin

Chair, ISC'25 Organizing Committee

Atilla Evcin, Ibrahim Güneş,
Ismail Yıldız, Yasemin Tabak
Editors

Proceedings of the 5th International Symposium on Characterization (ISC'25, Cappadocia, Türkiye)

Evcin R&D

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Herein, the book presents the main contributions of researchers who participated in the 5th International Symposium on Characterization (ISC'25), held during August 27-29, 2025, in Cappadocia, Türkiye.

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Evcin R&D Türkiye 2025

Aims and Scope

The International Characterization Symposium aims to serve as a global platform for researchers, academicians, industry professionals, and policymakers to exchange knowledge, foster collaboration, and discuss advancements in material and system characterization techniques.

The symposium focuses on promoting interdisciplinary research by bridging gaps between various scientific disciplines, including physics, chemistry, biology, and engineering. Its key objectives include advancing the development of innovative characterization methods, enhancing the understanding of material properties at the nanoscale and macroscale, and encouraging the application of these methods in addressing global challenges such as energy sustainability, environmental conservation, and technological innovation. Additionally, the symposium aspires to create opportunities for young scientists and researchers to network with leading experts, fostering an environment conducive to the development of future pioneers in the field. Through keynote speeches, technical sessions, and workshops, the event aims to set the stage for groundbreaking discussions that drive the field forward and contribute to the collective progress of science and technology.

Editorial Policies

International Symposium on Characterization (ISC) follows the steps below in the proceedings book publishing process. In the first stage, the papers sent to the conferences organized by ISC are subject to editorial oversight. In the second stage, the papers that pass the first step are **reviewed** by at least two international field experts in the conference committee in terms of suitability for the content and subject area. In the third stage, it is reviewed by at least one member of the organizing committee for the suitability of references. In the fourth step, the language editor reviews the language for clarity.

When authors submit a manuscript to be considered for publication in the proceedings book of ISC, its content must not significantly overlap with any other papers from you or your co-authors' groups that are under consideration or in press at other journals, with the exception of symposium abstracts.

Themes

Theme 1: Materials Science and Engineering

Theme 2: Nanotechnology

Theme 3: Advanced Materials

Theme 4: Energy Materials and Applications

Theme 5: Polymers

Theme 6: Electrical, Optical, Magnetic Materials

Theme 7: Metals and Alloys

Theme 8: Biotechnology and Biomaterials

Theme 9: Quantum Materials

Theme 10: Composite Materials

Theme 11: Ceramics, Glasses, Building Materials, Cement and Concrete

Theme 12: Additive Manufacturing

Theme 13: Materials Science and Engineering for AI

Theme 14: Archaeometry

Theme 15: Others

ACKNOWLEDGMENT

We would like to express our sincere gratitude to **Prof. Dr. Mehmet Karakaş**, Rector of Afyon Kocatepe University, and **Prof. Dr. Semih Aktekin**, Rector of Nevşehir Hacı Bektaş Veli University, for their valuable contributions and kind support to the symposium; their academic leadership, institutional support, and commitment to scientific collaboration have significantly contributed to the successful organization and high academic quality of the event, and we are honored by their engagement in fostering inter-university cooperation and promoting a strong research culture.

We would like to express our deepest gratitude to all individuals, institutions, and partners whose invaluable support has made the 5th International Symposium on Characterization (ISC'25) in Cappadocia a remarkable success. We extend our sincere appreciation to our esteemed Co-Chairs—Prof. Dr. Fayaz Hussain, Prof. Dr. İbrahim Güneş, Prof. Dr. Zahide Bayer Öztürk, and Assoc. Prof. Yasemin Tabak—for their exceptional leadership, scientific guidance, and unwavering dedication throughout the preparation and execution of this symposium. Their expertise and collaborative spirit have been instrumental in shaping the scientific program and ensuring the high quality of ISC'25.

We extend our deepest appreciation to our distinguished keynote speakers for their invaluable contributions to the 5th International Symposium on Characterization (ISC'25). Prof Dawei Wang, Prof. Ziad Melhem, Prof. Kaixin Song, Prof. Dr. Sinan Akgöl, Prof. Dr. Ali Koşar, Prof. Dr. Alpagut Kara, Assoc. Prof. Şeyda Polat, Dr. A. Gökçe Özbay and Ing. (MSc) Monika Vitvarova were keynote speakers. Their visionary perspectives, thought-provoking presentations, and cutting-edge insights have significantly enriched the scientific depth and intellectual rigor of this symposium. By sharing their expertise and addressing frontier topics that bridge fundamental research with advanced applications, they have inspired our participants, fostered new discussions, and opened pathways for future collaboration. The impact of their contributions extends far beyond the sessions themselves, strengthening the global characterization community and advancing the scientific dialogue that ISC aims to promote. On behalf of the ISC'25 Organizing Committee, we express our sincere gratitude for their time, dedication, and exemplary leadership in shaping this year's symposium.

We also gratefully acknowledge the contributions of our sponsors, (ERA Metallurgy, Atomika Teknik, Q&Co and Tekafos Teknolojik Sistemler) whose generous support has strengthened this event and enhanced its international visibility; their commitment to advancing scientific research and fostering global collaboration is deeply appreciated. Our heartfelt thanks further extend to the local supporting institutions and companies of Cappadocia and the surrounding region for enriching the symposium with their strong spirit of cooperation and regional engagement.

We are profoundly grateful to the members of the organizing team—Prof. Dr. Fayaz Hussain, Prof. Dr. Ibrahim Güneş, Prof. Dr. Zahide Bayer Öztürk, Assoc. Prof. Dr. Yasemin

Tabak, Assoc. Prof. A. Vahap Korkmaz, Prof. Dr. Ş. Hakan Atapek, Assoc. Prof. Begüm Ünveroğlu Abdioğlu, Assoc. Prof. Ekrem Altuncu, Assoc. Prof. Zeynep Taşlıçukur Öztürk, Dr. İsmail Yıldız, Dr. Büşra Tuğba Çamiç, Dr. Mehmet Albaşkara, Dr. Ahmet Burçin Batıbay, Dr. Recep Kurtuluş, Dr. Cansu Kurtuluş, MSc. Oğuzhan Evcin, Emre Evcin, Melike Evcin, for their tireless efforts, professionalism, and exceptional dedication, which have been essential to the planning, coordination, and flawless execution of ISC'25.

We also gratefully acknowledge the support of the the **TÜBİTAK 2223-D Program for the Organization of Events within the Framework of Bilateral Cooperation Agreements**, whose contribution has greatly facilitated the realization of this international scientific event.

On behalf of the ISC'25 Organizing Committee, we thank all participants, contributors, and supporters for their enthusiasm and commitment, which have made this symposium a meaningful and memorable gathering for the global scientific community.

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27 - 29 August 2025
Cappadocia, Türkiye
KEYNOTE SPEAKER
PROF. ZIAD MELHEM
Professor of Physics at Lancaster University & Founder/CEO of Oxford Quantum Solutions Ltd
Prof. Ziad Melhem is the Founder and CEO of Oxford Quantum Solutions Ltd, providing expertise in superconducting, cryogenics, and quantum technologies across various sectors. He is also a Professor at Lancaster University, focusing on advanced technology transfer in low-temperature physics and quantum systems, and serves as a Non-Executive Director at Intelliconnect Europe Ltd.
TALK TITLE:
Cryogenics Driving Innovation in Quantum Materials and Technology

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KEYNOTE SPEAKER
PROF. DAWEI WANG
Professor at Harbin Institute of Technology, China
Dr. Dawei Wang, Professor at Harbin Institute of Technology, China, holds a PhD from Beijing Institute of Technology and was a Visiting Scholar at Penn State, USA. Formerly a Research Associate at the University of Sheffield, UK, he serves as Associate Editor and Editorial Board Member for leading materials science journals.
TALK TITLE:
Bismuth ferrite based lead-free ceramics for energy conversion and storage.

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KEYNOTE SPEAKER
PROF. KAIXIN SONG
Professor at the School of Electronic Information, Hangzhou Dianzi University, China
Kaixin Song, professor at Hangzhou Dianzi University and West Lake Scholar, specializes in dielectric materials, RF components, LED optoelectronics, and energy storage. He has led major R&D projects, published 200+ SCI papers, and holds 50+ patents.
TALK TITLE:
Low K ceramic filter for 5G/6G communication.

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KEYNOTE SPEAKER
PROF. ALI KOSAR
Professor at Sabanci University FENS
Prof. Dr. Ali Kosar is a Full Professor at Sabanci University FENS, leading the Microthermal and Microfluidic Systems Lab since 2015 and co-directing EFSUN since 2016. Previously, he was an Associate Professor (2010–2015) and Assistant Professor (2007–2010) at Sabanci University and an Adjunct Faculty Member at Rensselaer Polytechnic Institute, USA (2007).
TALK TITLE:
Phase Change Phenomena on Functional Surfaces and their Applications

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Cappadocia, Türkiye
INVITED SPEAKER
PROF. DR. ALPAGUT KARA
Director of Sabancı University Nanotechnology and Application Center (SUNUM)
Prof. Dr. Alpagut Kara is a Faculty member in the faculty of Engineering and Natural Sciences, at Sabanci University since February 2025., also serves as Director of SUNUM. He holds a PhD from the University of Bath (1999) and an MSc from the University of Leeds (1991). Previously, he was a lecturer at Eskişehir Technical University, focusing on industrial and advanced ceramics, with around 100 publications and multiple patents.
TALK TITLE:
Effect of microstructural features in SiAlON ceramics on machinability of nickel-based superalloys

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KEYNOTE SPEAKER
PROF. SINAN AKGÖL
Professor at Ege University, Türkiye
Dr. Sinan Akgöl, Professor at Ege University Biochemistry Department and part-time researcher at Sabancı University Nanotechnology Center, specializes in biochemistry and nanotechnology. With 140+ SCI publications, 8 patents, 3900+ citations, and an h-index of 39, he has supervised 35 graduate students and delivered 55 international talks.
TALK TITLE:
Green carbon dots: synthesis, characterization, properties and biomedical applications

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INVITED SPEAKER
ASSOC PROF SEYDA POLAT
Associate Professor, High-Temperature Materials Lab, Metallurgical and Materials Engineering, Kocaeli University
Assoc. Prof. Dr. Şeyda POLAT is presently a guest researcher of the High Temperature Materials Laboratory at Kocaeli University. She worked on phase transformations in metal alloys using x-ray and neutron scattering techniques during her Ph.D. studies at University of Illinois at Urbana-Champaign. She continued her research studies in the Technology Department of BRISA A.Ş. where she focused on tire materials. She joined the Metallurgical and Materials Department of Kocaeli University in 2002 where she worked as a faculty member till her recent retirement. Her research interests involve the development and characterization of functionally graded materials, rubber-based materials, biomaterials and high temperature materials. She is a member of Turkish Society for Electron Microscopy (TEMD) and European Microscopy Society (EMS)
TALK TITLE:
Characterization of Rubber Based Materials

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INVITED SPEAKER
ING. (MSC.) MONIKA VITVÁROVÁ
LCA and Energy Specialist at Bowmen Consulting
Ing. (MSc.) Monika Vitvarová is a specialist and scientist in Techno-Economic Analysis (TEA), Life Cycle Assessment (LCA), Techno-Economic Analysis (TEA), and systems design and development, working with Bowmen Consulting Company and other companies as an independent expert. Her expertise centres on high-energy-intensive industries such as power generation, metallurgy, and minerals. She focuses on developing and implementing novel approaches and decarbonisation strategies, including Carbon Capture, Utilisation and Storage (CCUS), renewable technologies, and optimisation of industrial processes through systems like waste heat recovery.
TALK TITLE:
Life Cycle Thinking Approach in Minerals and Metals Production: Current Challenges and Future Directions for Sustainable Transitions

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KEYNOTE SPEAKER
DR. AISHA GOKCE OZBAY
Head of Quantum Metrology Laboratory, Turkey's National Metrology Institute (UME)
Dr. Aisha Gokce Ozbay, Head of the Quantum Metrology Laboratory at Turkey's National Metrology Institute (UME), holds a PhD in Physics from the University of Delaware. Her research spans quantum tunneling-based magnetic data storage, spintronics, and phase-change memory. Currently, she focuses on diamond-based sensors, superconductors, and microwave devices for metrology and sensing.
TALK TITLE:
Quantum Nanoscience: New definitions for the SI with novel materials and devices
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3D-Printing of Lanthanum-Doped Akermanite/Poly (Lactic Acid)-Based Biocomposites as Potential Wound Dressing

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ABSTRACT

In this study, biocomposites for potential wound dressings were developed using the three-dimensional bioprinting (3DP) method by incorporating different concentrations of lanthanum-doped akermanite (La-AK) powders, synthesized by the sol-gel method, into a poly(lactic acid) (PLA) matrix. The produced samples were then subjected to a comprehensive characterization process, encompassing morphological, structural, and in vitro biological properties. The homogeneous distribution of La-AK particles within the PLA matrix was confirmed by scanning electron microscopy (SEM), and structural interactions specific to the bioceramic phase were revealed by Fourier transform infrared spectroscopy (FTIR). Furthermore, an inquiry was initiated to investigate the swelling behaviour of the obtained biocomposites. It was determined that the incorporation of La-AK led to a reduction in the rate of swelling within the PLA matrix. This finding suggests that the structure became more resistant to water absorption and provided a controlled degradation process. Biodegradability tests revealed that the biocomposites possess suitable profiles for biomedical applications. It was further observed that the La-AK additive exerted a favourable influence on the degradation behaviour of PLA, concurrently ensuring a more balanced dissolution in the biological environment. The findings indicate that La-AK/PLA biocomposites are candidate materials with high potential for biomedical applications, particularly in wound healing.

Keywords: Poly(lactic acid), Akermanite, Lanthanum, Wound Dressing, 3D-printing.

Lantan Katkılı Akermanit/Poli (Laktik Asit) Bazlı Biyokompozitlerin Potansiyel Yara Örtüsü Olarak 3B Baskısı

ÖZET

Bu çalışmada, potansiyel yara örtüsü uygulamalarına yönelik biyokompozitler, üç boyutlu biyobaskı (3DP) yöntemiyle üretilmiştir. Bunun için, sol-jel yöntemiyle sentezlenen farklı konsantrasyonlardaki lantan katkılı akermanit (La-AK) tozları poli(laktik asit) (PLA) matrisi içerisine dahil edilmiştir. Üretilen numuneler morfolojik, yapısal ve in vitro biyolojik özellikler açısından kapsamlı bir karakterizasyon sürecine tabi tutulmuştur. La-AK partiküllerinin PLA matrisi içerisinde homojen dağılımı taramalı elektron mikroskobu (SEM) ile doğrulanmış, biyoseramik faza özgü yapısal etkileşimler ise Fourier dönüşümlü kızılötesi spektroskopi (FTIR) ile ortaya konmuştur. Ayrıca elde edilen biyokompozitlerin şişme davranışı incelenmiş ve La-AK katkısının PLA matrisindeki şişme oranını azalttığı belirlenmiştir. Bu durum, yapının su absorbsiyonuna karşı daha dirençli hale geldiğini ve kontrollü bir bozunma süreci

sağladığını göstermektedir. Biyolojik bozunabilirlik testleri, biyokompozitlerin biyomedikl uygulamalara uygun profillere sahip olduğunu ortaya koymuştur. Ayrıca, La-AK katkısının PLA'nın bozunma davranışını olumlu yönde etkileyerek biyolojik ortamda daha dengeli bir çözünme sağladığı gözlenmiştir. Elde edilen bulgular, La-AK/PLA biyokompozitlerinin özellikle yara iyileştirme alanında yüksek potansiyele sahip aday malzemeler olduğunu göstermektedir.

Anahtar Kelimeler : Poli(laktik asit), Akermanit, Lantan, Yara örtüsü, 3B-baskılama.

1. Introduction

Chronic and acute wounds present significant clinical challenges, frequently resulting in prolonged hospitalisation, increased healthcare costs, and high morbidity. The ideal wound dressing should regulate exudate, maintain a moist healing environment, allow gas exchange, protect against microbial invasion, and support cellular events essential for tissue regeneration [1]. Recent advances in polymer processing, particularly pneumatic extrusion-based three-dimensional (3D) printing, have enabled the design of wound dressings with controlled porosity, tailored mechanical performance, and multifunctional properties adapted to the requirements of complex wound sites. This technique facilitates the precise deposition of solution-based biomaterials through the utilisation of controlled air pressure, thereby enabling the regulation of filament diameter, pore interconnectivity, and scaffold architecture to optimise fluid management and cellular infiltration [2].

In the field of 3D printing, poly(lactic acid) (PLA) is a noteworthy polymer due to its advantageous properties, including biodegradability, biocompatibility, and mechanical strength [3, 4]. However, the inherent hydrophobicity of PLA, coupled with its relatively sluggish degradation under physiological conditions, may impede its efficacy in moist wound environments and prolong tissue integration [4]. In order to address these limitations, bioactive ceramic fillers have been incorporated into PLA matrices with a view to enhancing bioactivity, adjusting degradation kinetics and introducing additional functionalities such as ion release. Akermanite, a silicate-based bioceramic, has demonstrated potential in promoting tissue regeneration through the controlled release of Ca^{2+}, Mg^{2+}, and SiO_{4-} ions, which stimulate angiogenesis, cell proliferation, and migration [5-7]. Its incorporation into polymeric scaffolds has been reported to improve re-epithelialization and cellular responses in wound healing models [6], [7].

The addition of lanthanum (La) to bioceramics has been demonstrated to yield further functional outcomes (Smith . As demonstrated in the relevant literature, the presence of LA has been shown to exert a positive influence on surface reactivity, thereby promoting the formation of a hydroxyapatite-like layer. Furthermore, it has been demonstrated that LA contributes to the promotion of both osteogenic and antibacterial effects [8–10]. Furthermore, La^{3+} ions have been demonstrated to influence cellular behaviour, including the differentiation of osteoblasts and mesenchymal stem cells, thus suggesting their potential role in tissue repair [10, 11].

The present study was predicated on this rationale, with the objective being to develop porous wound dressings by incorporating sol–gel–derived La-doped akermanite (La-AK) powders into PLA at different weight ratios (0, 1, 3, and 5% w/w) using pneumatic extrusion-based 3D printing. The fabricated scaffolds were systematically characterised in terms of morphology (SEM), chemical interactions (FTIR), swelling behaviour, and degradation properties. The findings demonstrate that La-AK incorporation not only enhances the degradation profile of PLA, but also produces bioactive composites with considerable potential for wound healing applications.

2. Materials and Methods

2.1 Materials

Tetraethyl orthosilicate (TEOS; $(C_2H_5O)_4Si$), magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$), and calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) were obtained from Alfa Aesar™ (USA). Nitric acid (HNO_3) was procured from Merck™ (Germany). Lanthanum III nitrate hexahydrate ($La(NO_3)_3{\cdot}6H_2O$, purity approximately 99%) was obtained from abcr GmbH (Germany). The production of wound dressings involved the utilisation of two primary materials: the PLA granules (Luminy™ LX175), a biopolymer, and chloroform (≥99.8%, Fisher™ Chemical, Germany), a solvent. Phosphate-buffered saline (PBS, pH 7.4), utilised in the swelling tests, was procured from Gündüz Kimya (Turkey).

2.2 Synthesis of the powders

As outlined in our preceding study [12], the synthesis of AK powders was accomplished through the utilisation of the sol-gel method. In summary, TEOS, distilled water, and HNO_3 were mixed in a molar ratio of $TEOS:H_2O:HNO_3$ = 1:8:0.16 and stirred for 30 minutes. Subsequently, $Mg(NO_3)_2{\cdot}6H_2O$ and $Ca(NO_3)_2{\cdot}4H_2O$ were added to the mixture at a molar ratio of $TEOS:Mg(NO_3)_2:Ca(NO_3)_2$ = 2:1:2. The resulting solution was then subjected to a drying process at a temperature of 60 °C for a duration of 24 hours. The experiment was conducted within an oven specifically designed for this purpose (Ecocell™). The synthesis of La-doped AK powders, with doping concentrations of 0.01 M, 0.03 M and 0.05 M, followed a similar procedure [13]. The fundamental distinction pertained to the incorporation of $La(NO_3)_3{\cdot}6H_2O$ as the La source into the precursor solution. The solutions were then subjected to a drying process at a temperature of 60 °C for a duration of 24 hours, followed by a subsequent drying process at 120 °C for a period of 48 hours. The dried gels were subsequently exposed to a heat treatment at 1300 °C in air using a chamber-type laboratory furnace (Protherm™ PLF 160/7) with a heating rate of 5 °C/min. It is evident from the La content present in the powders that they were designated as AK-1La, AK-3La, and AK-5La, respectively.

2.3 Preparation of the 3D-printing solutions

Initially, PLA solutions were prepared independently. PLA was dissolved in chloroform at a concentration of 30% (w/v). The solution was then subjected to magnetic stirring at 50 °C for a period of 24 hours. In order to produce the composite PLA solutions with the powders, both neat and La-doped AK powders (AK-1La, AK-3La, and AK-5La) were firstly dispersed in chloroform, and then mixed until a uniform suspension was achieved. Subsequently, PLA granules were incorporated into each suspension at a weight ratio of 95:5 (PLA:AK-La) and stirred at 50 °C for a further 24 hours. The technique facilitated the production of PLA/AK-La composite suspensions that were both homogenous and stable.

2.4 Fabrication of the 3D-printed wound dressings

The PLA/AK-La-based wound dressings have been produced using a high-precision pneumatic extrusion 3D printer (Axo A1™, Turkey). Prior to the initiation of the printing process, the geometry and dimensions of the samples were created using computer-aided design (CAD) software (PrusaSlicer™), and the models were saved in stereolithography (STL) format. Subsequently, the STL files were transferred to the printer. The composite solutions, namely the PLA, PLA/AK, PLA/AK-1La, PLA/AK-3La and PLA/AK-5La, were meticulously injected into the sterile 3 mL syringe cartridges (Loctite™ Henkel, Rocky Hill, CT, USA). The printing parameters that were selected are outlined below: The pneumatic pressure has been set to 45 psi, the printing speed to 8 mm/s, and the nozzle diameter to 210 µm (27G). All printing operations were conducted at ambient temperature. The method was replicated for each formulation utilised in the study. Figure 1 provides a schematic overview of the experimental method, and Table 1 summarises the compositions and associated experimental codes of the produced wound dressings.

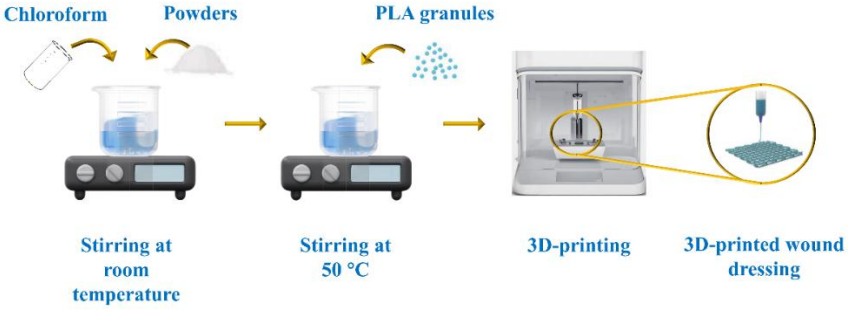

Figure 1. The schematic illustration of the preparation of the wound dressings.

Table 1. Sample compositions and their experimental codes used in this study.

Sample Code	Sample Compositions (w/w %)
PLA	Poly(lactic acid)
PLA/AK	Poly(lactic acid)/Akermanite (95:5)
PLA/AK-1La	Poly(lactic acid)/Akermanite- Lanthanum (1%) (95:5)
PLA/AK-3La	Poly(lactic acid)/Akermanite- Lanthanum-(3%) (95:5)
PLA/AK-5La	Poly(lactic acid)/Akermanite- Lanthanum (5%) (95:5)

2.5 Characterization

The macroporous 3D architecture of the wound dressing samples was visualized using a Zeiss™ Discovery V12 stereomicroscope (SM) equipped with a Zeiss™ Axiocam ERc5s high-resolution digital imaging system. The surface morphology of the samples, which had previously undergone sputter-coating with a thin layer of Au–Pd, was examined using a Carl Zeiss™ Gemini 300 scanning electron microscope (SEM) operated at an accelerating voltage of 5 kV. The chemical structural analysis of the samples was performed using Fourier-transform infrared spectroscopy (FTIR; Thermo™ Nicolet iS50) equipped with an attenuated total reflectance (ATR) accessory. The FTIR spectra of the scaffolds were recorded over a wavenumber range of 650–4000 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 16 scans.

The *in vitro* swelling behaviour of the samples was evaluated based on a modified version of a protocol previously employed by our research group. Initially, the samples were cut into rectangular specimens measuring 10 mm × 5 mm, and their initial dry weights were recorded. Subsequently, the samples were immersed in phosphate-buffered saline (PBS) at a pH of 7.4 at temperatures of 37 °C for 24, 48, and 72 hours. At each designated time point, the samples were removed from the PBS, and excess surface liquid was gently blotted with filter paper. The weights were measured immediately after being removed from the oven. The swelling ratio of the samples was calculated using the following equation (1):

$$W_S = (W_T - W_0)/\, W_0 \quad (1)$$

where W_T is the weight of the swollen sample at time t, and W_0 is the initial dry weight of the sample.

The in vitro hydrolytic degradation behaviour of the PLA/AK-La-based samples was investigated by means of immersion of the samples (10 mm × 5 mm) into a Falcon tube containing 10 mL of PBS solution (pH 7.4, 37 °C). Initially, the samples were subjected to a drying process at a temperature of 37 °C until a constant mass (Wi) was attained, prior to the commencement of the test. At predetermined intervals, the samples were extracted from the degradation medium, thoroughly rinsed with distilled water, and the surplus water present at the surface was meticulously removed using filter paper. Subsequently, the samples were subjected to desiccation at 37 °C until constant mass (Wf) was attained, at which point the weight loss was determined. The medium was replaced on a weekly basis with a fresh medium.

Subsequent to the conclusion of each period of degradation, the samples were characterized with regard to weight loss. The weight loss of the samples was determined during the degradation process according to the following equation (2):

$$\text{Weight loss } (\%) = \left(\frac{Wi-Wf}{Wi}\right) x\ 100 \quad (2)$$

where Wf and Wi correspond to the dry weight of the sample, after and before the degradation process respectively.

3. Result and Discussion

Optical micrographs of 3D-printed wound dressing samples (Figure 2) reveal that all samples include precisely specified support geometries (~µm width) and uniformly square pores (~µm edge length). All formulations—composed of PLA solution (30% w/v) and AK with 1, 3, and 5 % La display numerous micron-scale bubbles along their supports, irrespective of La concentration. Porosity challenges are attributed to air entrapment and rapid solvent evaporation during the extrusion of high-viscosity bioinks; this issue may be addressed by vacuum degassing and regulated drying processes [14]. Notwithstanding the increased filler concentration and various rheological characteristics, all composite formulations present continuous, defect-free filaments, demonstrating the resilience of pneumatic extrusion printing in fabricating bioactive ceramic-reinforced samples [2].

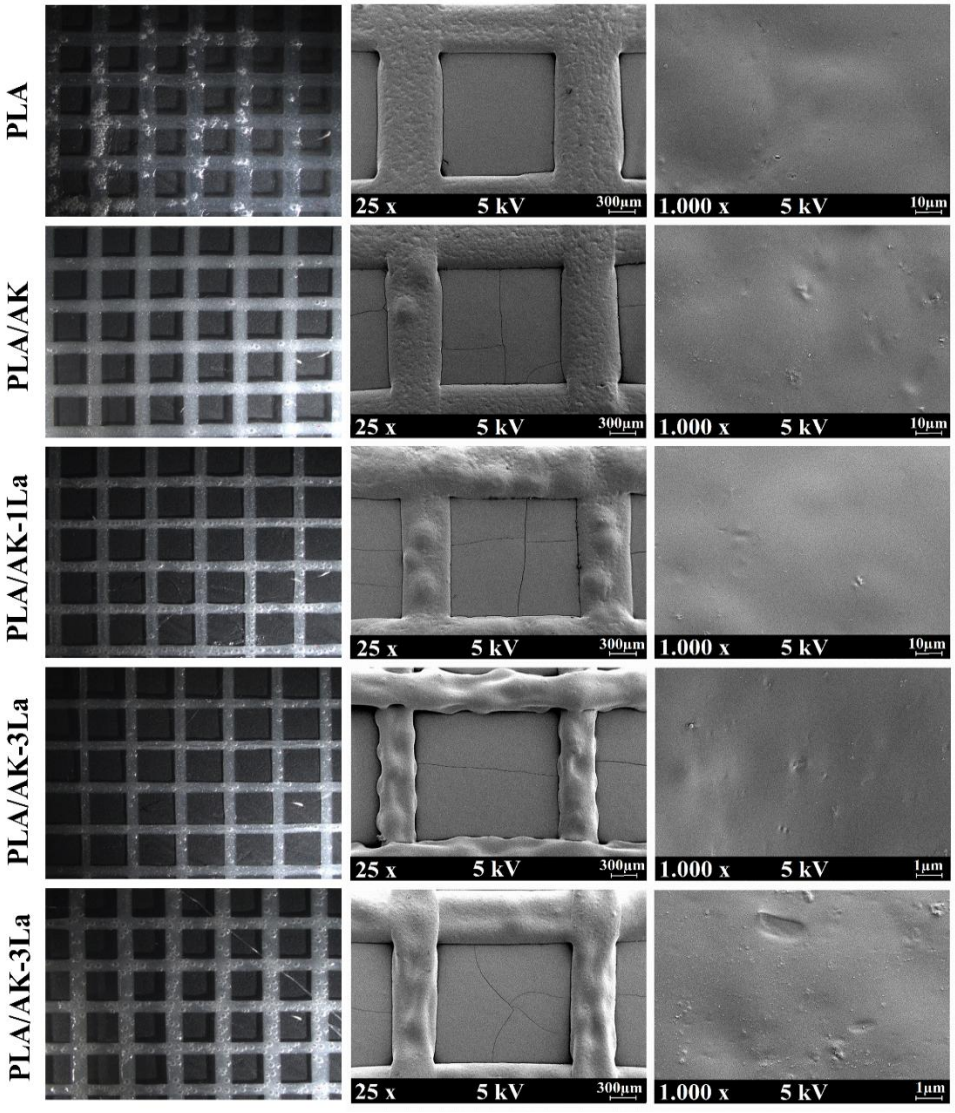

Figure 2. SM and SEM images of the wound dressings.

SEM analysis has been used to demonstrate that 3D-printed open, grid-like dressings, characterized by continuous supports and square pores, ensure high geometric accuracy for the designed exudate management architecture (Figure 2) [2]. A pristine sample of PLA is distinguished by its relatively smooth surfaces, which are interspersed with the occasional solvent-drying crack. These cracks are aligned with polymer shrinkage occurring during solvent evaporation [15, 16]. The incorporation of AK powders results in rougher support surfaces and distinct micron-scale protrusions associated with exposed ceramic particles. This particle exposure and enhanced roughness are frequently observed in polymer-bioactive filler composites, contributing to increased surface area and wettability [17]. The administration of doping substances at concentrations ranging from 1-5% serves to accentuate these effects: SEM images reveal an increased density of surface granules and a greater occurrence of shallow depressions. This phenomenon can be attributed to additive-dependent alterations in powder morphology, porosity, and dissolution behaviour, which enhance particle surface exposure following solvent consolidation [18], [19], [20]. The presence of microcracks and filament voids, as previously documented, is indicative of shrinkage resulting from solvent evaporation, interfacial stress concentration around hard inclusions, and sporadic air entrapment during pneumatic extrusion. The processing defects are exacerbated by ink viscosity and inadequate degassing [15], [21], [22]. The SEM results demonstrated that the pneumatic extrusion approach yielded dressings with open pores that exhibited geometrical accuracy. The addition of AK powders has been shown to result in the creation of a rougher support surface, thereby exposing bioactive particles. The incorporation of La leads to a marginally more pronounced effect. The presence of microcracks and surface pits can be attributed to the effects of solvents and drying, as well as the mechanics of the particle-polymer system.

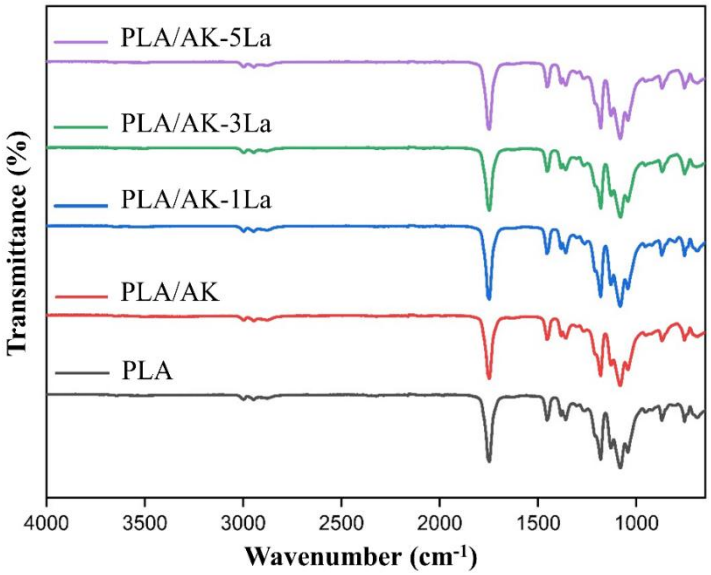

Figure 3. FTIR spectra of the wound dressings.

FTIR spectra of the neat PLA and the PLA/AK–La composites (Figure 3) indicate that all formulations preserve the special absorption bands of PLA. To elaborate further, the spectra indicate that the carbonyl (C=O) stretching vibration occurs at approximately 1750 cm^{-1}, the asymmetric and symmetric C–O–C stretching modes occur at 1180^{-1} and 1080 cm^{-1}, respectively, and the methylene ($–CH_2–$) stretching vibration occurs near 2995 cm-1 [3, [23]. In the 1000–1100 cm^{-1} range, additional bands corresponding to the antisymmetric Si–O–Si stretching modes of the sol–gel-derived akermanite phase are observed, thereby confirming the effective incorporation of the silicate network within the PLA matrix [24]. The absence of any supplementary absorption peaks, indicative of novel functional groups, suggests that the akermanite is physically diffused, rather than being chemically bound, and that the polymer backbone remains unaltered. Furthermore, only minor variations in band intensity are observed in the silicate bending region, consistent with the lattice distortions characteristic of La-substituted sol–gel alumina

[25]. The collective findings demonstrate the integration of both undoped and La-AK into the PLA matrix, thereby imparting bioactive silicate functionality without compromising the polymer's structural integrity.

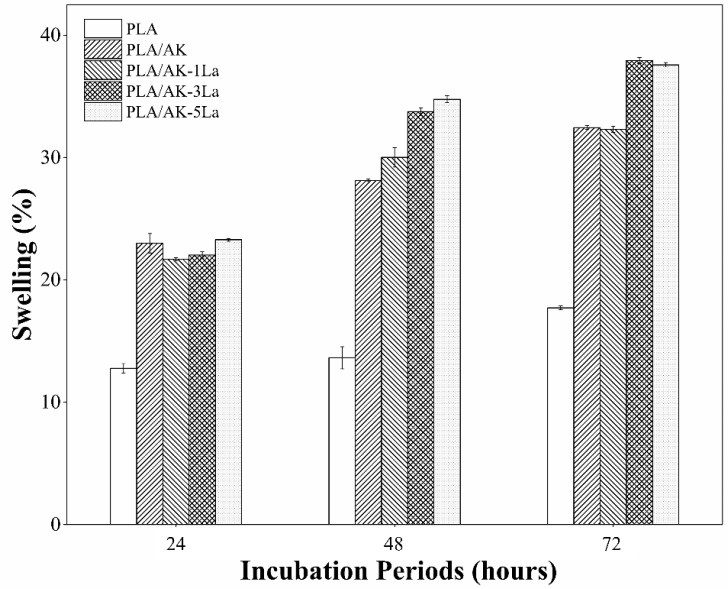

Figure 4. Degree of swelling of the wound dressings.

The swelling behaviour of the 3D-printed wound dressings was dependent upon the formulation (Figure 4): undoped PLA exhibited minimal absorption (approximately 12.8%, 13.6%, and 17.7% at 24, 48, and 72 hours, respectively), aligning with PLA's inherently hydrophobic characteristics and low intrinsic fluid absorption until altered [26]. The integration of AK powders resulted in a substantial enhancement of water absorption, with PLA/AK levels reaching approximately 23.0%, 28.1%, and 32.5% at 24–72 hours. This increase in absorption was found to be concentration-dependent, aligning with the enhanced absorption characteristics observed in bioactive-glass/silicate-infused wound dressings and foams [27, 28]. Substitution of La^{3+} at a level of 1–5 moles per cent resulted in enhanced late-stage uptake (48–72 hours). The samples exhibiting a molar percentage ranging from 3 to 5% demonstrated the most substantial equilibrium swelling within this series. This finding is indicative of dopant-induced alterations in particle surface chemistry, porosity, and dissolution behaviour, which in turn influence wettability and sustained ion-mediated osmotic forces [18]. The observed behaviour is mechanistically explained by two factors. Firstly, enhanced wettability is observed, resulting from silanol-rich silicate surfaces. Secondly, particle-induced microstructural channels and interfacial free volume that facilitate water ingress. These mechanisms have been previously identified in the context of bioactive ceramic-polymer dressings [27, 28].

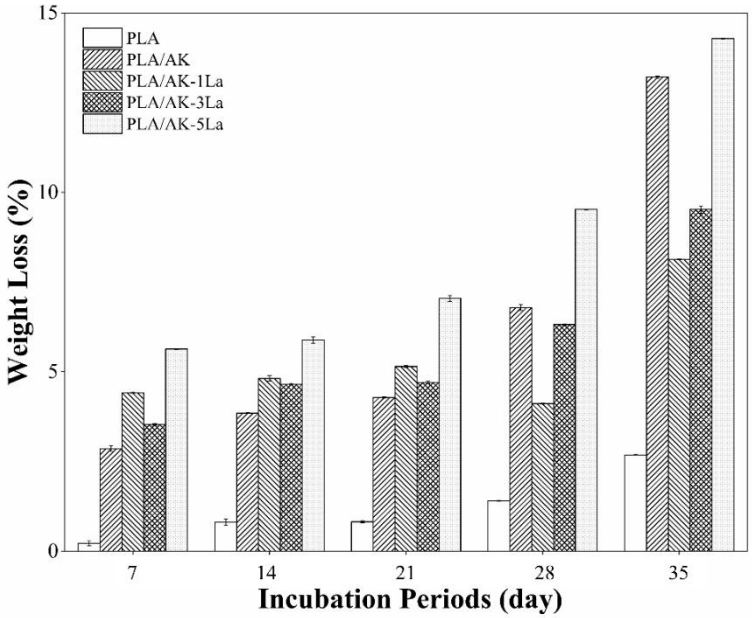

Figure 5. Biodegradation behavior of the wound dressings.

The hydrolytic degradation of 3D-pneumatically extruded wound dressings was found to be significantly influenced by the formulation (Figure 5). The neat PLA sample exhibited minimal mass loss (0.2–2.7%) after 35 days, which is consistent with the established slow hydrolysis of PLA under physiological aqueous conditions. The incorporation of sol–gel derived AK powders resulted in a dose-dependent increase in mass loss: formulations with moderate La concentrations exhibited approximately 4–9% mass loss, while samples with 5 moles % La-AK reached approximately 14% mass loss after 35 days. This tendency is likely facilitated by two complementary processes: Firstly, it is evident that the incorporation of bioceramic powders into the composite material serves to enhance its hydrophilic properties and augment its capacity for water absorption. This process, in turn, serves to promote the hydrolytic breakdown of ester bonds within the polymer matrix. Secondly, the release of ions by reactive silicate phases results in alterations to the local interfacial chemistry (pH, ionic strength). This, in turn, facilitates chain scission at the polymer-ceramic interface and increases apparent mass loss. These methods correspond with previous findings on bioactive glass/silicate-filled polymer dressings, whereby filler-induced wetting and ion transport expedite breakdown and the transfer of functional ions [27], [29]. The doping of AK with La provides an additional compositional mechanism for the customisation of degradation. The addition of La^{3+} has been demonstrated to influence ion speciation and release kinetics, alter local dissolution chemistry and surface reactivity, and can increase wettability and water accessibility. Consequently, La doped AK composites exhibit somewhat greater hydrolytic mass loss in comparison to their undoped counterparts [9], [18], [30]. Consequently, the AK composition, when employed in conjunction with rare-earth doping, provides a means to adjust parameters in order to achieve the desired outcome.

4. Conclusion

The 3D-printing of PLA/AK-La wound dressings demonstrated manufacturability and geometric precision, thereby preserving the intended open pore structure. The utilisation of FTIR analysis disclosed that the distribution of the AK powder occurred in a physical manner, exhibiting no compromise to the polymer backbone. The incorporation of AK, particularly with 1–5 mol% La^{3+} doping, has been demonstrated to enhance the swelling capacity (e.g., PLA ≈ 13–18% → PLA/AK ≈ 23–33%, 24–72 h) and hydrolytic weight loss (neat PLA ≈ 0.2–3%, La-AK samples ≈ 4–14% after 35 days). Consequently, this has led to an improvement in the biodegradation behaviour of the material. The utilisation of lead-doped, AK-reinforced, PLA composites facilitates the modulation of swelling and the promotion of biodegradability, thereby establishing a pragmatic, adaptable, and preclinical-ready framework for the fabrication of 3D pneumatic extrusion-manufactured wound dressings.

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Experimental Investigation of Internal Corrosion in X60 Pipeline Before and After Desalination Treatment

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ABSTRACT

Corrosion is one of the significant problems in many industries, particularly in the transport of fluids through steel pipelines, resulting in high maintenance costs, safety hazards and environmental damage. Welded joints are particularly susceptible to corrosion due to the heat activated physico-chemical changes they undergo while being produced. The present study focuses on the investigation of internal corrosion in a pipeline (API 5L X60 PSL1) with a diameter of 1400 mm. The proposed pipeline is used to transport drinking water between the "Fouka 02" seawater desalination plant, with a capacity of 300,000 m³/day, and the "El Sahel" reservoir in the Tipaza province. In this context, a comprehensive analysis of environmental factors, material properties, and pipeline operational conditions is conducted in a laboratory setting. A range of characterisation techniques was employed, including chemical composition analysis, optical microscopy, and microhardness testing.

Keywords: Corrosion, Potentiostat/Galvanostat, Pipeline, $X60$ steel, Flexal and Bohler electrodes, Drinking water, Desalination stations, NaCl solutions, Tafel curves, Curves of OCP.

1. Introduction

Pipelines play a crucial role in transporting liquids such as hydrocarbons or water, but they are subject to various forms of degradation over time, including corrosion, erosion, cracking, and other phenomena [1]. The issue of corrosion in pipelines is becoming increasingly problematic for infrastructure management [2, 3] due to pipeline failures, resulting in substantial economic losses and significant risks to public safety and the environment. This phenomenon results from complex chemical and electrochemical reactions between the metal of pipelines and the environmental conditions to which they are exposed, which can lead to serious incidents such as leaks and ruptures [4].

The factors influencing corrosion are multiple and vary according to environmental conditions, the composition of the pipeline, and the properties of the fluid transported [5], additionally, soil characteristics also play a crucial role in the rate and type of corrosion observed [6, 7]. For solving problems, it's crucial to develop and implement effective prevention and monitoring strategies. A thorough understanding of corrosion mechanisms and protection methods is essential to ensure the durability and safety of these infrastructures [8]. This study aims to examine the degradation affecting pipelines (steel X60) and the two filler metals (Bohler and Flexal), used in the welding, Figure 01.

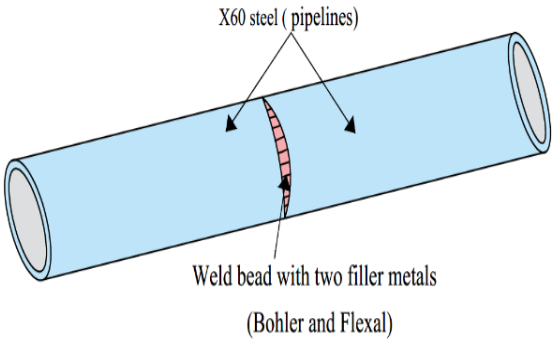


Figure 1: Illustration showing the assembly of pipeline and the two filler metals.

It should be noted that the pipeline (API 5L 60 PSL1) was originally designed for the transport of hydrocarbons, but in this case it has been retained for the transport of drinking water from several desalination stations recently commissioned (2023) and "El Sahel" reservoir Figure 02. Several samples (Drinking water and X60 steel) were therefore taken for testing from the new 300,000 m^3/day desalination station at Fouka 02, Tipaza Department - Algeria. This station, which was commissioned on 22 February 2025, is designed to meet the drinking water needs of the population until 2050.

Figure 2. Satellite image of pipeline trace between the desalination stations and the El Sahel Reservoir

2. Materials and Method

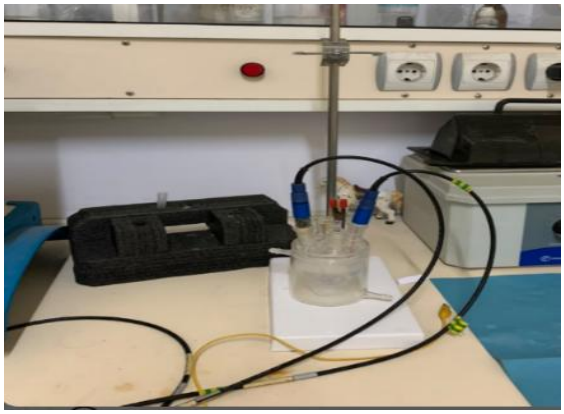
Initially, a number of samples were prepared for each experiment, with the three materials (X60 steel, Bohler and Flexal) being used. In the first experiment, a section of the X60 pipeline was extracted, after which samples measuring approximately 0.5 cm^2 were cut into square shapes. The samples of the welding daughters with a diameter of 0.5 mm (Bohler and Flexal) were then melted in a square mould, with the objective of obtaining samples measuring approximately 0.5 cm^2.

Prior to the electrochemical study, the samples of the various materials were prepared by mechanical polishing. The experimental characterisation was then initiated. Initially, the chemical composition of the three materials under study was determined using an Oxford Instruments device. This was then compared with the manufacturer's data sheets. Subsequently, the samples of the various materials were subjected to observation through the utilisation of optical microscopy. The utilisation of NITAL as an attack solution was also a component of the experimental procedure. The hardness of the three materials constituting the subject of this study was determined through the implementation of micro-hardness testing, employing a Vickers indenter from the Wilson Hardness brand. The electrochemical methods employed

in the study of the corrosion can be categorised into two distinct classifications: stationary and transient methods.

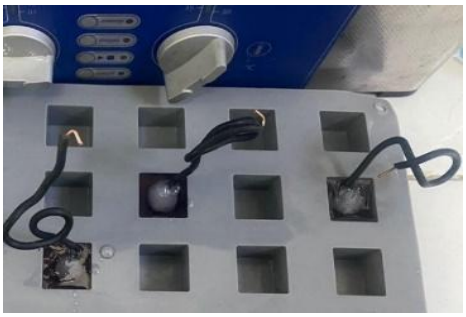
In this study, the stationary method with a three-electrode electrochemical cell, the classic assembly for performing electrochemical measurements was implemented in a cylindrical double-walled glass cell. The cell is kept at constant temperature by means of a bath, and equipped with a cover with five lapped inlets allowing the entry of three electrodes, in particular working electrodes ($X60$ steel; Flexal electrodes and Bohler electrodes). The reference electrode, also known as the auxiliary electrode is of the "$\mathrm{Ag/\ AgCl_2}$ / $\mathrm{KCl\ 4M}$ " type.

The potential of this electrode is measured at +0.205 V, in comparison to the standard hydrogen electrode. In the present application, the Radiometer Analytical brand electrode, designated as the XR 110, is utilised. The primary function of this electrode is to facilitate the transmission of electric current within the three-electrode assembly, thereby minimising the occurrence of polarization effects and accurately locating the ohmic drop in the immediate vicinity of the working electrode [9, 10].



Figures 3. The assembly of the electrochemical cell used.

It is imperative that the working electrodes of the X60 pipeline, Flexal and Bohler samples are prepared. The metallic surface is connected by a wire of a conductive nature, i.e. copper, which is covered with an insulating sheath. Samples and copper electric wire are coated with a cold resin, as illustrated in Figure 04, with the objective of leaving only the surface of the straight section of each sample exposed to the corrosive environment (the attack surface). The active surface area of the working electrode is measured to be S=$01m^2$ [9, 11]



Figures 4. Working electrodes, different samples in a mold, cold coated with resin.

All experiments are carried out using different equipments Figure 05. The first equipment is AUTOLAB-type Potentiostat/Galvanostat servo system, integrating both software for stationary measurements. This device is connected to a microcomputer to allow the control of the potentiostat, data acquisition and processing [12].

Figure 5. Experimental device used for electrochemical measurement.

Two experimental approaches are commonly utilised in which reactions are governed by charge transfers. The extrapolation of Tafel lines enables the determination of key electrochemical parameters, such as corrosion current and corrosion potential, by extrapolating anodic and cathodic polarization curves [13, 14]. The measurement of polarization resistance provides an indication of the electrolyte's resistance to polarization, a process which is directly related to the rate of corrosion. This method is especially efficacious in systems where corrosion is governed by load transfer reactions [15]

Potentiodynamic polarization studies were performed from the cathodic potential $(800\mathrm{mV})$ to the anodic potential $(-800\ \mathrm{mV})$, compared with the corrosion potential (Ecorr) at a scan rate of $(\ ^{10\ \mathrm{mV}}/_{\mathrm{S}}\ )$ for $35\ \mathrm{min}$ for all samples. Due to the presence of a degree of nonlinearity in the Tafel slopes, the Tafel coefficients $(\mathrm{Ba}$ and $\mathrm{Bc})$ were calculated from the slope of the points after $50\ \mathrm{mV}$ of (Ecorr) corrosion potential.

It should be noted that the protocol of electrochemical measurements is determined based on the principle and working conditions. The parameters were $(25°\mathrm{C})$, Electrovalence : 3 ; Density : $7.85\ \mathrm{g/cm^3}$ and Electrolytes: drinking water samples from desalination station in FOUKA 02 and the second plant, which was commissioned on 22 February 2025 and Seawater (the NaCl solution $(35\mathrm{g/l})$ prepared in the laboratory). The chemical composition analysis result of the samples is shown in Table 1, 2 and 3.

Table 1. Chemical Composition of pipline ($X60$ steel)

Fe	**C**	**Mn**	**Mo**	**Co**	***Ni***	***Si***	***Pb***	***Cu***	***Nb***
97.68	*0.186*	*1.56*	*0.02*	*0.03*	*0.11*	*0.203*	*0.02*	*0.34*	*0.02*

The comparison of Table 01, with the results of Y. Chemani et H.Hamaidia [11, 16], also answers and confirms the specification imposed by the $API\ 5L\ PSL1$ standard [17]. It is clear that the pipline (X60 steel) has slightly higher amount of Mn and lower C content in order to improve weldability through reducing sulphide stress cracking susceptibility and higher Cu content to lower the susceptibility to hydrogen induced cracking [18].

Table 2. Chemical Composition of weld metal deposited using Bohler electrode

Fe	**C**	**Mn**	**Mo**	**Co**	**Ni**	**Si**	**Pb**	**Cu**	**Nb**	**W**
97.9	*0.175*	*1.44*	*0.0084*	*0.0061*	*0.11*	*0.193*	*0.0090*	*0.0612*	*0.0065*	*0.0074*
V	**Ti**	**Cr**	**NbV**	**CEpc**	**Al/N**					
0.0038	*0.057*	*0.0452*	*0.016*	*0.263*	*10.830*					

Table 3 Chemical Composition of weld metal deposited by Flexal welding electrode using

Fe	***C***	***Mn***	***Mo***	***Co***	***Ni***	***Si***	***Pb***	***Cu***	***Nb***	***W***
97.9	*0.164*	*1.40*	*0.0098*	*0.0064*	*0.161*	*0.178*	*0.0089*	*0.0568*	*0.0070*	*0.005*
V	***Ti***	***Cr***	***NbV***	***CEpc***	***Al/N***					
0.0025	*0.0057*	*0.0453*	*0.016*	*0.251*	*11.050*					

The results are given in tables 02 and 03 which were also csompared with the results by FERRADJI, Z. and A. ZELLOUF [19]; tests were carried out according to AWS 5.1, AWS A5.18 and EN ISO 14341-A standards. It is clear that weld metal compositions deposited by Bohler and Flexal welding electrodes are similar to pipline (X60 steel) composition, which encouraged in order to obtain problem free welds.

3. Results and Discussion

3.1. Microscopic observation

Figures 06, 07 and 08 show the optical images from the $X60$ steel samples and the weld metals deposited by two welding electrodes Bohler and Flexal, at different magnifications in as received form.

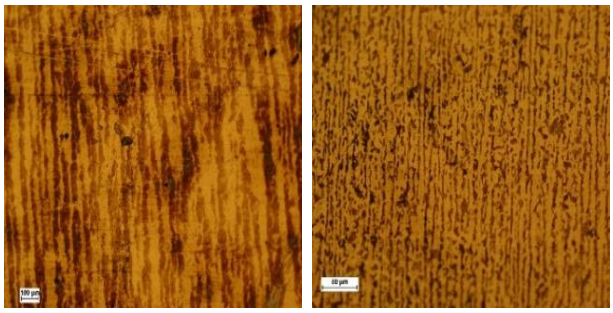


Figure 6. microscopic observation of $X60$ steel, with different magnification.

In Figure 06, we can see that the structure is elongated structure of grains formed due to rolling process at temperatures where rolling is allowed, with the presence of two zones of different colors and shapes; light coloured zone is ferrite with very low onten of C whereas dark coloured region is the pearlite where cementite and ferrite are aligned to form laminated structure. The presence of black spots, apart from pearlite zones in bulk form, are various types of inclusions that are formed during the production of steel [20]. It is clear that chemical analysis indicates a hypoeutectoid steel [21]. On the other hand, the electrode from Flexal also has similar morphology and elongated form of grains due to rolling effect during the wire drawing. Contrary to Bohler electrode steel and X60 steel morphology, the Bohler steel electrode shows equiaxed structure where grain boundaries are visible by the formation of ferrite phase.

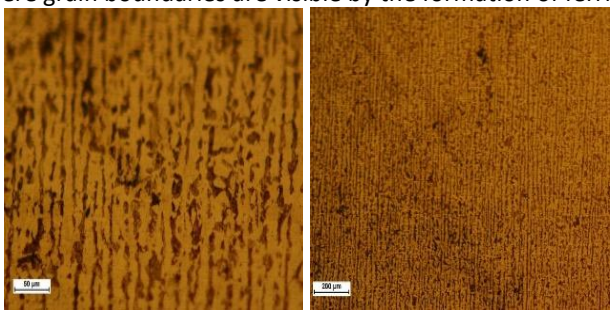


Figure 7. optical microscopy images of the Flexal electrode.

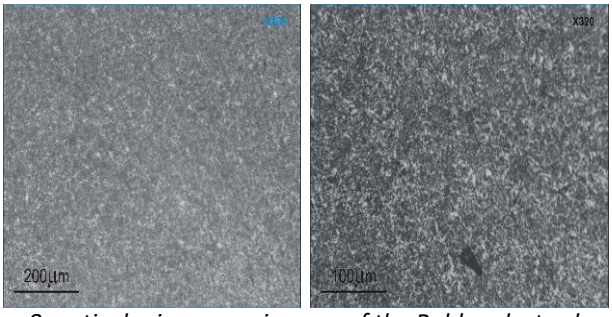
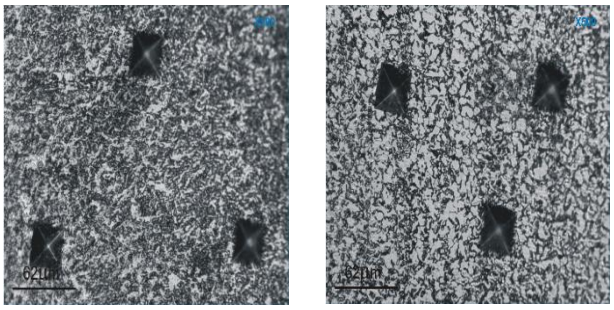


Figure 8. optical microscopy images of the Bohler electrode.

3.2. Micro-hardness

Figures 09 and 10 represent the locations where the micro-hardness (HV) measurements were carried out; it should be noted that a load $100gf\ mm^{-2}$ was used for the hardness measurement with a tip of Vickers.



(a) *(b)*

Figure 9. the microhardness Vickers tip indentation on (a) Bohler, (b) Flexal samples.

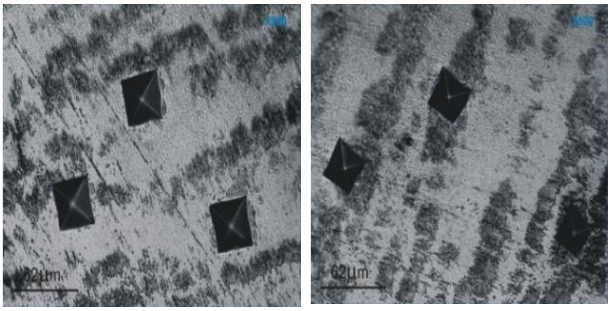


Figure 10. The microhardness Vickers tip indentations applied to the $X60$ steel.

The results of this micro-hardness are shown in tables 4, 5 and 6.

Table 4. Bohler micro-hardness results

Les zones	***Hv*** $(\frac{kgf}{mm^2})$	***Average of Micro-hardness***
Zone 1	*198*	*Hv = 193.66*
Zone 2	*199*	
Zone 3	*184*	

Table 05: Flexal micro-hardness test results

Les zones	***Hv*** $(\frac{kgf}{mm^2})$	***Average of Micro-hardness***

Zone 1	*189*	*Hv = 190.33*
Zone 2	*186*	
Zone 3	*196*	

Table 6. Micro-hardness test results of the clear parts of $X60$ steel

Les zones	$Hv\ (\frac{kgf}{mm^2})$	***Average of Micro-hardness***
Zone 1	*164*	*Hv = 159.66*
Zone 2	*165*	
Zone 3	*150*	

Table 7. Results of the micro-hardness values of the dark parts of $X60$ steel

Les zones	$Hv\ (\frac{kgf}{mm^2})$	***Average of Micro-hardness***
Zone 1	*207*	*Hv = 220.66*
Zone 2	*241*	
Zone 3	*214*	

Based on the chemical composition of $X60$ steel, which contains about 0.2% carbon, it can be said that it is a hypo-eutectoid steel. According to the phase diagram of the iron-carbon system. In the hypo-eutectoid zone, perlite is the hardest phase, while ferrite is the least hard phase. Therefore, the dark phases observed in the $X60$ steel sample probably correspond to perlite, and the light phases to ferrite. This phase differentiation explains the variations in hardness measured, with perlite conferring a higher hardness compared to ferrite. The analysis of the hardness values obtained from the indentations made on the $X60$ steel sample shows a clear distinction between dark and light areas (Figure 10). Tables 06 and 07 show that the hardness values measured in the dark parts are higher than those in the light parts. As a result, the average hardness of dark areas is higher than that of light areas, indicating that dark phases possess higher hardness than light phases. It is also important that the thickness of pearlite (cementite + ferrite) patches are very relevant to the hardness measurements; thinner the laminate/cementite layer the higher the hardness test measurements in steels. It is important to observe such changes as it indicates the cooling rate of steel, however, the morphology of pearlite zone is indistinguishable and hence claim no effect. On the other hand, X60 steel steel contains 10 times higher Cu content than Flexal and Bohler electrode compositions (Tables 2 and 3), which is known for solid solution hardening and stability of pearlite by reducing the dissociation of C through outward diffusion process [22].

The similarity of the micro-hardness results given in Tables 4 and 5 between the two filler metals are noticeable, given, which explains their use as filler metal in the welding of $X60$ steel. Micro-hardness results are in agreement with the results by A. ACHOURI [21].

3.3. Electrochemical tests

3.3.1. Tafel curves

The Tafel curves of the three samples are grouped and plotted on the same graph for the two electrolyte solutions (drinking water after desalination treatment and $NaCl$ with 35g/l).

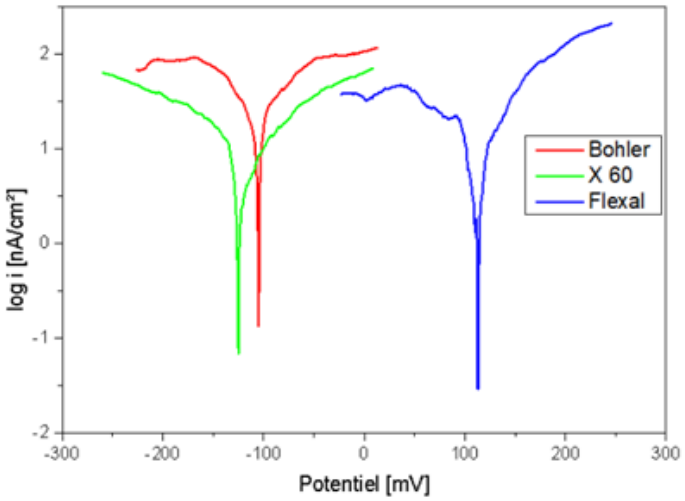


Figure 11: Tafel curve of the three specimens in drinking water

Table 8. Tafel values E_{ab}, E_{corro}, I_{corro},B_a B_c, V_{corro} of electrochemical polarization in water

Samples in the water	***Ecorr (mV)***	***Icorr (nA/cm2)***	***Ba (mV)***	***Bc (mV)***	***Vcorr (nm/Y)***	***Coeff***
Bohler	*-105.0*	*22.1663*	*87.7*	*-78.1*	*259.2*	*0.9925*
X 60	*-124.9*	*18.0685*	*228.9*	*-243.7*	*211.3*	*0.9970*
Flexal	*112.8*	*24.1593*	*121.9*	*-246.4*	*282.5*	*0.9972*

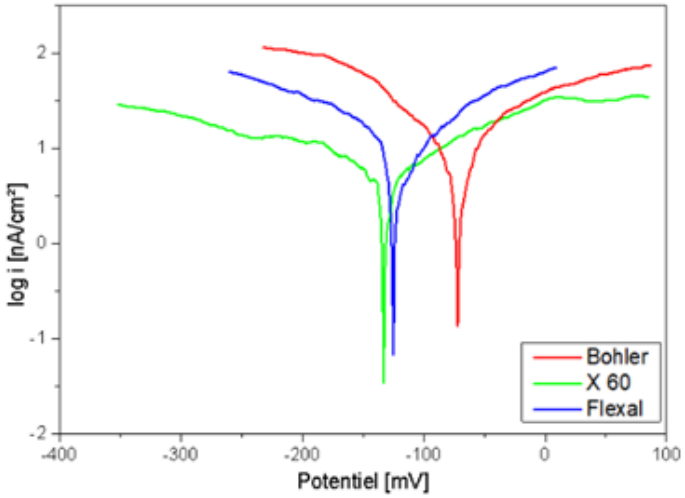


Figure 12. Tafel curve in $NaCl$ solution.

Table 9. Tafel values E_{ab}, E_{corro}, I_{corro},B_a B_c, V_{corro} of electrochemical polarization in $NaCl$

Samples in the Na Cl	***Ecorr (mV)***	***Icorr (nA/cm2)***	***Ba (mV)***	***Bc (mV)***	***Vcorr (nm/Y)***	***Coeff***
Bohler	*-71.2*	*20.0492*	*254.2*	*-163.0*	*234.5*	*0.9975*
X 60	*-133.2*	*6.2935*	*192.5*	*-306.4*	*73.61*	*0.9969*
Flexal	*-81.7*	*40.8082*	*99.7*	*-94.8*	*477.3*	*0.9973*

3.3.1.a Behavior of X60 steel

Figure 12 and Figure 13 show the corrosion behaviours of Böhler, X60 and flexal steels. The $X60$ steel curves in both solutions have two distinct branches in which may indicate that there are different

corrosion mechanisms or the presence of multiple metallurgical phases. However, current densities remain relatively low in both solutions suggesting good corrosion resistance with a slight increase in water[20].

The values of E_{corr} are relatively similar in both environments; The slopes of Tafel show significant variation, suggesting distinct corrosion mechanisms in the two environments. This metal shows better corrosion resistance in saline environments compared to water, which is indicated by a lower corrosion rate in $NaCl$.

3.3.1.b. Behavior of Flexal Electrode

The curves in both solutions have a simpler shape with a single linear branch, the current densities are higher compared to $X60$ steel, indicating a greater susceptibility to corrosion especially in the saline medium ($NaCl$), than in water, it should also be noted that the current densities of the two curves in Flexal are the highest among the three materials.

The Ecorr values indicate a better corrosion resistance of Flexal in $NaCl$, which is contrary to the trend observed for corrosion rate and corrosion current density.

3.3.1.d. Behavior of Bohler electrode steel

The curve is similar to Flexal's, with a single linear branch. However, the current densities are slightly lower, suggesting better corrosion resistance, particularly in saline solutions. Both curves resemble those in drinking water, but with higher current densities.

The values of E_corr are found to be relatively similar in both environments. The slopes of Tafel demonstrate significant variation, particularly cathodic, indicating distinct corrosion mechanisms in the two environments. The values are found to be relatively constant between the two media, indicating relative stability in terms of corrosion resistance.

3.3.1.e. Comparison between the three metals

Overall, $X60$ steel seems to have the best corrosion resistance in this aqueous solution, while the Flexal electrode shows the good performance, Bohler, on the other hand, shows stable performance in both types of environments.

Comparing the two solutions, it is clear that the saline environment accelerates corrosion for all materials tested, but with different proportions.

Further analyses would be required to fully understand the underlying corrosion mechanisms in each case [23, 24].

3.3.2. Open Circuit Potential $(\boldsymbol{OCP})$ Curves

Figures 13 and 14 show the OCP curves of the three metals for the two solutions, on each figure we have grouped the three graphs.

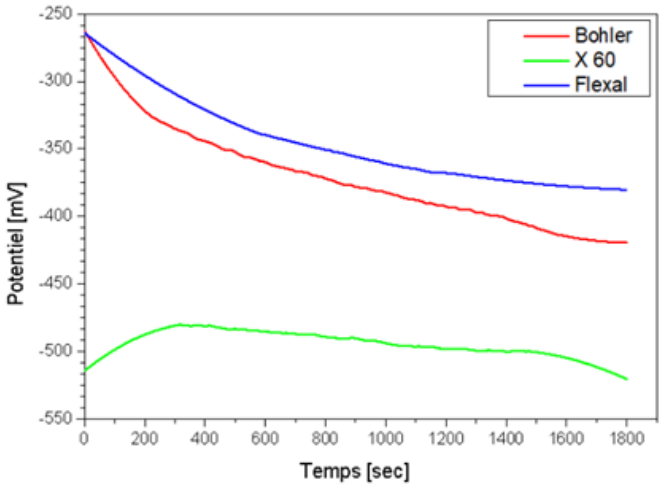


Figure 13: Curves of OCP for the specimens tested in water.

In an aqueous environment, Figure 13, the Bohler electrode exhibits optimal corrosion resistance and maintains a consistent and stable potential. The X60 material used for pipelines has been found to demonstrate satisfactory behaviour, exhibiting intermediate potential. The Flexal electrode exhibited the lowest resistance, with the lowest potential and a constant decrease, rendering it unsuitable for this environment.

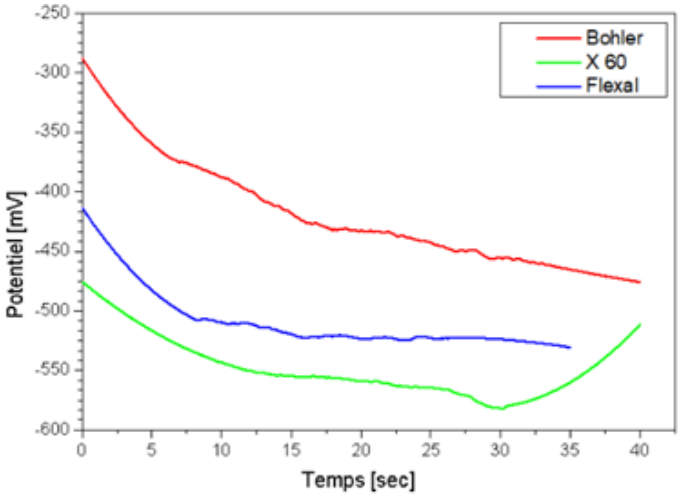


Figure 14: Curves of OCP for the specimens tested in $NaCl$.

In the NaCl solution, Figure 14, all curves are shifted to more negative potentials due to the more corrosive environment. However, the Bohler electrode still retains the best performance, followed by the $X60$ material. The Flexal electrode exhibits a unique behavior with a rapid initial drop and then a rise in potential, which raises questions about its reliability in this solution.

For optimal corrosion resistance in both tested environments, the Bohler electrode is the best choice. The $X60$ material is a viable option for pipelines, offering acceptable intermediate performance. On the other hand, the Flexal electrode is not recommended due to its low resistance, especially in corrosive saline[25].

3.3.3. Micrograph of the corroded surface

By using the optical microscope a second time after the corrosion in the two solutions, we can obtain the following results :

3.3.3.1. Corrosion in water

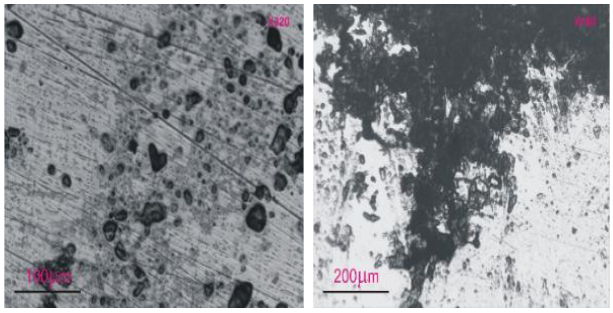


Figure 15: Microscopic observation after corrosion of X60 steel.

We notice that the surface is relatively smooth with some small marks, streaks, which are probably due during surface preparation, we also notice that there are few signs of significant corrosion.

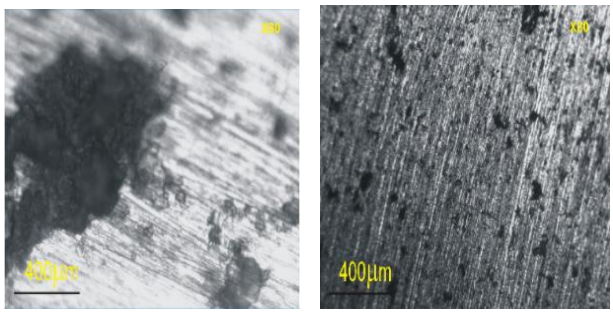


Figure 16: Microscopic observation after corrosion of the Bohler electrodes

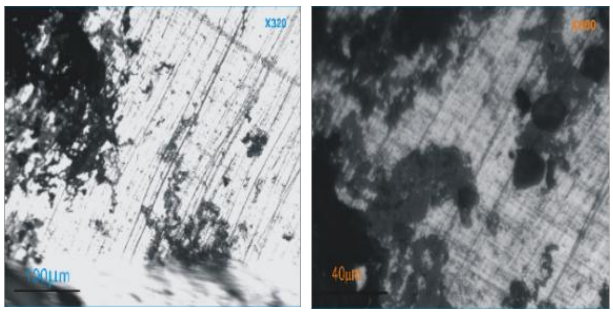


Figure 17: Microscopic observation after corrosion of the Flexal electrodes

In both the Bohler and Flexal electrodes we notice some isolated dark areas, indicating minor localized corrosion with an overall intact surface.

3.3.3.2. Corrosion in NaCl

From microscopic observations, we notice that the sample surfaces of the specimens corroded in the $Nacl$ solution, In X60 steel, the presence of numerous small cavities and pitting is observed on the surface. These defects are distributed in an uneven manner and are characterised by irregular dark areas, which are indicative of localised corrosion. Furthermore, the presence of linear scratches on specific parts is noted. It is evident that the phenomenon of corrosion is more pronounced in certain areas, resulting in a heterogeneous manifestation. The surface of the Bohler electrode exhibits substantial irregular dark areas, indicative of significant corrosion. This corrosion is more extensive and aggressive than that observed on X60 steel. The attack is deeper and more localized, forming craters or crevices. The corrosion process is characterized by its severity and widespread nature, encompassing the entire surface of the Flexal electrode. The presence of a large, extended, dark area is indicative of significant material dissolution. The original structure is obscured due to the intensity of the corrosion, making it challenging to discern.

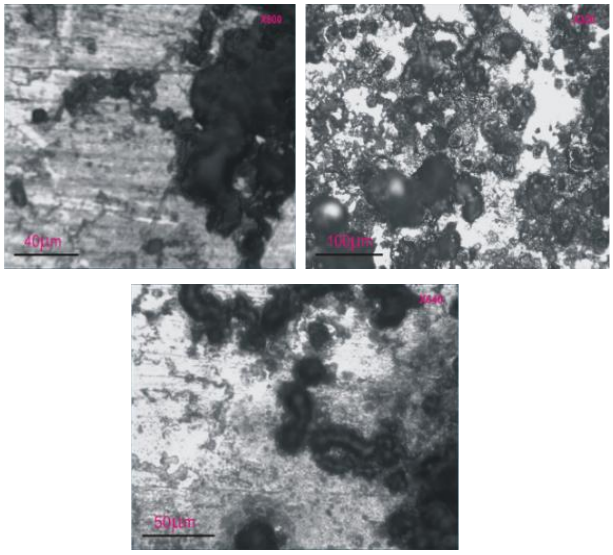


Figure 18: Microscopic observation after corrosion of X60 steel.

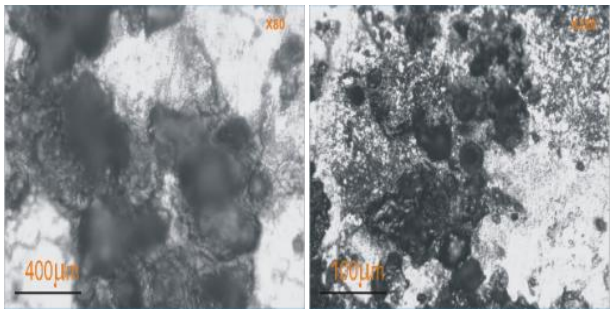


Figure 19: Microscopic observation after corrosion of the Bohler electrodes

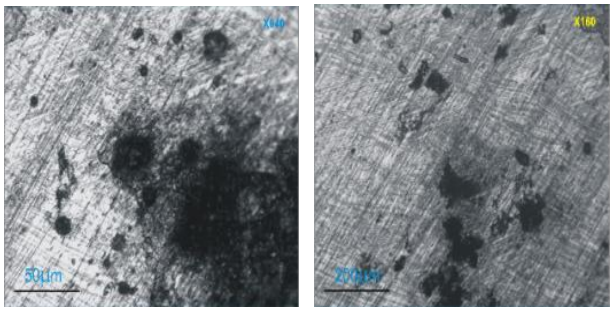


Figure 20: Microscopic observation after corrosion of the Flexal electrodes.

The surface of the material exhibits a coarse and porous appearance. It is evident, based on the observations presented above, that Flexal has been subject to the most severe and widespread corrosion. The Bohler specimen displays substantial, albeit more circumscribed, corrosion. X60 steel has been demonstrated to exhibit the optimal relative strength, accompanied by a greater surface area and a reduced susceptibility to extensive corrosion. The findings of this study indicate that X60 steel demonstrates the optimal resistance to corrosion in the environment under investigation, with Bohler steel exhibiting a secondary level of corrosion resistance. Conversely, Flexal steel exhibits the least resistance to corrosion under these conditions. It is noteworthy that the NaCl solution causes significantly more severe corrosion than normal water on all materials tested. It has been established that water, in its normal state, causes only a minimal amount of corrosion, which is largely superficial. By contrast, NaCl has been shown to lead to significant surface degradation, the effects of which vary depending on the material concerned. This discrepancy underscores the substantial impact of chloride ions on the acceleration of corrosion processes [25, 26].

4. CONCLUSIONS

In this study, the various test results performed on X60 grade steel samples and Bohler and Flexal electrodes were discussed.

The analysis of the chemical composition of the three materials enabled the identification of the requirements of the different API 5L talc standards. There was a high degree of concordance for the main elements, such as iron, carbon, silicon and manganese. Notable discrepancies were observed for certain trace elements: phosphorus and sulfur exhibited slightly elevated levels, while chromium was present at approximately double the standard value. In addition, nickel, cobalt, and copper were found to be present at marginally lower levels.

Microscopic analysis has revealed distinct structural features in X60 steel (pipeline). The material exhibits a laminated structure comprising two distinct phases. Flexal electrode displays a surface that is comparable to that of X60 steel, while the Bohler electrode presents a motled appearance with a grainy and irregular texture.

The results of the micro-hardness measurements demonstrated a clear distinction between the dark and light areas of the X60 steel specimen. The dark areas exhibited higher levels of hardness. Despite the average hardnesses of the Flexal and Bohler electrodes being similar, the Flexal electrode was found to be closer to the hardness of the X60 steel.

The corrosion study, which was conducted via electrochemical tests, demonstrated that X60 steel exhibited the optimal corrosion resistance in both the normal water and NaCl solutions. The Bohler electrode exhibited a marginally diminished corrosion resistance in comparison to X60 steel, yet it demonstrated higher corrosion resistance than that of Flexal. Notably, the Flexal electrode demonstrated the least corrosion resistance, particularly in saline environments.

5. Acknowledge

The authors would like to acknowledge that this work was carried out independently as part of the Master's program at the University of Science and Technology Houari Boumediene during the 2023/2024 academic year. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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Effect of Localized Hot Forging and Welding Processes on Structural Integrity and Fracture Behavior of C40+C Screws in Scissor Jacks

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ÖZET

Makas kriko, ARIKAN AUTOMOTIVE 'de önemli bir üretim bileşenidir ve araç bakımı ve acil durum operasyonlarında hayati bir rol oynamaktadır. Krikonun kritik elemanı olan vida mekanizması C40+C çeliğinden üretilmektedir. Çalışma sırasında kullanımını mümkün kılmak için bir ucuna sıcak dövme ile kanal açılır ve kaynak ile döndürme aparatı monte edilir. Gerçekleştirilen bu çalışmada, prototip aşamasındaki kalite testlerinde başarısız olmuş ve müşteri gereksinimlerini karşılamamış krikonun vida mekanizmasının hasar analizi ve performans iyileştirme çalışmaları yapılmıştır. Sertlik testleri, malzeme karakterizasyonu ve tasarım analizini bir araya getirerek hasarın temel nedenlerini araştırmış, mevcut tasarım veya üretim sürecindeki potansiyel zayıflıkları belirlemek ve makaslı krikonun yapısal performansını ve güvenilirliğini artıracak iyileştirmeler önerilmiştir. Bu amaçla, dövme ve kaynak işlemlerinden kaynaklanan mikroyapısal değişiklikleri ve hasar mekanizmalarını incelemek için optik mikroskop (OM) ve taramalı elektron mikroskobu (SEM) kullanılmıştır. Mekanik özelliklerdeki değişiklikleri değerlendirmek için mikro sertlik testi uygulanmıştır. Ayrıca, döngüsel yükleme koşulları altında krikonun çalışma performansını değerlendirmek için gerçek zamanlı yorulma testleri yapılmıştır. Bu çalışmanın bulguları, hasar mekanizmaları hakkında değerlendirme yaparak üretim süreçlerinin optimizasyonuna ve güvenilir kalite kontrol uygulamalarının geliştirilmesine katkıda bulunacaktır. Bu çalışma, ARIKAN AUTOMOTIVE tarafından AR-25002 numaralı proje tarafından desteklenmiştir.

Anahtar Kelimeler: Kriko, Hasar analizi, Kaynak, Sıcak dövme

ABSTRACT

The scissor car jack is an essential production component at ARIKAN AUTOMOTIVE and plays a vital role in vehicle maintenance and emergency operations. A key element of this mechanism, known as the lead screw, is typically manufactured from cold-worked C40+C steel and subsequently subjected to hot forging and welding at one end to ensure proper alignment during operation. Despite its functional importance, the jack, intended for a new application, failed during quality testing in the prototype phase and did not meet the customer requirements. This study investigates the root causes of the failure through a combination of mechanical testing, material characterization, and design analysis. The primary aim is to identify the potential weaknesses in the current design or manufacturing process and to propose improvements that enhance the structural performance, reliability, and overall safety of the scissor jack. To this end, optical microscopy (OM) and scanning electron microscopy (SEM) were employed to investigate the microstructural changes and failure mechanisms associated with the forging and welding processes. Microhardness testing was conducted to assess the changes in mechanical properties resulting from the forging and welding operations. Additionally, real-time fatigue tests were conducted to assess the jack's operational performance under cyclic loading conditions. The findings of this study provide valuable insights into failure mechanisms and contribute to the optimization of production processes, as well as the

development of more robust quality control practices for future manufacturing. This study was supported by ARIKAN AUTOMOTIVE under Grant Number AR-25002.Bu çalışmanın bulguları, hasar mekanizmaları hakkında değerlendirme yaparak üretim süreçlerinin optimizasyonuna ve güvenilir kalite kontrol uygulamalarının geliştirilmesine katkıda bulunacaktır. Bu çalışma, ARIKAN AUTOMOTIVE tarafından AR-25002 numaralı proje tarafından desteklenmiştir.

Keywords: Scissor car jack, Failure mechanisms, Welding, Hot forging

1. Introduction

The reliability of shafts in heavy-duty mechanical systems has been the subject of considerable research due to their critical function in power transmission [1-3]. These components are often subjected to complex loading conditions, including high rotational speeds, fluctuating stresses, and elevated temperatures, all of which can accelerate damage accumulation and reduce service life [4-6]. Failures in such shafts not only lead to costly downtime but can also compromise the safety and efficiency of the entire system [7-8]. Consequently, detailed failure analysis is essential to identify the underlying mechanisms, prevent recurrence, and improve the design and maintenance strategies of these critical components.

Several studies have focused on failure analysis and service life improvement of shafts used across various industries. For example, Muhammad et al. [9] investigated a high-speed pinion gear shaft used in a natural gas compression machine. While macroscopic examination of the fracture surface indicated fatigue features, scanning electron microscopy (SEM) analysis revealed predominantly brittle intergranular cracking without the presence of striations. Complementary fatigue testing under service conditions confirmed fatigue as the dominant failure mechanism, initiating from a stress concentration region located beneath the bearing race. In another study, Pantazopoulos and Papaefthymiou [10] investigated the failure of an austenitic stainless steel marine propeller shaft. Their analysis revealed that rotating bending fatigue was the dominant failure mechanism, with cracks initiating at surface defects in the vicinity of the keyway. Stress concentrators such as dents and scoring lines were found to accelerate crack propagation, while fractographic features including beach marks and ratchet marks provided clear cyclic loading effects. To mitigate such failures, the authors recommended stricter maintenance practices and enhanced surface inspection procedures. Miranda et al. [11] examined the fatigue failure of a speed reduction gearbox shaft used in mining operations. The shaft exhibited improper heat treatment, resulting in a banded microstructure with numerous inclusions, which significantly reduced its fatigue resistance. The fracture was attributed to low-cycle fatigue, initiating from inclusions and surface pores. This study highlights the critical importance of proper metallurgical control in ensuring the reliability of shafts employed in mining applications. Amer et al. [12] investigated high-silicon austempered steels to improve shaft performance. Both experimental testing and computational analysis demonstrated that increased silicon content (min. 1.5 wt.%) promoted the stabilization of retained austenite, refinement of the bainitic structure, and suppression of carbide formation. In particular, steel with 1.59 wt.% Si exhibited an excellent balance of properties, achieving a yield strength of 1088 MPa, an elongation of 16.4%, and high toughness. These findings confirm the strong correlation between alloy composition and fatigue resistance. Kant et al. [13] studied the premature failure of pinion shaft in TMT rebar mill. Fatigue cracks were found to initiate at a geometric irregularity that produced a severe stress concentration. The failure was further aggravated by improper repair welding, a non-uniform microstructure, and the presence of detrimental inclusions such as MnS and Ca–Si. The study concluded that the primary causes of the premature failure were the inadequate welding procedure and poor material quality.

Collectively, these studies demonstrate that shaft failure is strongly influenced by material composition, heat treatment quality, the presence of inclusions, and geometric irregularities. Effective prevention therefore requires a multifaceted approach, including optimized compositional design, uniform microstructural control, appropriate surface treatments, and rigorous inspection during both manufacturing and maintenance. In the present work, during a rear axle vehicle lift test, the scissor jack experienced a critical failure as a result of excessive load and displacement. Specifically, the rotating head

separated from the main body of the screw shaft during the tests. Following this failure, design and processing improvements were implemented to enhance the reliability of the component.

2. Materials and Methods

A scissor jack consists of four main components, as illustrated in Figure 1: (i) the top step, which interfaces with the vehicle's jacking point, (ii) the base, which provides stability on the ground, (iii) the arms, which rotate to increase the jack's height, and (iv) the screw, the most critical component, as it drives the mechanism and carries the majority of the load.

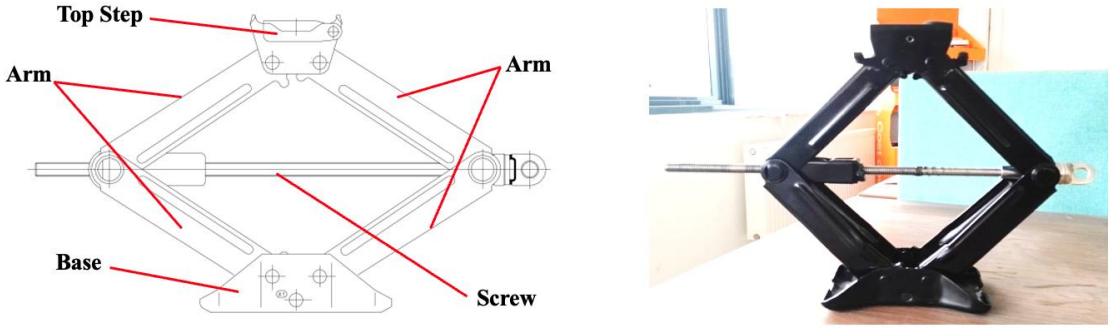

Figure 1. Scissor jack main components

The screw is manufactured from cold-drawn C40 steel. The as-received form of C40 steel and its microstructure, as examined by optical microscopy (OM), are shown in Figures 2a and 2b, respectively. The OM images reveal a microstructure consisting of pearlite and ferrite, consistent with the steel's carbon content.

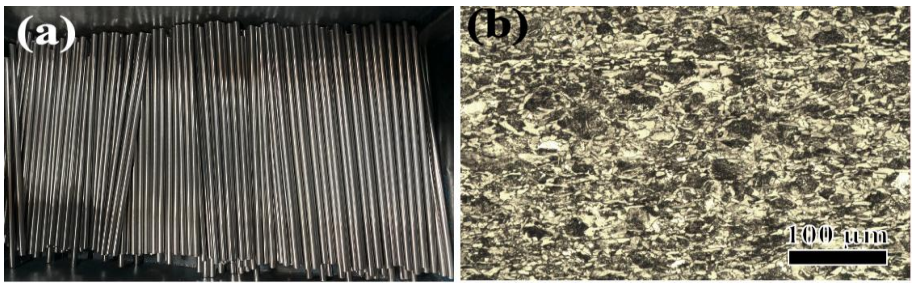

Figure 2. (a) the as-received form of C40 steel and (b) its microstructure.

In the current production process, the screw head is first hot forged, as illustrated in the sequential production shown in Figure 3. The forging procedure begins by heating the screw head to approximately 900–1000°C (Figure 3a). While the material is in this heated state, a groove is formed through forging (Figures 3b and 3c), into which a turning fixture is later welded. After forging, the screw is allowed to cool in air alongside the other screws (Figures 3d and 3e). Figure 3f shows the final form of the forged region of the screw, with a clearly visible groove.

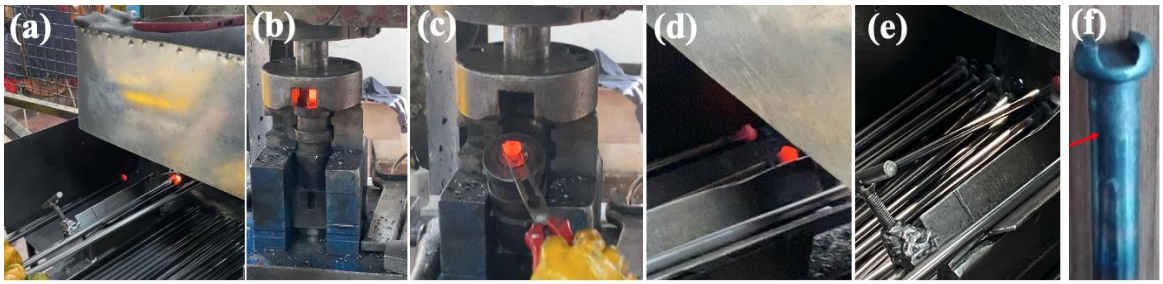

Figure 3. (a) Heating of the screw head, (b-c) a groove is formed through forging, (d-e) the forged screws are allowed to cool in air alongside the other screws, and (f) the final form of the forged region of the screw, with a clearly visible groove.

After the forging is complete, the screw, ring locator, and washer are welded together. The ring locator and washer are positioned on the fixture along with the screw during the forging process and subsequently welded together. This welding creates a wide planar surface to support the bearing and provides a locator for the jack handle. Due to the presence of these three components, additional welding wire was used to ensure a secure joint between the ring locator and the washer. Figure 4a presents the modeling of forged region, Figure 4b shows the cross-section modelling of the screw head after welding, and the complete screw assembly is illustrated in Figure 4c.

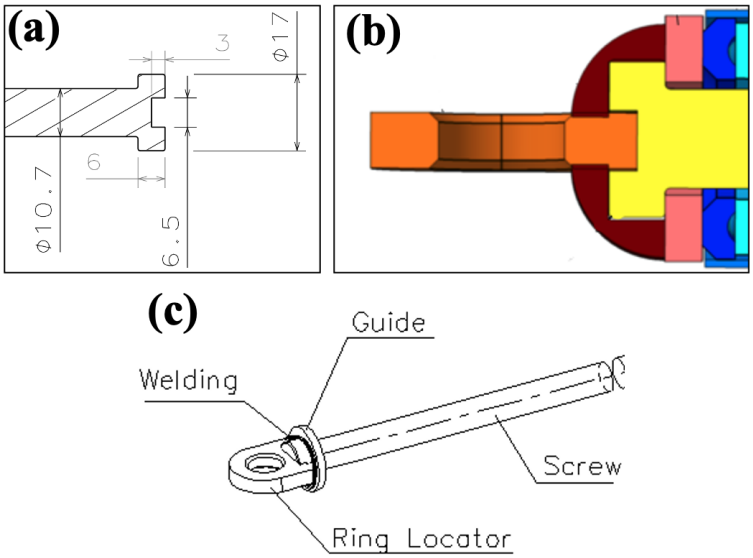

Figure 4. (a) forged head, and (b) the cross-section modelling of the screw head after welding, and (c) the complete screw assembly.

The microstructure of the screw material after various processing steps was examined using optical microscopy (OM). Conventional metallographic sample preparation procedures were followed for the microstructural analysis, including grinding the samples down to 2500-grit abrasive paper, followed by polishing. Additionally, a nital solution was used to etch the samples prior to optical microscopy (OM) investigations [14-15]. In addition, fractography analysis of the failed screws was conducted using scanning electron microscopy (SEM) to characterize the features of the fractured surface.

For the microhardness test, the samples were first cut radially from approximately 100 mm away from the forging location. Each sample was then divided into three equal pieces (approximately 33 mm each) to allow secure mounting in sample holder. Microhardness test was used for hardness measurements with 9.807N load and 10 s duration.

3. Results and Discussion

The screw component, an essential part of the mechanical system of jacks, ensures the safe and smooth lifting of the vehicle. The vertical movement of the jack is mechanically achieved via the screw shaft. Depending on the vehicle type and lifting capacity, the screw shaft in different jacks must be able to move the jack up and down for a specified number of cycles without sustaining damage. In the current design and production for a specific customer, the screw shaft's lifetime did not meet the required performance criteria. The fractured screw head during the quality control and life-time assessment in our R&D department is given in Figure 5. SEM analysis was conducted on the fracture surfaces to determine the type of failure, also shown in Figure 5. The SEM images reveal a brittle fracture characterized with minimal plastic deformation. The observed cleavage planes and granular features are indicative of rapid crack propagation typical of brittle failure. The root causes were identified as defects originating from the welding process and the inhomogeneous microstructure generated during hot forging. This fracture tendency suggests that the crack was initiated in the welded region during vehicle lifting via the screw

component [16]. However, further investigations, including microstructural analysis and hardness testing, were conducted to assess the root cause of the failure.

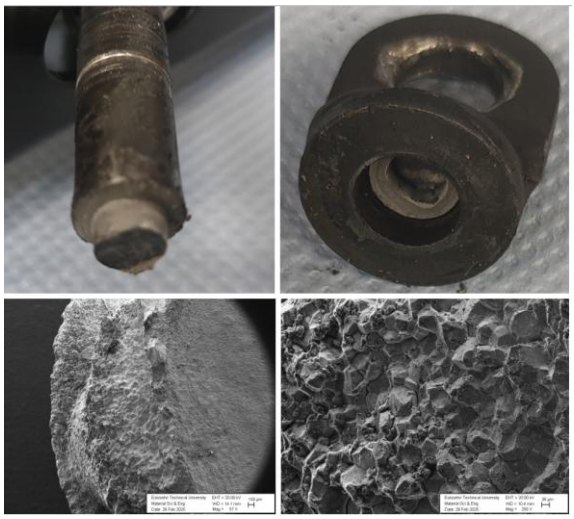

Figure 5. The fractured screw head was examined during quality control and lifetime assessment in our R&D department, and a fractography analysis was conducted using SEM.

Optical microscopy analysis was conducted to investigate the microstructural evolution following forging and welding, as well as to evaluate the effect of forging on raw material and the welding quality between the screw and the turning fixture. Figure 6 shows the microstructural changes in the screw across the forged region, from low magnification (left) to high magnification (right). In the indicated area in Figure 6, the grain structure is noticeably coarser. This is because, during hot forging, this region was exposed to heat for a longer period and cooled more slowly, promoting more grain growth through diffusion.

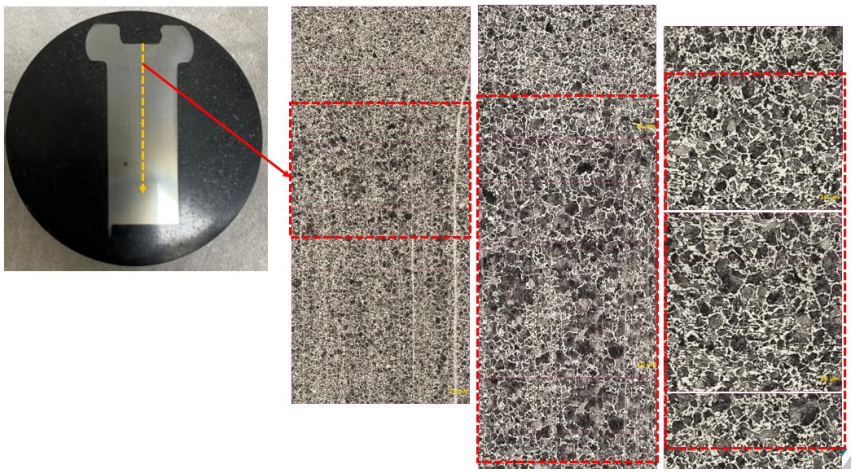

Figure 6. Optical microscopy (OM) images of the hot-forged steel, from low magnification (left) to high magnification (right).

Figure 7 presents optical microscopy images of the welded screw and the welding gaps. Small gaps between the screw head and the turning fixture are clearly visible, which can act as stress concentrators under load and serve as potential initiation sites for cracks. During repeated cycles of vehicle lifting, the localized stresses around these gaps may cause structural damage, ultimately compromising the screw's integrity and increasing the risk of premature failure.

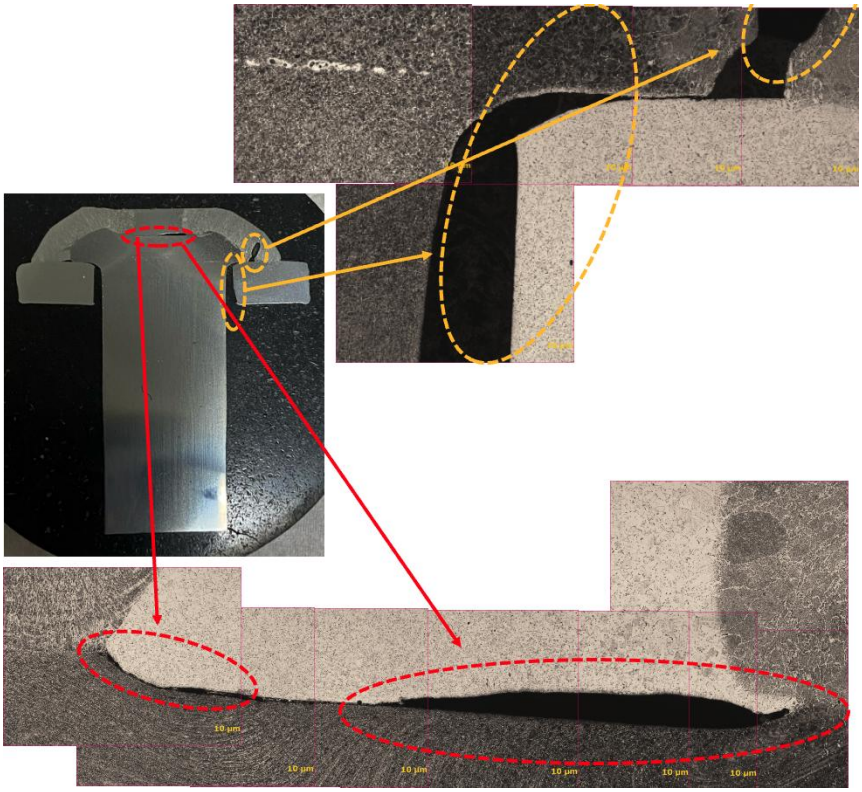

Figure 7. Optical microscopy (OM) images showing the welded screw and the welding gaps.

It is also expected that the microstructural changes occurring during forging and welding, due to excessive heat exposure, may alter the mechanical properties of the screw [17]. This was evaluated through microhardness tests. As shown in Figure 8, the hardness of the steel decreases from 260 HV to around 200 HV as the measurement location approaches the forged head. The measurements were taken from the surface as indicated by the dashed horizontal line, while the vertical dash-dotted line represents the cross section along which the hardness variation was measured. The X axis of the graph indicates the measurement location in mm, and the Y axis shows the corresponding HV hardness values. This variation represents the transition from the heat-affected zone to the cold-drawn region, resulting in a deterioration of the cold-drawn properties and reduced material durability. Furthermore, the sudden change may introduce additional stress concentration in this section. After forging, the turning fixture is welded to the end of the screw shaft, where hot forging was performed. In this region, the hardness is reduced to approximately 180 HV near the welded joint as shown in Figure 9. This significant reduction in hardness indicates that the combination of high-temperature forging and subsequent welding has caused microstructural softening in the heat-affected zone. Such softening may compromise the local mechanical strength and increase the susceptibility of the welded region to stress concentration, crack initiation, and premature failure under cyclic loading conditions.

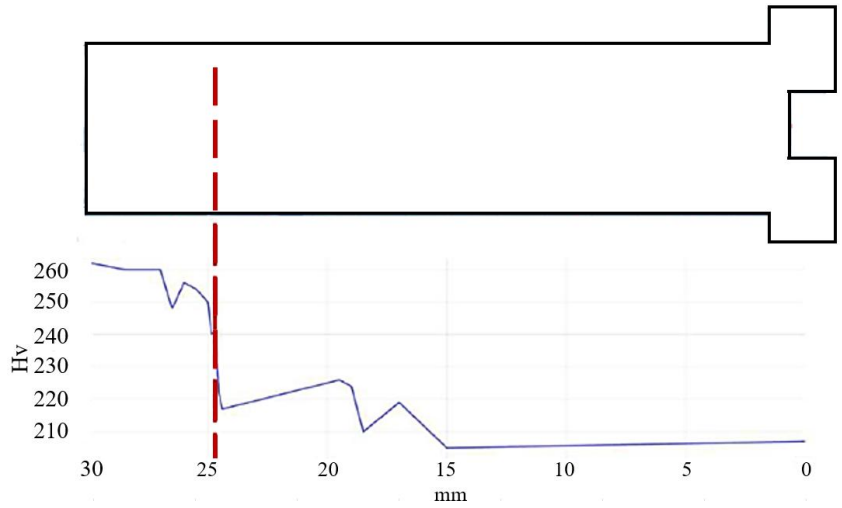

Figure 8. Hardness test results after forging. The dashed box indicates the forged head, vertical dashed line marks the sudden hardness change, located 25mm from the forged head where induction heating ends.

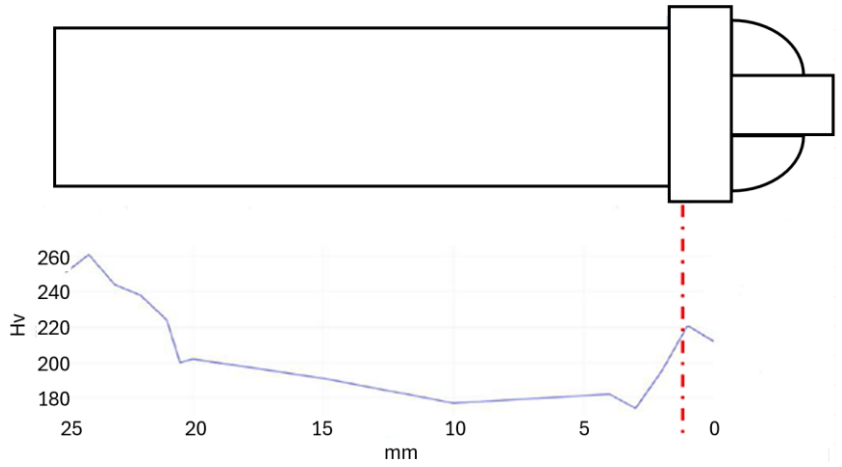

Figure 9. Hardness test results after welding. The vertical dashed line indicates the welding location.

In addition to the potential softening of the screw material caused by heat exposure during forging and welding, and the presence of welding gaps, bending of the scissor jack during lifting may also impose additional stresses on the screw. During lifting, stress is concentrated on the screw head, as shown in Figure 10. This occurs because the screw head is constrained against the pivot: while the head cannot bend, the shaft can, resulting in stress concentration at the head. Figure 10 (right) illustrates the shaft bending and the locations of stress concentration, while Figure 10 (left) shows screw bending observed during an actual test.

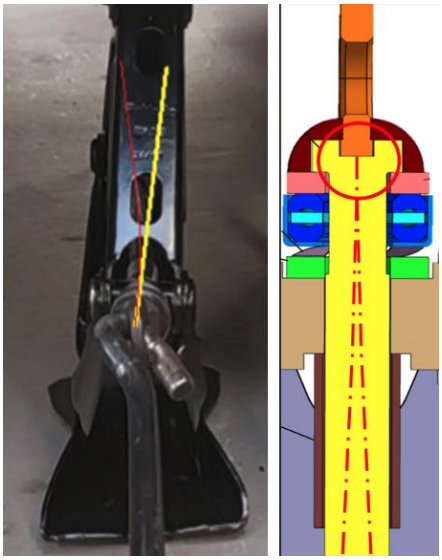

Figure 10. Extreme displacement of screw during vehicle test (yellow line shows the screw head planar face normal, red line shows how the screw bends under load) and stress concentration on the screw head

4. Conclusions

The scissor car jack is a critical component in vehicle maintenance and emergency operations, with the lead screw playing a central role in ensuring safe and reliable lifting. In this study, the failure of the screw during prototype testing was systematically investigated through mechanical testing, microstructural characterization, and design analysis. The results indicated that stress concentrations, microstructural inhomogeneities from hot forging and welding, and geometric weaknesses associated with the welded canal contributed to premature failure.

Based on these findings, targeted design and process improvements were proposed. Modifications to the canal feature, including either increasing its thickness or eliminating it entirely while enlarging the unthreaded section, are expected to reduce stress concentrations and improve fatigue performance. Additionally, post-processing heat treatment is planned to homogenize the microstructure and recover the mechanical strength reduced during forging and welding. Together, these measures offer a clear pathway to improving the durability and reliability of the lead screw, ensuring it can withstand the rigorous demands of its intended application.

5. Acknowledge

The authors sincerely thank the ARIKAN Automotive for their invaluable support throughout the AR-25002 project.

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Fren Balatalarında Alt Tabaka Formülasyonunun Mekanik Özelliklere Etkisi

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ÖZET

Bu çalışmada, fren balatalarının alt tabaka (underlayer) formülasyonu yeniden tasarlanarak, maliyetin düşürülmesi ve mekanik performansın artırılması amaçlanmıştır. Aramid elyaf yerine daha ekonomik ve çevre dostu olan selülozik elyaf kullanılarak geliştirilen yeni formülasyon, dört farklı araç grubu için uygulanmıştır. Üretilen balatalar üzerinde ECE R90 standardına uygun yapışma/kopma (shear) testleri ve ISO 6310 standardına uygun sıkıştırılabilirlik testleri gerçekleştirilmiştir. Kopma testlerinde, alt tabaka kullanılan balatalarda referanslara kıyasla %30'un üzerinde dayanım artışı gözlenmiştir. Sıkıştırılabilirlik testlerinde ise tüm örnekler, hem ortam sıcaklığında hem de 400 °C'de ISO 6310 sınır değerleri içinde kalmıştır. Sonuçlar, alt tabaka katkısının fren balatalarında hem güvenilirliği hem de performansı artırdığını göstermektedir.

Anahtar Kelimeler : Fren Balatası, Alt Tabaka (Underlayer), Kopma Dayanımı, Sıkıştırılabilirlik

The Effect of Underlayer Formulation on the Mechanical Properties of Brake Pads

ABSTRACT

This study aimed to redesign the underlayer formulation of brake pads to reduce costs and improve mechanical performance. A new composition using cellulose fiber, a more economical and eco-friendly alternative to aramid fiber, was applied to four different vehicle groups. Brake pads were tested in accordance with ECE R90 for shear strength and ISO 6310 for compressibility. Shear tests showed that pads with the underlayer exhibited more than a 30% increase in strength compared to reference pads. In compressibility tests, all samples remained within ISO 6310 limits at both ambient and 400°C conditions. The results demonstrate that the modified underlayer formulation enhances both reliability and performance, offering a cost-effective and environmentally sustainable solution for brake pad manufacturing.

Keywords: Brake Pad, Underlayer, Shear Strength, Compressibility

1. Introduction

Vehicles that contain engines—such as cars, motorcycles, wind turbines, and airplanes—require braking systems to decelerate or come to a complete stop. In automobiles, braking is not only about speed reduction but also directly related to driver safety. Therefore, brake pads play a crucial role in controlling vehicle speed. During braking, the pads are exposed to friction and wear, which means the materials selected for their production must be high-performance and durable. The materials used in brake pads are categorized into four main groups: friction modifiers, binders, fillers, and reinforcing materials (Jadhav and Sawant, 2019). These materials are blended in varying proportions to produce composite materials for brake pad manufacturing. A wide range of materials have been identified in the literature for this purpose.

In our previous study, the copper present in brass chips—commonly used in brake pads—was removed due to its negative environmental impact and replaced with ULTIMATE TS material. The physical and chemical properties of the produced brake pads were tested. The test results fell within standard ranges, and an improvement in braking performance was observed. These findings indicated that environmentally friendly alternatives to copper can be effectively used in brake pad production (Dalar et al., 2024).

Juan and his colleagues developed an organic brake pad composite using coconut shell, candlenut shell powders, pineapple fiber, iron sand, carbon, and resin. The composite was pressed using a hydraulic press to form brake pads. Their test results showed reduced wear on the brake pads, leading them to conclude that the service life of the pads had increased (Irawan et al., 2022).

Singh and his team produced six different brake pad composites using rice husk, rice husk ash, and *Grewia optiva* fibers. These composites were evaluated for their tribological performance according to the SAE J2522 standard and analyzed using multi-criteria decision-making methods. The analysis showed that the composite containing rice husk ash had the best friction and wear properties. This demonstrated that agro-waste-based materials could serve as effective and sustainable alternatives in brake pad manufacturing (Singh et al., 2024).

Varriale and colleagues examined the effect of different brake pad components on particle emissions. Their tests revealed that materials containing metal fibers and abrasives emitted significantly more $PM_{2.5}$ and PM_{10} particles compared to those containing aramid fibers and lubricants. This highlights the critical role of brake pad composition in terms of environmental impact (Varriale et al., 2023).

The underlayer in brake pads acts as a crucial link between the friction material and the backing plate. This layer helps to reduce the transfer of heat generated during braking to the metal backing plate, thereby minimizing the risk of thermal damage and extending the life of the pad. Additionally, it enhances the mechanical bonding between the friction material and the plate, preventing separation. The underlayer also contributes to driving comfort by reducing noise and vibration. During the manufacturing process, it helps optimize material usage, contributing to cost-effectiveness. Thus, the underlayer is a vital structural element that directly affects the performance, durability, and user experience of brake pads (Rajaei et al., 2020)

In used brake pads, an unused surface of friction material (pad dust) approximately 3 mm thick typically remains. This residual material represents economic and environmental waste and limits the optimization of brake pad performance. This study aims to develop a cost-effective and mechanically enhanced underlayer formulation to replace this unused portion. As part of this effort, expensive aramid fiber—commonly used in brake pad formulations—was replaced with a more economical and natural alternative: cellulosic fiber. The newly developed underlayer formulation not only offers cost advantages but also demonstrated high shear strength. This formulation was applied to brake pads for four different vehicle types, along with a reference (original) formulation, and industrial-scale production was carried out. The produced brake pads were tested for shear/bonding strength in accordance with ECE R90 regulations and for axial compressibility according to ISO 6310 standards. The results showed that the new underlayer formulation offers both economic benefits and mechanical performance that is comparable to or superior to existing standards.

2. Materials and Method

In the production of brake pads, typically between 10 to 15 different raw materials are used. These materials are classified into four main groups according to their functional properties: friction modifiers, fillers, binders, and reinforcements. Each group has a direct impact on the tribological performance, thermal stability, mechanical strength, and cost-effectiveness of the brake pad. In this study, production was carried out based on the reference formulation provided in Table 1, in order to enable a comparative evaluation of experimental studies.

Table 1. Materials used in the brake pad composition and their functions

Material Name	**Function**
Phenolic resin	Binder
Aramid	Reinforcement
Graphite	Lubricant
Friction dust	Filler
Oxide groups	Abrasive
Steel powder	Abrasive
Petroleum coke	Lubricant

Lime	Filler
Zinc powder	Abrasive
Brass chips	Abrasive
Metal sulfite mixture	Abrasive

In this study, the underlayer composition was reformulated to be more cost-effective, while also improving shear strength performance. The newly developed underlayer formulation aims to provide economic advantages as well as enhance the mechanical bond strength, thereby improving the integrity of the brake pad. The components and ratios of this new formulation are presented in detail in Table 2.

Table 2. Materials used in the underlayer composition and their functions

Material Name	**Function**
Phenolic resin	Binder
Cellulosic fiber	Reinforcement
Graphite	Lubricant
Friction dust	Filler
Oxide groups	Abrasive
Steel powder	Abrasive
Petroleum coke	Lubricant
Lime	Filler
Zinc powder	Abrasive
Grinding dust	Recycled material
Metal sulfite mixture	Abrasive

The first stage of the brake pad manufacturing process involves the preparation of the material mixture. All raw materials included in the formulation were weighed sequentially according to their designated proportions. The mixing process began with the pre-mixing of fiber in the mixer for approximately 4 minutes. This step was performed to prevent fiber agglomeration and to ensure homogeneous dispersion.

Subsequently, all remaining raw materials were added to the mixer, and the mixing process was continued for an additional 6 minutes. The same mixing procedure was applied identically for the underlayer formulation as well.

The production of the brake pads was carried out using the hot-pressing method, which is based on the principles of powder metallurgy. Figures 1 and 2 show the pressing and mixing equipment, respectively.

Figure 1. Pressing equipment

Figure 2. Mixing equipment

In this process, the prepared mixture was placed into molds and pressed at a temperature of 150 °C under a pressure of 8 MPa. This step was applied to ensure homogeneous compaction of the material components and to initiate the pre-curing process.

A total of 96 brake pads were produced:

- 12 reference pads and 12 pads with underlayer were manufactured for each of 4 different vehicle types,
- For each vehicle type, 10 pads were allocated for shear (adhesion) tests, and 2 pads for compressibility tests.

After pressing, the pads underwent a curing process in a furnace. The temperature was gradually increased from 125 °C to 200 °C in 25 °C increments, and the pads were cured for 7 hours. The cured brake pads were tested in accordance with the ECE R90 regulation for shear strength and the ISO 6310 standard for axial compressibility. Figure 3 shows the produced brake pads, while Figure 4 displays the metal plate surface after the shear test.

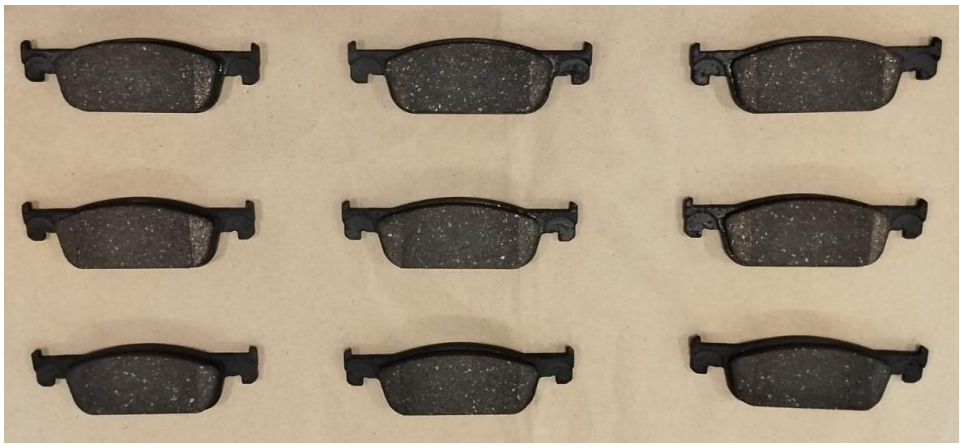

Figure 3. Manufactured brake pads

Figure 4. Shear test result – metal plate surface

3. Results and Discussion

3.1 Shear Test

The reference brake pads and those containing an underlayer were examined using the shear test in order to compare their mechanical strength. Figure 5 presents the shear test results for both sample groups. The data obtained is significant for demonstrating how the use of an underlayer affects the structural integrity of the brake pad. These results were analyzed in detail to evaluate the impact of the underlayer addition on mechanical performance. Figure 5 shows the shear test results for vehicle group 1.

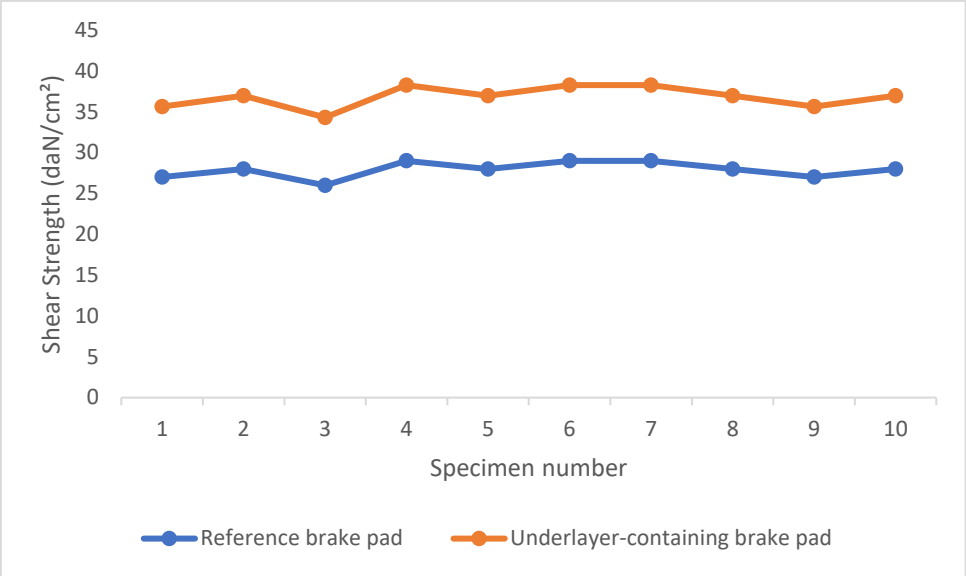

Figure 5. Shear test result of vehicle group 1

The shear test results presented in Figure 5 provide a comparative analysis of the shear strength between the reference pads and the pads containing an underlayer. According to the obtained data, the average shear strength of the pads with underlayer was determined to be 36.8 daN/cm², while the reference pads showed an average value of 27.9 daN/cm². Moreover, it was observed that the measurement values for the underlayer pads were distributed within a narrower range, indicating a more stable and consistent performance. These findings reveal that the use of an underlayer not only improves the average shear strength, but also enhances production consistency. Figure 6 presents the shear test results for vehicle group 2.

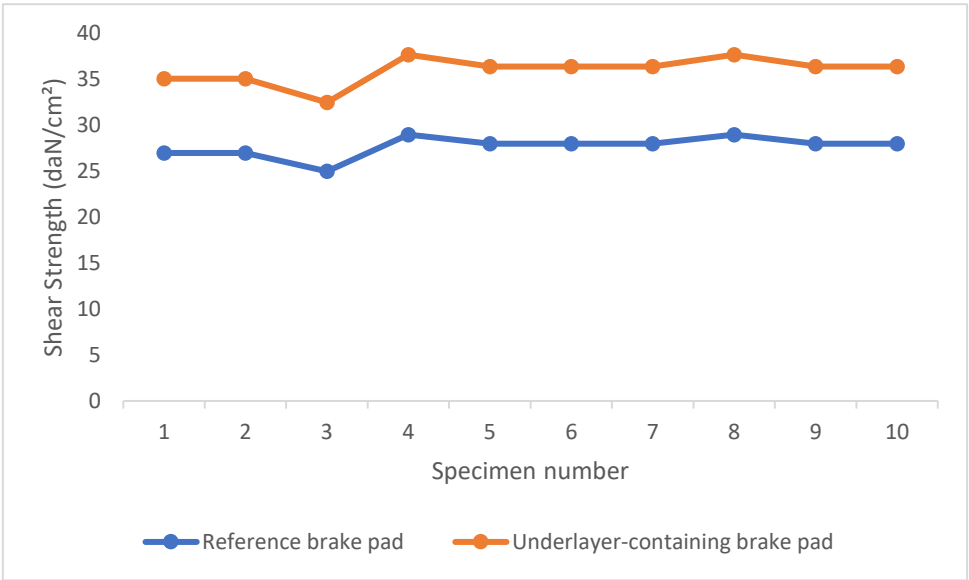

Figure 6. Shear test result of vehicle group 2

The results presented in Figure 6 provide a comparative evaluation of the shear strength between the reference brake pads and those containing an underlayer for vehicle group 2. The findings indicate that the shear strength of the pads with underlayer falls within the range of approximately 35–38 daN/cm², whereas the reference pads remain within the 27–30 daN/cm² range. The consistently higher shear strength observed in all underlayered samples demonstrates that this structure significantly enhances the bonding between the brake pad and the backing plate. Figure 7 shows the shear test results for vehicle group 3.

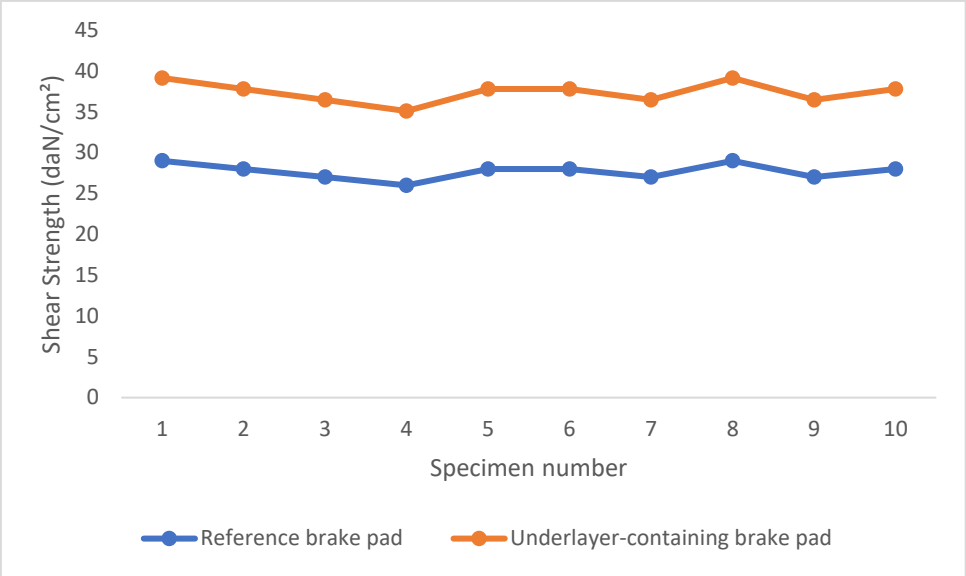

Figure 7. Shear test result of vehicle group 3

The data presented in Figure 7 provide a comparative overview of the shear strength of the reference pads and the pads containing an underlayer for vehicle group 3. According to the results, the shear strength of the underlayered pads ranged between 35–39 daN/cm², whereas the reference pads remained within the 25–30 daN/cm² range. This difference clearly demonstrates that the application of an underlayer significantly contributes to strengthening the bond between the friction material and the backing plate, thereby enhancing adhesion resistance. Figure 8 presents the shear test results for vehicle group 4.

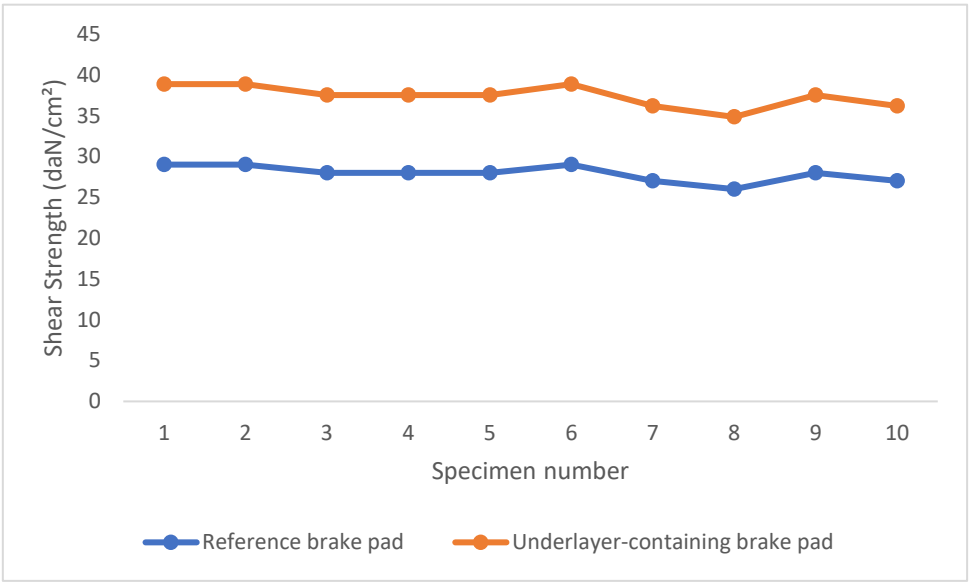

Figure 8. Shear test result of vehicle group 4

The results presented in Figure 8 provide a comparative analysis of the shear strength of the reference pads and the pads containing an underlayer for vehicle group 4. Upon examining the measurements, it was observed that the shear strength of the underlayered pads ranged between 35–40 daN/cm², while the reference pads remained within the 27–30 daN/cm² range. This clearly indicates that the use of an underlayer enhances the adhesion strength between the brake pad and the backing plate, resulting in higher shear resistance.

3.2. Compressibility Test

One of the key parameters in evaluating the mechanical performance of brake pads is their compressibility. In this context, compressibility tests were conducted in accordance with the ISO 6310 standard to determine the extent of deformation that occurs in the brake pads under a specified load. This test measures the change in pad thickness under controlled temperature and load conditions, providing insight into the elastic and plastic deformation behavior of the material. For friction materials operating under thermo-mechanical conditions, having an appropriate compressibility value is a critical design criterion, as it directly affects both braking comfort and noise control. Through this test, the structural integrity and operational adaptability of brake pads with different formulations can be evaluated and compared. In this study, a total of five compressibility tests were performed for each of the four vehicle groups, using brake pads produced in accordance with the ISO 6310 standard. Table 3 presents the compressibility test results.

Table 3. Compressibility test results

	Compressibility (ISO 6310) %									
Sample number:	**1**		**2**		**3**		**4**		**5**	
	Ambient	**Hot (400°C)**	**Ambient**	**Hot (400°C)**	**Ambient**	**Hot (400°C)**	**Ambient**	**Hot (400°C)**	**Ambient**	**Hot (400°C)**
Vehicle group number 1	1.55	2.03	1.60	2.05	1.53	2.04	1.50	2.00	1.53	2,03
Vehicle group number 2	1.56	2.03	1.63	2.04	1.52	2.04	1.49	2.00	1.57	2,13
Vehicle group number 3	1.47	2.05	1.62	2.01	1.57	2.10	1.52	2.02	1.55	2,07
Vehicle group number 4	1.58	2.11	1.56	2.08	1.56	2.07	1.53	2.03	1.56	2,11
ISO 6310: Max. Ambient rate=2,00% Max. Hot rate=5,00%										

4. Conclusions

The shear tests were conducted in accordance with the ECE R90 standard, and the results were systematically evaluated across four different vehicle groups. The findings reveal that brake pads with the underlayer exhibited significantly higher shear strength compared to the reference pads in all groups. Specifically, the use of the underlayer resulted in increases in shear strength of 32% in vehicle group 1, 30% in vehicle group 2, 35% in vehicle group 3, and 34% in vehicle group 4. These results indicate that the underlayer application not only enhances the average strength but also provides a more stable and reliable performance during the manufacturing process. Therefore, it can be concluded that brake pads with the underlayer offer safer, more durable, and standards-compliant usage by improving the adhesion strength between the friction material and the backing plate.

Compressibility tests were performed on samples from four different vehicle groups in accordance with the ISO 6310 standard. Measurements were taken at both ambient temperature and at 400°C (hot), with the results presented in Table 3.

According to the ISO 6310 standard, compressibility values should not exceed 2.00% at ambient temperature and 5.00% at elevated temperature. In the tests conducted, compressibility values at ambient temperature ranged from 1.47% to 1.63% for all vehicle groups, thus remaining below the 2.00% limit. This indicates that the samples possess sufficient rigidity and mechanical strength under normal ambient conditions.

At 400°C, the compressibility values ranged between 2.00% and 2.13%, with no sample exceeding the 5.00% limit. The highest value of 2.13% was observed in sample number 5 from vehicle group 2; however,

this value is still well below the ISO 6310 threshold. These findings demonstrate that the samples maintain their mechanical integrity even under high-temperature conditions.

5. Acknowledge

I would like to sincerely thank Beşer Balata for their valuable collaboration and support throughout the project. The production and testing of the brake pads were successfully carried out at Beşer Balata, enabling reliable and consistent results.

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Microstructural and Chemical Effects of Mechanical Grinding on Magnesium Slag

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ABSTRACT

Magnesium slag (MS), generated as a by-product in the Pidgeon process at approximately 7–8 tons per ton of magnesium metal, represents a significant industrial solid waste with both environmental challenges and valorization potential. Owing to its high CaO and SiO_2–MgO content, MS has attracted increasing attention as a supplementary cementitious material; however, its low intrinsic reactivity and stability issues limit its direct use. In this study, mechanical activation through laboratory-scale ball milling was employed to enhance the reactivity of MS and evaluate its potential as a clinker substitute in cement systems. Portland cement clinker, gypsum, and MS were characterized via XRF analyses, then subjected to controlled grinding and standardized cement testing procedures (TS EN 196-1, TS EN 196-2, TS EN 196-3). Cement mortars containing 30% and 55% MS were prepared, and their setting time, volume stability, water demand, and compressive strength were systematically assessed. The results demonstrated that mechanical activation significantly reduced particle size, increased specific surface area, and induced partial amorphization, thereby improving the hydraulic reactivity of MS. Overall, the study confirms that mechanically activated magnesium slag can be effectively used as a sustainable, technically feasible, and environmentally beneficial additive in cement systems. Its incorporation reduces clinker consumption, lowers CO_2 emissions, and contributes to circular economy strategies in the cement industry, thereby presenting both scientific and industrial value.

Keywords: Magnesium slag, Mechanical activation, Microstructure analysis, Waste based binders

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1. Introduction

In the production of magnesium metal via the Pidgeon process, approximately 7-8 tons of "magnesium slag (MS)" are generated for every 1 ton of Mg [1]. MS, a common industrial solid waste, is widely used in various industrial areas such as cement additives, chemically activated cementitious compounds, fertilisers, calcined porcelains, inorganic fibres and desulfurization processes [2-5]. Literature studies have shown that magnesium slag is primarily utilised in cement and binder systems due to its high CaO and SiO_2–MgO contents. CaO is generally present above 50% in magnesium slag, and β/γ–C_2S (dicalcium silicate) phases, free lime and periclase (MgO) are commonly observed. This phase distribution indicates the potential binder behaviour of MS, but also brings the risks of low specific reactivity and volume stability [6-7]. Literature studies report that iron ore tailings, bauxite residues, and other metallurgical wastes can be effectively activated through mechanical activation, increasing their substitution rates in cement production and significantly contributing to binder performance. In this context, industrial byproducts functionalized through mechanical activation appear to improve cement performance and provide a strategic advantage in terms of sustainable production and reducing environmental burdens [8-12].

MS as a mineral additive or clinker raw material by increasing its reactivity through mechanical activation is considered an environmentally sustainable approach that reduces energy consumption and

CO_2 emissions [6,13]. In this context, mechanical grinding/activation stands out as one of the most effective methods for transforming the microstructural and chemical properties of MS through high-energy ball mills and mechanochemical methods. Studies have reported that mechanical activation reduces particle size, increases specific surface area, decreases crystallinity and partial amorphisation, and consequently increases defect density [11,14]. These changes contribute to releasing reactive Ca–Si sites and forming new nucleation sites for the nucleation of C–S–H and calcium carbonate derivative products during hydration/carbonation processes [15,16]. The resulting fineness and increased reactivity strengthen the binding capacity by increasing MS's hydraulic activity and accelerating the cement matrix's early-age hydration kinetics. Recent studies have shown that significant increases in early-age and ultimate mechanical strengths are achieved by using "modified magnesium slag (MMS)" and also that denser and lower-voidage microstructures are developed [17-18]. In particular, mechanochemical approaches based on ball milling increase the hydration and carbonation rates in slag-added cements, resulting in measurable mechanical gains quickly and optimising binder performance [19].

The primary reason for choosing mechanical activation in this study is to overcome the problems of magnesium slag's low specific reactivity and volume stability, making it a more effective and usable mineral additive in cement. The increased fineness, high surface area, and partial crystallinity achieved through a rise in mechanical activation of the hydraulic activity of magnesium slag accelerate the formation of C–S–H phases during cement hydration [20-21]. Thus, the aim is to improve early-age strengths, densify the microstructure, and enhance long-term mechanical performance. Furthermore, using magnesium slag in cement systems reduces energy costs by lowering natural raw material consumption and contributes to limiting CO_2 emissions through lower clinker requirements. In this context, the study aims to establish a scientific basis for using MS as a high-value-added component that reduces carbon footprint in low-clinker systems by revealing the causal relationships between grinding parameters and cement binder performance.

2. Materials and Methods

The magnesium slag samples used in this study were obtained from the waste site of a magnesium metal production facility established in Eskişehir, Turkey. The PC clinker, natural gypsum, and standard sand used in the production of cement samples were supplied by the Afyon Cement Factory. Chemical analyses of the samples used in cement production were conducted in accordance with TS EN 196-2. An ARL-8680+ model X-ray spectrophotometer was used to determine elemental composition. The chemical analysis results of the raw materials used in the preparation of the cement samples are presented in Table 1.

Table 1. Chemical analysis results of raw materials used in cement production

Components	PC Clinker	Gypsum	Magnesium Slag
	%	%	%
SiO_2	21.38	5.50	26.90
Al_2O_3	5.20	1.20	0.39
Fe_2O_3	3.79	0.5	3.48
CaO	66.30	39.0	62.85
MgO	1.80	1.0	3.60
SO_3	0.48	43.0	0.0
K_2O	0.75	0.2	0.03
Na_2O	0.33	0.1	0.04
Loi	0.28	7.50	11.50

As shown in Figure 2.1, cement raw materials were initially subjected to a natural air-drying process. These raw materials are directly air-dried and incorporated into the production process without undergoing any thermal drying steps. Therefore, the raw materials contain a certain amount of moisture.

Preliminary studies have determined that air-dried clinker contains 0.1% moisture, magnesium slag contains 0.1%, and gypsum contains 1.8%.

Figure 2.1 Portland cement raw materials used in grinding experiments

Before commencing the grinding experiments, the raw materials were passed through a jaw crusher and a roller crusher, respectively, to reduce particle sizes below 8 mm. Afterwards, the raw materials were sieved through a 1 mm screen. After the under-sieve fraction was separated, only the over-sieve material was used in the grinding experiments. This method prevented the direct feeding of material below 1 mm into the mill, ensuring a homogeneous and controlled feed in each experiment. Thus, the particle sizes of the raw materials used in the grinding experiments were -8 + 1 mm (d80 ≈ 6 mm), resulting in a narrower distribution.

The fraction in question was subjected to grinding times of 4, 8, 12, 15, and 30 minutes in the laboratory-scale ball mill shown in Figure 2.2. Dry sieve analyses were performed after the grinding processes, and undersieve distribution curves were generated accordingly. The primary objective in grinding cement raw materials is to meet the particle size requirements sought in the cement production process. In this context, it has been considered a necessary criterion for standard cement production: at least 80% of the final product is below 75 µm (0.075 mm).

Figure 2.2 Laboratory scale sieve device, jaw crusher and ball mill used in the studies

In this study, blended cement samples were prepared by substituting magnesium slag at 30% and 50% ratios to investigate the usability of magnesium slag as an additive in cement production. Portland cement clinker and gypsum were weighed per TS EN 197-1 "Cement - Part 1: General Cements - Composition, Properties and Suitability Criteria" and mixed homogeneously with magnesium slag in the determined proportions. The setting times of the prepared cement samples were determined using a Vicat apparatus in accordance with TS EN 196-3; the beginning and end of setting were measured. Volumetric expansion tests were also conducted using the Le Chatelier method within the scope of TS EN 196-3, thus evaluating the volume stability of the samples. A standard consistency test was performed to determine the water requirement, and workability properties were determined. Mortar samples prepared for mechanical properties were produced per TS EN 196-1 "Cement Testing Methods - Part 1: Determination of Strength," stored under curing conditions, and subjected to compressive strength tests at ages 2, 7, and 28 days. All

experimental studies were conducted to determine the effects of magnesium slag addition on hydration behaviour, volumetric stability, and compressive strength development.

3. Results and discussions

3.1. Effect of Mechanical Activation Time on Grain Size in Cement Raw Materials

The grinding experiments carried out after drying the clinker raw material in the oven were ground in a ball mill for different times of 4, 8, 12, 15 and 30 minutes, and the grain size curves of the products were drawn. The cumulative under-sieve curves corresponding to these grinding times are shown in Figure 3.1. In cement technology, sufficient fineness of clinker grinding, especially a d_{80} value below 75 µm, is considered a critical parameter regarding the hydration kinetics, early strength development and binder performance of the final cement [22-24]. It is emphasised in the literature that the increase in the specific surface area of finely ground clinker significantly increases the hydration rate of the C_3S phase, thus providing high early strength [25-26]. However, it has been reported that insufficiently finely ground clinker causes irregularities in the setting time and limits the strength development [27-28]. The results obtained in this study are consistent with the literature, with the clinker d_{80} value decreasing to below 75 µm after approximately 30 minutes of grinding. This demonstrates the decisive role of grinding time in particle fineness and further demonstrates the importance of optimising energy consumption and product performance in the cement industry.

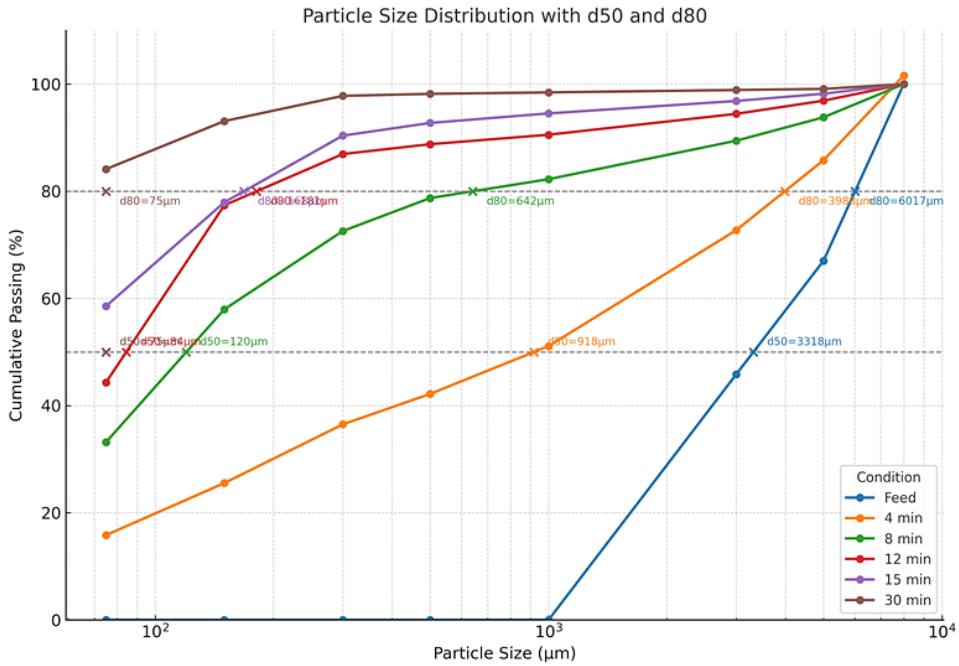

Figure 3.1 The relationship between clinker particle size distribution and grinding time

Figure 3.1 shows the particle size distributions obtained by grinding clinker for different durations. It is clearly seen that cumulative undersize values increase as grinding time increases, meaning the material becomes finer. The starting material, the feed, exhibits a relatively coarse-grained structure, with a significant portion of particles remaining above 1000 microns. Although significant fineness occurs when grinding is continued for four minutes, this time is insufficient for the clinker to reach a fineness suitable for cement production. Fineness becomes more pronounced at eight minutes of grinding, but the particle distribution still exhibits a wide range. At twelve and fifteen minutes of grinding, cumulative undersize values reach 80–90%, indicating that the clinker is approaching a fineness level suitable for cement. After thirty minutes of grinding, almost all the material falls below 100 microns, resulting in a fine fraction exceeding 95%. While this provides a relatively high fineness, it may not always be preferred in practice because it increases energy consumption, and excessive fineness can negatively affect the cement's

setting time and hydration behaviour. An examination of Figure 3.1 generally reveals that the particle size distribution narrows with increasing grinding time, and the fine fraction decreases significantly.

After drying the magnesium slag in the oven, different grinding times of 4, 8, 12, 15, and 30 minutes were applied in the ball mill, respectively, and the particle size distributions of the resulting products were plotted. The cumulative under-sieve curves corresponding to these grinding times are shown in Figure 3.2. As can be clearly seen from the figure, only approximately 8 minutes of grinding time is sufficient for the magnesium slag to reach a d_{80} value below 75 µm. This result shows that the mechanical degradability of magnesium slag is high and can be ground approximately 3.5 times faster to achieve the desired optimum fineness compared to clinker, a traditional cement raw material.

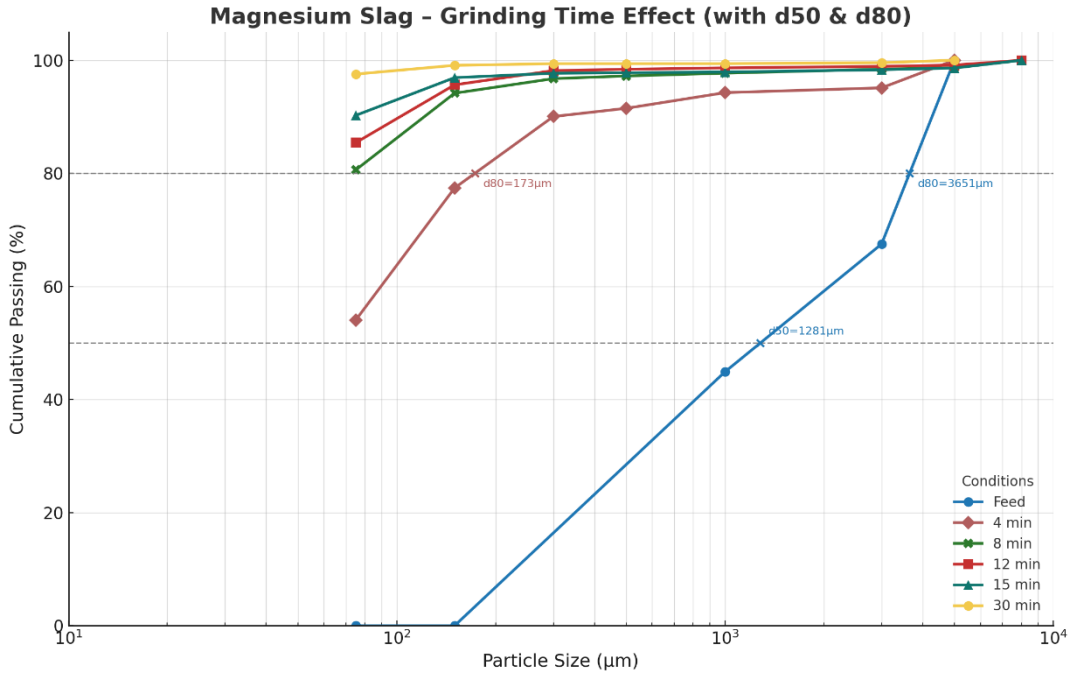

Figure 3.2. The relationship between the grain size distribution of magnesium slag and grinding time.

The literature states that materials with high friability are generally characterised by a low work index and a high grindability coefficient (HGI) [36-38]. In this context, the ability of magnesium slag to reach the desired fineness in a short time demonstrates that this material is advantageous in terms of energy consumption, meaning that it can be reduced to target sizes with lower specific energy requirements during the grinding process. Furthermore, its rapid friability indicates that magnesium slag can provide significant economic and environmental advantages as a potential pozzolanic or mineral additive. Thus, results were consistent with the fundamental goals emphasised in the literature [22-24] of reducing energy costs in cement production processes, reducing CO_2 emissions, and sustainably utilising industrial by-products. After drying the gypsum raw material in an oven, different grinding times of 4, 8, 12, 15, and 30 minutes were applied in a ball mill, and the particle size distributions of the resulting products were plotted. The cumulative sieve curves corresponding to these grinding times are shown in Figure 3.3. Keeping the d_{80} size of gypsum, one of the cement raw materials, below 75 µm is of great importance, especially for increasing the effectiveness of Portland cement in regulating the setting time [29]. As presented in Figure 3.3, it was determined that despite approximately 30 minutes of grinding, the particle size of gypsum could not be reduced below 75 µm. This finding indicates that beyond a certain duration, the grindability of the material reaches a limitation, restricting further size reduction.

In the literature, the grinding behaviour of gypsum varies depending on both its mineralogical structure and crystal water content; it is generally reported to be relatively more friable due to its lower hardness and lower value on the Mohs scale compared to other raw materials such as limestone and clay [30]. However, the grinding fineness of gypsum is a critical parameter not only in terms of mechanical energy consumption but also in terms of cement hydration mechanisms. Gypsum that has not reached

sufficient fineness cannot prevent the uncontrolled hydration of the C_3A phase. At the same time, excessively finely ground gypsum, due to its high solubility, can be consumed quickly, leading to imbalances in setting time [31].

In this context, the experimental results show that gypsum reaches the desired fineness after approximately 30 minutes of grinding, thus achieving an optimal balance between energy consumption and performance. This ensures process efficiency in cement production and fulfils the functionality defined in the literature regarding setting control. SEM images of the microstructures of clinker and magnesium slag as a result of mechanical activation are given in Figure 3.4.

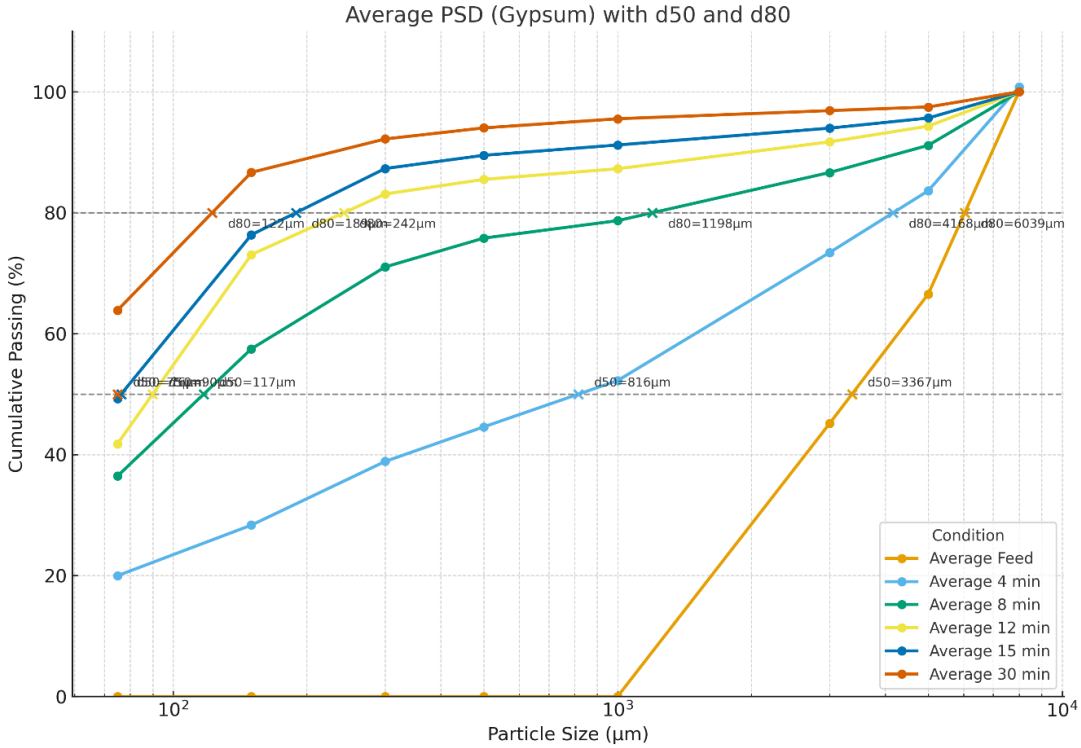

Figure 3.3. The relationship between the particle size distribution of gypsum and grinding time.

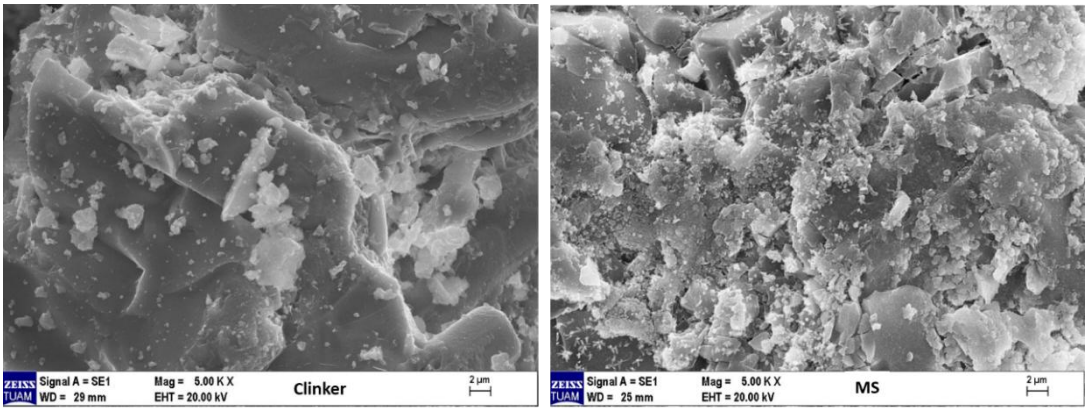

Figure 3.4 SEM images of clinker and magnesium slag after mechanical activation

3.2. Hydraulic Properties

Cements containing magnesium slag exhibit different behaviours during the hydration process. At 30% magnesium slag replacement, clinker phases (especially C_3S and C_2S) still dominate, allowing hydration reactions to proceed effectively. At this rate, the slag's hydraulic and partial pozzolanic properties come

into play, supporting the formation of the C–S–H gel. Furthermore, adding magnesium and aluminium ions causes modifications to the C–S–H structure, while the formation of hydrotalcite-like phases refines the pore structure [11,23-24]. Thus, the heat of hydration is more controlled compred to pure Portland cement, increasing product durability.

In cements containing 55% magnesium slag, the significant decrease in the clinker content results in a significant decrease in the hydration rate. Initial hydration reactions occur more slowly, setting times are extended, and the early-age hydration temperature decreases. This composition primarily consists of M–S–H (magnesium silicate hydrate), hydrotalcite-like phases, and carbonate derivatives. Although hydration is limited at an early age, this provides an advantage in reducing the risk of thermal cracks in mass concrete applications due to the low heat of hydration [32,33]. The literature has also reported that high slag replacement slows down hydration kinetics but improves pore structure in the long term [34].

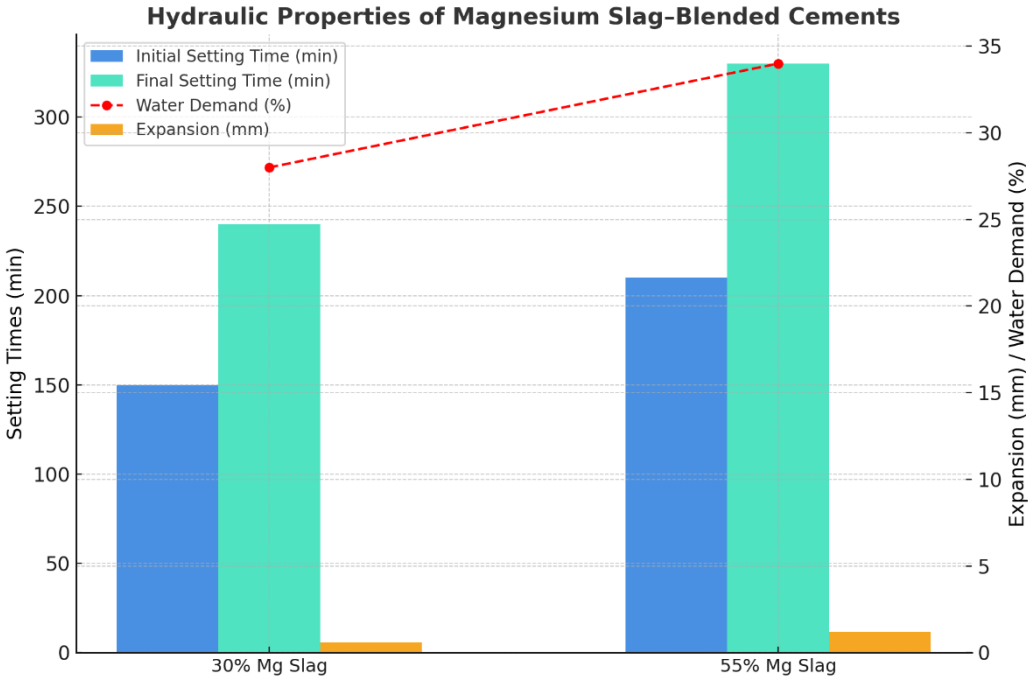

Figure 3.5 Hydraulic properties of cements produced with MS

According to Figure 3.5, the hydraulic properties of magnesium slag-added cements vary significantly depending on the additive content. For cement containing 30% magnesium slag, the initial setting time is approximately 150 minutes, and the final setting time is around 240 minutes. In comparison, for cement containing 55% slag, these values increase to 210 and 330 minutes, respectively. This indicates that high slag replacement slows the rate of hydration and prolongs setting times. Furthermore, volumetric expansion increases from 0.6 mm for 30% slag cement to 1.2 mm for 55% slag cement, meaning that a higher slag content negatively impacts volume stability. Regarding water requirement, the value increases from approximately 28% for 30% slag cement to 34% for 55% slag cement. These results show that as the magnesium slag ratio increases, the cement requires more water, the setting times are significantly prolonged, and the expansion tendency increases, thus indicating that careful design should be made regarding workability and volume stability in high-substitution systems.

3.3 Mechanical Properties

Regarding mechanical properties, cements containing 30% magnesium slag exhibit strengths similar to or slightly lower than those of Portland cement at early ages (Figure 3.6). However, strength values increase significantly after 28 days, especially in the long term (90 days and beyond), surpassing the

control cement's. This is due to both the activation of the slag's pozzolanic reactions over time and the filling of voids by microfilling [34].

In cements containing 55% magnesium slag, however, early-age strength development is significantly weaker. This is due to the limited formation of C_3S-derived hydration products due to the low clinker content [34,35]. The 28-day strength is generally below that of standard Portland cement, but a slight increase is observed in the long term. However, the mechanical performance of these cements with a high slag content remains lower than that of mixtures containing 30%. For this reason, cements with 55% magnesium slag additive are unsuitable for structures requiring high strength. However, they can be used more in mass concrete applications, low-temperature, or environmental durability areas.

When the compressive strength results of pure Portland cement (OPC) and 30% and 55% magnesium slag replacement cements are compared, it is shown that early age strengths decrease with increasing magnesium slag ratio. However, the 30% replacement cement reaches values close to OPC in 28 days.

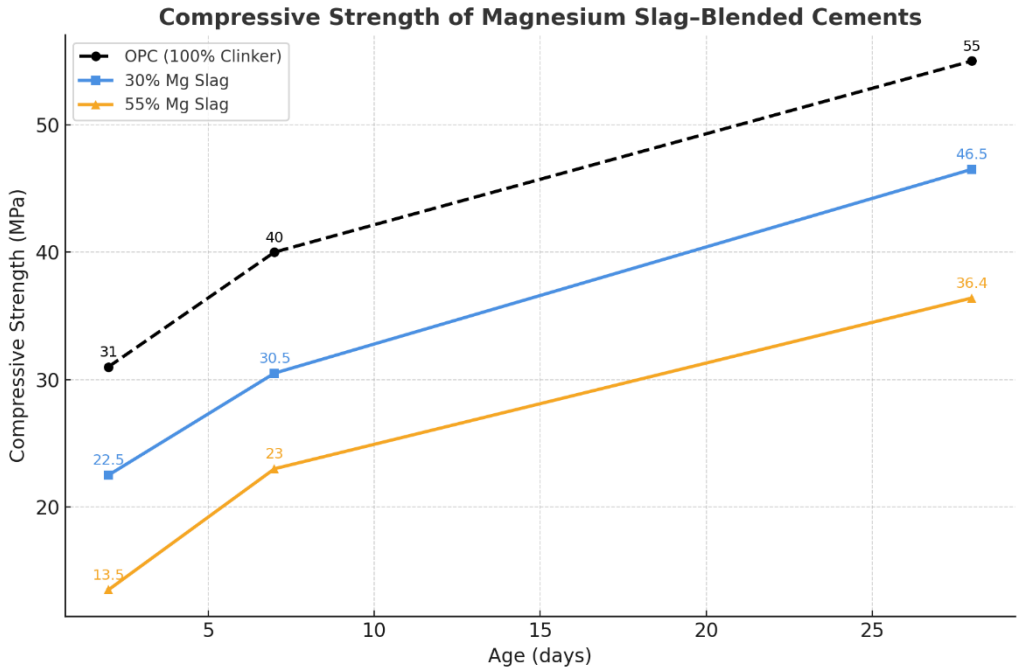

Figure 3.6. Compressive strength development of magnesium slag added cements.

4. Conclusion

The findings obtained within the scope of this study revealed that the hydraulic reactivity of ground magnesium slag with mechanical activation increases due to grain size refinement, provides acceptable values in setting time and volume stability at 30% and 55% substitution rates, and supports the development of compressive strength especially at 30% use, and is a sustainable, environmentally advantageous and technically feasible additive material in cement systems. Furthermore, the results indicate that the enhanced surface area and partial amorphization induced by mechanical activation accelerate hydration kinetics and promote denser microstructural formation, leading to improved long-term performance. The incorporation of magnesium slag not only reduces clinker demand but also contributes to lowering energy consumption and CO_2 emissions, aligning with global sustainability goals in the cement industry. In addition, the study highlights that while higher substitution levels may extend setting times and reduce early-age strength, they offer potential benefits in applications such as mass concretes where low hydration heat is desirable. Overall, the systematic evaluation underscores the potential of mechanically activated magnesium slag as a high-value supplementary cementitious material that bridges both performance enhancement and environmental responsibility.

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Characterization of Waste-Derived Foam Ceramics Using Red Mud and Alumina Coating Wastes

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ÖZET

Bu çalışma, endüstriyel atık malzemeleri (özellikle kırmızı çamur ve alümina kaplama atıkları) alternatif hammadde olarak kullanarak sürdürülebilir köpük seramiklerinin geliştirilmesini araştırmaktadır. Silisyum karbür (SiC), hem standart hem de atık bazlı formülasyonlarda köpük oluşturucu madde olarak kullanılmıştır. Karışımlar, su ve sodyum silikat ile ıslak öğütme ile hazırlanmış, ardından kurutma, granülasyon ve kontrollü koşullar altında sinterleme aşamaları takip edilmiştir. Hammaddelerin ve elde edilen karışımların kimyasal bileşimleri X-ışını floresans (XRF) analizi kullanılarak belirlenmiştir. Sinterleme sonrası, köpük seramik tabletlerin fiziksel özellikleri (yığın yoğunluğu, ağırlık ve yükseklik) değerlendirilmiştir. Mikroskobik incelemeler, kırmızı çamur bazlı numunelerde daha büyük ve düzensiz gözenekler, alümina kaplama atığı bazlı numunelerde daha küçük ve standarda benzer gözenek dağılımları ve standart formülasyonda ise ince, homojen gözenekler ortaya koymuştur. Bu farklılıklar, atıkların oksit içeriğine, pişirme sıcaklığındaki erime davranışına ve gaz salınımının etkisine bağlanmıştır. Sonuçlar, kırmızı çamur ve alümina kaplama atıklarının köpük seramik üretiminde belirli oranlara kadar (%5 ağırlıkça ve %7 ağırlıkça) kullanımının mümkün olduğunu, geleneksel formülasyonlara benzer gözeneklilik ve işlevsel performans sağladığını, seramik üretiminde atık değerlendirmesini ve kaynak verimliliğini desteklediğini göstermektedir.

Anahtar Kelimeler : Köpük seramikler, atık, kırmızı çamur, hafif malzemeler.

ABSTRACT

This study investigates the development of sustainable foam ceramics utilizing industrial waste materials—specifically red mud and alumina coating waste—as alternative raw materials. Silicon carbide (SiC) was employed as a foaming agent in both standard and waste-based formulations. The mixtures were prepared by wet milling with water and sodium silicate, followed by drying, granulation, and sintering under controlled conditions. The chemical compositions of the raw materials and resulting mixtures were determined using X-ray fluorescence (XRF) analysis. Post-sintering, the physical characteristics of foam ceramic tablets—including bulk density, weight, and height—were evaluated. Microscopic examinations revealed larger and irregular pores in red mud-based specimens, smaller and more standard-like pore distributions in alumina coating waste-based specimens, and fine, homogeneous pores in the standard formulation. These differences were attributed to the oxide contents of the wastes, melting behavior at firing temperature, and the effect of gas release. The results demonstrate that the use of red mud and alumina coating wastes in foam ceramic production is feasible up to certain proportions (5 wt.% and 7 wt.%), providing comparable

porosity and functional performance to conventional formulations, while supporting waste valorization and resource efficiency in ceramic manufacturing.

Keywords: Foam ceramics, waste, red-mud, light-weight materials.

1. Introduction

Porous ceramics are widely employed in various structural and functional applications owing to their distinctive characteristics such as low density, high specific surface area, good thermal insulation, chemical durability, and controlled porosity [1-2]. These materials offer significant advantages, particularly in applications where weight reduction is critical, thereby enabling the development of lightweight and easy-to-install products for the construction industry [3-4]

The developed porous foam ceramic represents an innovative solution that simultaneously addresses the needs for sustainability and functionality in building materials. Although porous ceramics have been extensively studied in the context of sound and thermal insulation, filtration, and catalytic support in the construction sector [3, 5] the integration of porous foam ceramics with structural ceramics in a layered composite form remains a relatively underexplored area, presenting significant potential for novelty and innovation

In this context, various fabrication techniques—such as direct foaming, particle-stabilized foaming, and organic foam impregnation—allow the production of porous ceramics with high porosity levels (typically >80%), while offering precise control over their mechanical and physical properties [4, 6-7]. The integration of such porous frameworks with porcelain tiles enables the development of multilayered, multifunctional products that go beyond conventional tile production methods

In the field of structural ceramics, porcelain tiles are considered high-tech products with superior technical properties compared to standard floor and wall tiles. Their low water absorption and excellent resistance to acids and staining make them particularly suitable for outdoor applications [8]. However, compared to other types of tiles, porcelain tiles used as structural ceramics in residential or hotel garden installations have relatively higher density. This increased density poses challenges during transportation to the target location and during on-site installation. Additionally, the higher fuel consumption associated with transporting heavier materials leads to increased product costs. Furthermore, when users wish to replace the tiles, the weight of the products requires greater physical effort, making the process more labor-intensive and inconvenient. Since low-durability surface materials such as wood or carpet cannot be used in outdoor environments, there is a growing need for the development of innovative products that can address this limitation in exterior applications.

This study focuses on the development of double-layered tiles designed for outdoor use, consisting of a highly porous foam ceramic base and a porcelain surface layer. The resulting structure integrates the low-density and insulating properties of the foam ceramic with the high mechanical strength and aesthetic surface quality of porcelain. This combination not only offers material savings for manufacturers but also enhances user convenience by reducing transportation and installation costs. Due to their lightweight nature, these tiles can be installed by end-users without professional assistance, contributing to overall product accessibility. Thanks to its lightweight nature, this new product can be easily installed and has been designed to a level that allows users to carry out the installation themselves without the need for professional assistance. Within the scope of this study, the fabrication of laminated tiles combining foam ceramic and porcelain layers, the relationship between microstructure and mechanical performance, and the potential advantages of these novel products will be comprehensively investigated.

2. Materials and Method

In this study, the production of foam ceramics was carried out using silicon carbide (SiC) as the primary foaming agent. Silicon carbide (SiC) is preferred in foam ceramic production due to its low coefficient of thermal expansion, high thermal conductivity, and excellent mechanical strength [9]. Eight distinct formulations were prepared: a standard batch utilizing synthetic SiC, and experimental batches (K3-K5-K7 and A3, A5, A7, A8) incorporating waste-derived SiC powder as a sustainable alternative. Red mud waste (RMW) supplied from Azeraluminium LLC factory (Azerbaijan) and alumina coating wastes (ACW) from

factory Bilecik Iron Steel Factory (Bilecik/Turkiye) were used in new experimental batches. Alumina production, primarily through the Bayer process, generates significant amounts of solid residues. The most prominent by-product is red mud, some highly alkaline waste rich in iron oxides, alumina, silica, and trace metals. In iron–steel production, alumina-based coating (lining or coating) materials are widely applied to protect refractory linings and mold surfaces during casting. These coatings act as a barrier between molten steel and the mold, preventing chemical reactions, metal penetration, and thermal shock damage. After each casting cycle, the undercoat layer loses its protective function and is discharged as solid waste together with other refractory residues. This alumina-rich waste, mainly composed of Al_2O_3 with minor SiO_2 and other oxides, is generated in considerable amounts in large-scale operations. The chemical compositions of the waste materials used in the foam ceramic mixtures were determined using an X-ray fluorescence (XRF) spectrometer (Rigaku ZSX Primus model). The result of the chemical analysis is presented in Table 1. The formulations developed from these materials, along with their corresponding codes, are summarized in Table 2. Due to its high alkali content, red mud waste was incorporated into the formulations as a partial replacement for albite, while alumina coating waste was used as a substitute for clay based on its aluminum oxide content. The crystalline phase compositions of the waste materials used in the study were analyzed using an X-ray fluorescence (XRF) spectrometer and illustrated in Figs1-2. Based on the phase analysis of the wastes, hematite (Fe2O3), quartz (SiO2), albite (Al 1.02 Ca 0.02 Na 0.98 Si 2.98) and gibbsite (Al(OH)3) were identified as the dominant phases in the red mud waste, while corundum (Al2O3), analcime (Al 1.80 H 1.8 Na 1.71 Si 4.19), boggsite (Al 2.1 Ca 0.67H 4.78 O25.31 Si 9.9) and periclase (MgO) were observed in the alumina coating waste. The presence of these phases is consistent with the results of the corresponding chemical compositions. All batches were initially prepared by mixing 500 g of raw materials with 50 wt.% water and 1 wt.% sodium silicate as a binder. Due to its high alkali content, red mud waste was incorporated into the formulations as a partial replacement for albite, while alumina coating waste was used as a substitute for clay based on its aluminum oxide content. The mixtures were milled in laboratory-scale jet mills for 30 minutes to obtain homogeneous ceramic slurries. The resulting slurries were then oven-dried at 100 °C and sieved to obtain granulated powders suitable for shaping. The granulated materials were uniaxially pressed into disc-shaped pellets and sintered in a Protherm PLF 130/25 muffle furnace at 1250 °C for 30 minutes. Following the firing process, the porosity of the tablets and cross-sections of the samples was examined using an optical microscope.

Table 1. The chemical analysis of waste materials (RMW, ACW)

Oxides	**RMW**	**ACW**
Na_2O	3.39	0.13
MgO	0.33	14.50
Al_2O_3	19.43	83.46
SiO_2	14.81	0.60
P_2O_5	0.19	0.06
SO_3	1.24	0.01
K_2O	0.32	0.02
CaO	1.17	0.39
Fe_2O_3	40.93	0.49
TiO_2	5.68	-
Cr_2O_3	0.43	-
MnO	0.16	-
L.O.I.	11.86	0.29

Table 2. Standard and foam ceramic recipes

	Clays	Albite	Calcite	Pegmatite	SiC	RMW	ACW	Silica sand
STD	50	20	2	28	0.28	-	-	-
K-3	50	17	2	28	0.28	3	-	-
K-5	50	15	2	28	0.28	5	-	-
K-7	50	13	2	28	0.28	7	-	-
A-3	47	20	2	28	0.28	-	3	-
A-5	45	20	2	28	0.28	-	5	-
A-7	43	20	2	28	0.28	-	7	-
A-8	40	20	2	28	0.28	-	7	3

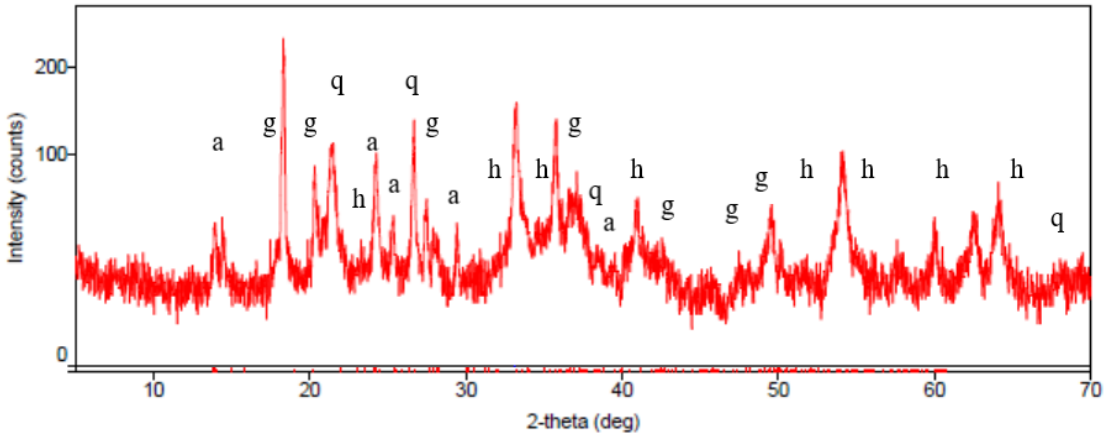

Figure 1. Phase analysis of red mud waste (h: hematite, q: quartz, a: albite, g: gibbsite)

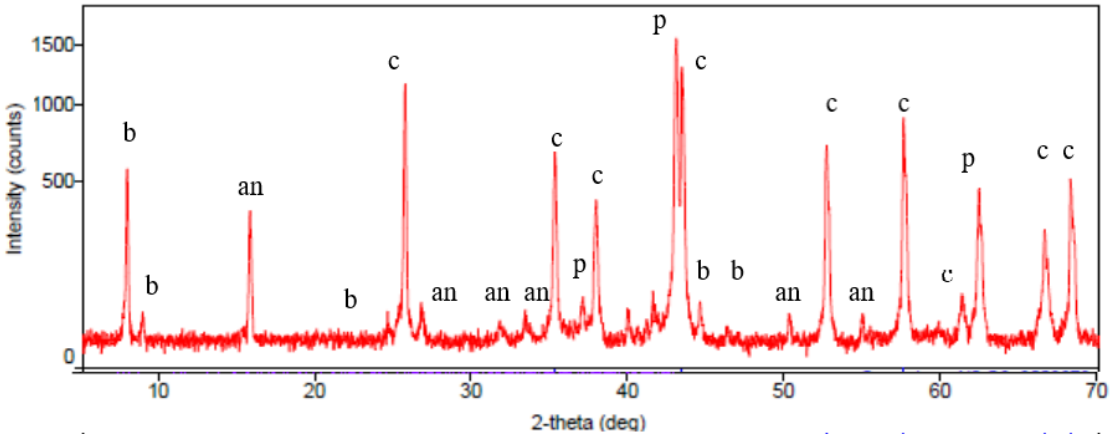

Figure 2. Phase analysis of alumina coating waste (c:corundum, b:boggsite, an:analcime, p:periclase)

3. Results and Discussion

In this study, red mud waste and alumina coating waste were successfully utilized as alternative raw materials for the production of foam ceramics. The incorporation of these industrial by-products into ceramic matrices aligns with previous research demonstrating the feasibility of solid waste valorization in foam ceramic applications [3,7]. The chemical compositions of the formulated mixtures, as determined by X-ray fluorescence (XRF) analysis, are presented in Table 3. The physical characteristics of the sintered foam ceramic tablets, including height, weight, and bulk density, are summarized in Table 4. Based on the results, the incorporation of red mud (K-series) led to the development of larger pore sizes compared to the standard formulation. Although the bulk density values of these samples were slightly higher than the standard, this can be explained by the presence of fewer but coarser pores, combined with the fluxing

effect of Fe_2O_3 and alkali oxides that enhanced local densification during sintering. In contrast, the alumina coating waste (A-series) resulted in smaller and more homogeneously distributed pores. This reduction in pore size limited overall porosity, leading to a noticeable increase in bulk density, particularly in sample A-5. The mechanical strength of A-series samples remained comparable to or slightly higher than the standard, owing to the stabilizing influence of Al_2O_3 during sintering. On the other hand, the K-series samples showed strength values similar to the standard, with minor variations that can be attributed to the higher alkali and iron oxide contents of red mud. These findings highlight the distinct roles of the two waste types: red mud promotes pore coarsening with moderate effects on density, while alumina coating waste suppresses porosity, yielding denser and mechanically stable foam ceramics.

Table 3. The chemical compositions of the prepared mixtures

	STD	K-3	K-5	K-7	K-8	A-3	A-5	A-7	A-8
LOI	9.02	9.36	9.58	9.81	9.84	8.79	8.63	8.48	8.28
SiO_2	62.88	61.17	60.03	58.89	59.22	60.95	59.67	58.39	59.26
Al_2O_3	16.30	16.41	16.48	16.56	16.48	18.17	19.42	20.67	20.16
Fe_2O_3	1.41	2.63	3.45	4.26	4.21	1.37	1.34	1.32	1.26
TiO_2	0.52	0.68	0.79	0.90	0.88	0.49	0.47	0.45	0.42
CaO	1.96	1.97	1.98	1.99	1.98	1.96	1.97	1.97	1.97
MgO	2.62	2.61	2.61	2.61	2.61	3.04	3.32	3.60	3.58
Na_2O	3.03	2.84	2.72	2.59	2.53	3.02	3.01	3.01	3.00
K_2O	2.10	2.10	2.10	2.09	1.98	2.04	2.00	1.95	1.89
P_2O_5	0.06	0.06	0.06	0.06	0.07	0.06	0.06	0.06	0.06
SO_3	0.04	0.07	0.10	0.12	0.13	0.04	0.04	0.04	0.04
MnO	0.01	0.02	0.02	0.02	0.03	0.01	0.01	0.01	0.01
Cr_2O_3	0.00	0.01	0.02	0.03	0.03	0.00	0.00	0.00	0.00

Table 4. Properties of post-sintering foam ceramic tablets

Properties	STD	K-3	K-5	K-7	A-3	A-5	A-7	A-8
Height(mm)	21.60	19.40	19.10	20.00	20.00	20.60	19.00	20.20
Diameter (mm)	72.30	75.40	76.20	77.10	74.30	73.00	72.20	75.20
Weight (g)	29.36	28.11	27.65	28.74	27.77	28.24	28.78	28.59
Density (g/cm^3)	0.403	0.418	0.443	0.439	0.451	0.540	0.418	0.456
Strength (N/cm^2)	13.81	-	-	13.76	-	-	-	13.79

Post-sintering tablet and cross-sectional images revealed that both waste-derived formulations led to the formation of porous structures typical of foam ceramics (Figs3-4). Optical microscopy (NSZ-606 Zoom Stereo Microscopy) of the sectioned samples confirmed the presence of interconnected pores distributed relatively uniformly across the matrix. The red mud waste-based samples exhibited a slightly coarser pore structure compared to those prepared with alumina coating waste, which may be attributed to differences in fluxing oxide, iron oxide content and phase composition of the wastes. In the cross-sectional evaluations (Figure 4) of the foam ceramic samples containing red mud waste, a noticeable shrinkage was observed. This phenomenon is likely associated with the high alkali and iron oxide content of the red mud, which may reduce the melt viscosity during sintering and promote densification in localized regions.

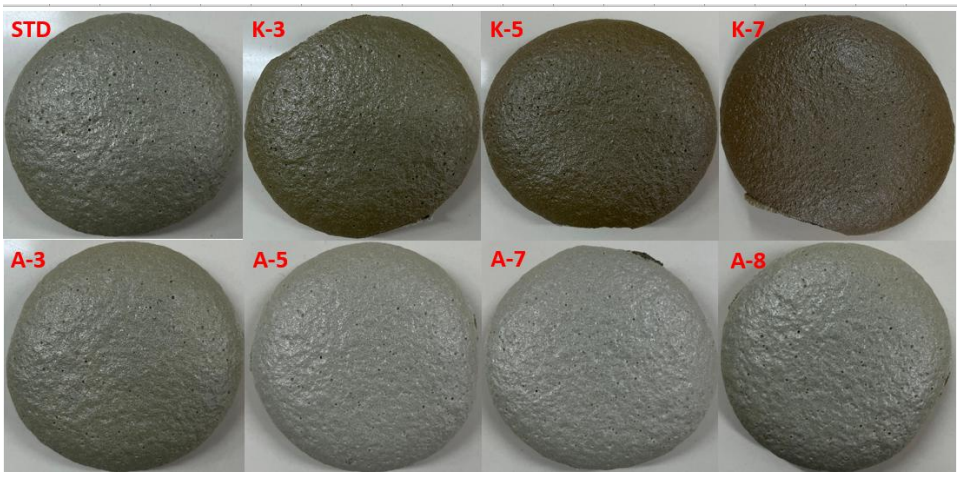

Figure 3. Post-sintering tablet images of foam ceramics

In the foam ceramic samples incorporating alumina coating waste, cross-sectional and pore morphology observations revealed structural features comparable to those of the standard formulation. This similarity is likely attributed to the stabilizing effect of the high Al_2O_3 content in the waste, which enhances the viscosity of the melt phase during sintering and supports the formation of a more uniform and controlled porous structure. Additionally, the lower content of fluxing oxides in the alumina coating waste, relative to red mud, likely contributes to reduced melt fluidity, thereby minimizing pore coarsening and promoting structural integrity throughout the foamed body [4].

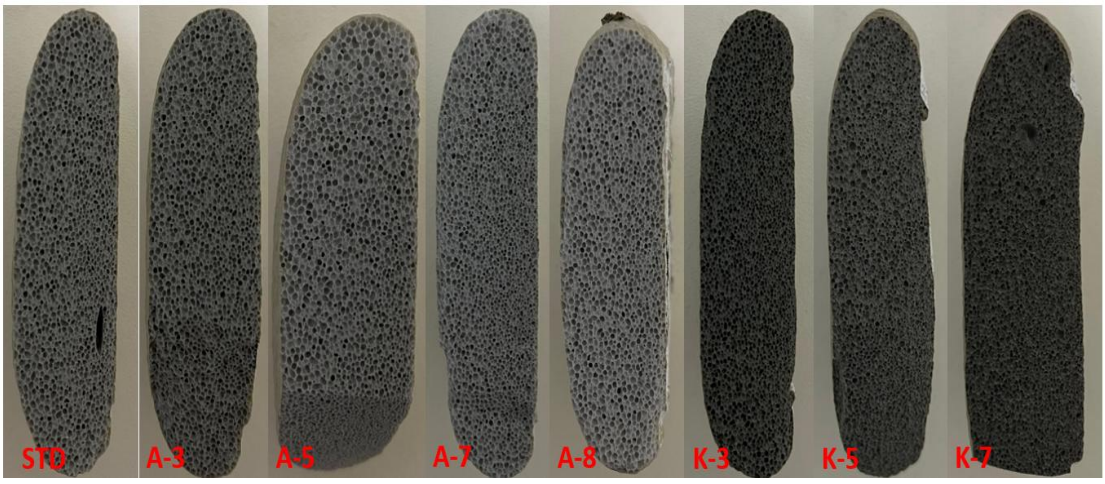

Figure 4. Cross-sectional images of foam ceramics

The observed pore morphologies were consistent with previous findings where SiC was used as a foaming agent and waste materials acted as primary ceramic precursors [4,6]. Specifically, the evolution of the porous microstructure appears to be governed by the gas release behavior of SiC during high-temperature sintering and the resulting viscosity of the molten phase

Moreover, the experimental compositions displayed porosity characteristics comparable to those reported in the literature (typically 70–85%), indicating that the selected formulations provided sufficient open pore volume for applications such as thermal insulation or lightweight construction materials [1,5].

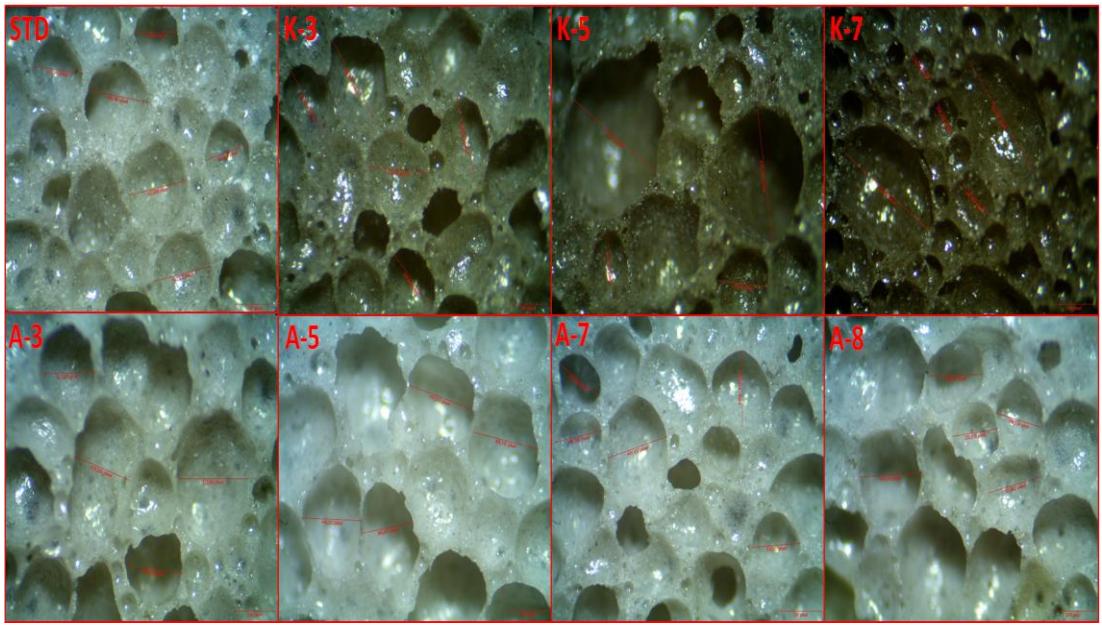

Figure 5. Cross-sectional microscope images of foam ceramics

Cross-sectional microscope images of foam ceramics were shown in 10X magnification (Figure 5). The pore morphologies of the waste-derived foam ceramic samples exhibited distinct characteristics when compared to the standard formulation. Optical microscopy analysis of the cross-sections revealed that the red mud and alumina coating waste compositions resulted in more irregularly shaped pores. This morphology is likely attributed to the higher content of iron oxide and alkali elements present in the red mud, which reduce the melt viscosity during sintering and facilitate gas expansion [3,7]. In contrast, the standard formulation containing synthetic SiC and refined raw materials produced a more uniform and finer pore structure, likely due to better control over gas generation and melt behavior during foaming

The alumina coating waste-based samples demonstrated intermediate behavior, with moderately interconnected pores and relatively homogeneous distribution. This can be linked to the stabilizing influence of alumina on the melt phase, which supports structural retention during gas evolution. These differences in pore architecture are consistent with prior studies showing that the oxide composition, especially SiO_2, Al_2O_3, and Fe_2O_3 content, significantly influences foam stability and final porosity [4,6].Although variations in oxide composition, particularly in Fe_2O_3, Al_2O_3, and alkali content, influenced the pore morphology to some extent, the waste-derived formulations exhibited comparable pore structures and mechanical properties to the standard formulation, suggesting that the use of industrial wastes does not significantly compromise the structural integrity of foam ceramics.

4. Conclusions

This study demonstrated that red mud and alumina coating wastes can be utilized in the production of foam ceramics. The sintered samples exhibited well-developed porous microstructures as confirmed by tablet and cross-sectional observations, including optical microscopy analysis. The pore distribution and morphology of the samples were comparable to those produced using conventional ceramic raw materials, indicating that these waste-derived formulations can serve as viable and sustainable alternatives. The findings are in agreement with prior studies emphasizing the compatibility of solid waste-derived compositions in foam ceramic applications, particularly in terms of porosity, processability, and structural integrity. Overall, the findings indicate that waste-derived formulations can achieve mechanical strength values comparable to the standard formulation. While the alumina coating waste led to higher bulk density due to reduced porosity, the red mud formulations maintained densities closer to the standard. These results suggest that both types of waste can be utilized in lightweight structural ceramic applications, with red mud favoring pore coarsening and alumina coating waste promoting densification, without significant compromise in mechanical performance. Future work may focus on

mechanical performance evaluation and thermal conductivity measurements to further assess the suitability of these materials for building and environmental applications.

5. Acknowledgement

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Effect of Nano Mineral Reinforced Filling Systems on Marble Slab Applications

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ABSTRACT

Today, various filling materials are used in the natural stone industry to process marble slabs and increase their service life. Traditional filling systems have limitations, especially in completely closing microstructural voids and causing surface deformations over time. This study investigated the effects of applying nano-sized structured minerals (such as nano silica and nano calcite) as a filling system on marble slabs. The filling material was aimed to form a stronger bond with the marble surface thanks to the high surface area and reactivity properties of nano minerals. Within the scope of the study, filling recipes containing different amounts of nanomineral additives were prepared and applied to standard marble slabs. The experimental phase examined surface adherence, porosity, colour matching and mechanical strength properties. The findings show that using nano minerals as filling materials provides a more homogeneous filling structure than traditional systems, where porosity decreases and surface integrity increases. These results reveal that integrating nanotechnology into the construction and natural stone sector can significantly contribute to aesthetics, durability and sustainability.

Keywords: Nano silica, nano calcite, marble slab, surface strength, microstructure.

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1.Introduction

Marble has been a preferred building material in the natural stone industry for centuries due to its aesthetic appeal and high durability. However, cracks, pores, and surface imperfections that arise during the blocks' cutting, processing, and application processes negatively impact aesthetic integrity and structural performance [1-3]. Various filling systems have been used for many years to address these imperfections, with polymer-based resins and cement-based mortars being particularly popular. While these filling systems effectively preserve marble's decorative value and increase its mechanical resistance in the short term, they have limitations in terms of long-term performance. Colour changes, cracking tendencies, and mechanical abrasion over time indicate that the compatibility of filling systems with marble surfaces needs improvement [4].

Studies in the literature reveal that traditional fillers cause problems such as yellowing, abrasion, and delamination, especially in flooring applications subject to high pedestrian traffic [6]. While polymer-based systems offer advantages with their transparent appearance and ease of application, they lose colour stability over time due to their low resistance to ultraviolet radiation. At the same time, cement-based fillers achieve satisfactory compressive strength values, high porosity, and a tendency to crack, which pose serious problems in long-term use. Therefore, developing more advanced filler systems that can meet both mechanical and aesthetic requirements in marble flooring applications has become inevitable [7]. At this point, nanotechnology's contributions to the building materials field are noteworthy. Thanks to their high specific surface area, reactive surface energy, and filling capabilities at the nanometer scale, Nano-sized mineral additives provide denser and more durable structures than traditional mineral additives by homogenously dispersing within the matrix. Studies using additives such as nano-silica, nano-alumina, nano-calcite, and nano-titania have reported positive results such as filling microvoids, slowing crack propagation, and increasing wear resistance [8-12]. Chen et al. [13] (2018) showed that crack

resistance improved by up to 30% in systems containing nano-silica additives, while Gu et al. [14] (2024) reported that the use of nano-calcite improved colour stability and UV resistance in marble filling resins. These findings demonstrate that nanominerals contribute not only to mechanical properties but also to aesthetic and environmental durability.

The existing literature generally examines nanoadditives in concrete, ceramic, or polymer-based composites [15-17]. Studies on compressive strength, hydration kinetics, shrinkage behaviour, and abrasion performance have revealed that nanominerals significantly improve material behaviour. However, studies on marble flooring applications are limited, and data on the long-term compatibility of filler systems with natural stone and their performance in use are insufficient. However, marble represents a unique material group compared to other building materials, with high aesthetic expectations and exposure to intense environmental and mechanical loads. Therefore, the evaluation of nanomineral-added filler systems in marble flooring applications fills the gap in the academic literature and significantly contributes to addressing the industry's current needs.

This study aims to address this literature gap and comprehensively examines the performance of nanomineral-added filler systems in marble flooring applications. The study provides a detailed evaluation of parameters such as the microstructural advantages imparted by nanoadditives to filler systems, increased mechanical strength, aesthetic integrity, and ultraviolet and thermal resistance. In this respect, comparisons are made with existing filling technologies, and scientific solutions are presented to meet the natural stone industry's long-term quality and durability-oriented expectations.

2. Materials and Methods

This study aims to demonstrate the potential use of nanoscale minerals as fillers for porous/porous travertine slabs and to determine the most suitable production methods. The research process was structured around four main components: (i) detailed characterisation of the physical and chemical properties of the raw materials used, (ii) development of optimal formulations, (iii) evaluation of the mechanical and hydraulic performance of the resulting systems, and (iv) holistic analysis of the optimization processes. This systematic approach formed the study's fundamental framework in terms of scientific consistency and practical effectiveness.

2.1 Mineral Characterization and Preparation Process

In the first stage, the chemical compositions of the nano-boron, nano-silica, micronised travertine, and white cement samples used in the experimental studies were determined using X-ray fluorescence (XRF). The obtained data are presented in Table 1, providing a scientific basis for the formulation studies to be conducted in the subsequent stages. This characterization was a critical step, particularly for understanding mineral additives' chemical compatibility and potential reactivity levels. As emphasized in the literatüre[18-20], the chemical composition of mineral admixtures has a decisive impact on early-age hydration and long-term strength.

Table 1. Chemical analysis results of raw materials used in cement filling mortar

Components	Cement	Nano-calcite	Nano-Boron	Travertine
	%	%	%	%
SiO2	21.60	0.28	5.20	0.32
Al2O3	4.50	0.11	0.16	0
Fe2O3	0.26	0.009	0.044	0
CaO	65.1	54.9	27.14	53.96
MgO	1.30	1.10	2.74	0.25
SO3	2.30	0.02	0.16	0
K2O	0	1.10	0	0
Na2O	0	-	0.2	0.32

P2O5	0	0.01	0.14	0
SrO	0	0	0.8	0
B2O3	0	0	40.23	0
Loi	5.30	42.5	23.17	44.62
Total	99.91	99.95	99.98	99.47

Following characterization, cement-based filling systems were designed to repair cracks observed in travertine slabs. The model presented in Table 2 is based on determining the components' proportions and optimizing the optimum compositions based on multidimensional parameters. This considers the synergistic effects of the mineral admixtures, aiming to optimize the system in terms of strength and volumetric stability.

Table 2. Raw materials and usage rates used in the preparation of cement mortar

cement filling mortars codes	Cement	Nano-calcite	Nano-Boron	Travertine
	%	%	%	%
CFM	70	1	1	28

2.2 Grinding and Granulometry Control

Travertine waste used in the experimental process was obtained from quarries in the Afyon region and ground in a laboratory-type steel ball mill. The grinding process was designed to ensure homogenization of the filler material, ensuring that 75% of the resulting product remained below 90 µm (Figure 1). This granulometry control increased reactivity and facilitated the uniform distribution of the components in the filler mortar. The literature emphasizes that fine-grained structures are critical, particularly in filling microcracks and ensuring matrix integrity [21].

Figure 1. Preparation of cement filling mortars

2.3 Filling Mortar Formulations

In the study's second phase, filling mortars were prepared by combining Cem I 42.5 R type Portland cement, micronized travertine waste, nanosilica, and nanoboron additives in predetermined proportions. Nanosilica, with its high specific surface area and pozzolanic reactivity, increased the density of the cement matrix; It contributed to the more effective filling of microcracks. Nano boron was chosen for its enhancing chemical stability, positively influencing hydration processes, and providing high-temperature resistance—the synergistic effect of these additives aimed to optimize the long-term performance of the developed systems.

The rheological behaviour, setting times, mechanical strengths, and chemical properties of the prepared mixtures were systematically examined; the findings demonstrated the suitability of the filling mortars in terms of workability and resistance to environmental conditions (Figure 2).

Figure 2. Application processes of cement filling mortars

2.4 Surface Preparation and Application Process

Travertine samples for the experimental applications were obtained from marble factories in the Afyon region. Surfaces with voids and cracks were chosen explicitly for sample selection. This approach ensured that the experimental process reflected realistic conditions. Before application, surface preparation was meticulously carried out; altered areas were mechanically cleaned, surfaces were smoothed using power tools, and prepared for grout application. The decisive role of surface preparation in grout/stone matrix adhesion is frequently emphasised in the literature and was a significant reason for the increased performance observed in this study.

During the grout application process, systematic filling of voids was ensured, ensuring optimal surface penetration. The techniques used in this phase created a homogeneous distribution and enabled a strong bond between the grout and the stone matrix .

2.5. Curing and Surface Treatments

Following the grout application, the samples were stored in a controlled curing chamber for 24 hours to ensure optimal cement setting. The curing process ensured the balanced progression of hydration reactions and significantly contributed to the early-age strength gain of the filler material. As noted in the literature [18-20], it is known that failure to provide appropriate curing conditions interrupts hydration, which both reduces early-age strength and leads to long-term crack formation.

After the setting process was completed, grinding and polishing were applied to enhance the surface aesthetics and integrity. Appropriate abrasive materials and gradual polishing techniques were used during this stage to reduce surface roughness and achieve a uniform shine. Ultimately, the filler application improved mechanical and chemical performance and enhanced the stone's decorative value.

3. Results and discussions

3.1. Cement Filler Application on Travertine Slabs

Cement-based fillers prepared for experimental studies were applied to travertine slabs to improve existing cracks, microcracks, and voids. The surface preparation phase before application included mechanical smoothing, removing loose particles from the surface, and cleaning dust residue. These processes contributed to improved adhesion by improving the chemical and mechanical compatibility of the filler with the stone matrix. As noted in the literature, pre-treatment processes performed on porous stone surfaces facilitate the integration of the filler with the microstructure and prevent strength loss during subsequent use (TS EN 1469, 2015).

During the application process, the cement-based filler homogeneously penetrated the highly porous structure of travertine, characteristically, and effectively sealed the pores (Figure 4.1 and Figure 4.2). This deep diffusion of the filler into the pores increased adhesion strength and distributed stress concentrations at the crack tips. This contributed to preventing potential crack propagation or surface peeling in later stages. Similarly, various studies emphasize that filling voids in natural stone with cement-based systems increases the material's durability and service life [7].

Experimental observations have revealed that the voids observed on the surfaces of travertine slabs following filling application are significantly reduced, and the stone's integrity and structural stability are significantly strengthened. This finding is consistent with the functionality of repair mortars defined in the TS EN 1504-3 (2010) standard. Consequently, cement-based filling materials have been determined to be an effective method for preserving the aesthetic integrity and improving mechanical performance in porous natural stone.

Figure 3.1 Cement mortar applied surfaces (low porosity)

Figure 3.2 Cement mortar applied surfaces (high porosity)

3.2. Setting and Setting Properties of Cement Filling Mortar

The setting behaviour of nano-enhanced cementitious grouts was investigated per the methodology defined in the TS EN 196-3 (2016) standard. Curing was performed at 20 ± 2°C and ≥95% relative humidity to ensure the orderly progression of hydration reactions. The findings revealed that the initial and final setting times were consistent with the standards, and the grout hardened homogeneously within the travertine matrix.

Analysing the grout's setting process is critical, especially for highly porous natural stones such as travertine. Setting speed is crucial for adequate filler penetration into voids, improved adhesion to the stone matrix, and volumetric stability. Observations demonstrated that hydration progressed evenly under controlled curing conditions due to the nanoadditives, eliminating sudden delays in the setting process or tensile stresses due to premature hardening. Consequently, the setting times of nano-modified cement-based infills applied to travertine slabs were consistent with standard values, and it was determined that proper curing conditions directly impact the microstructural integrity of the infill material and its adhesion to the stone. In this context, setting time management is considered one of the most critical processes for the sustainability of travertine infill applications' aesthetic and structural performance.

Figure 3.3 Hydraulic properties of cement mortar filler

3.3. Surface Polishing and Polishing Properties

The surface grinding and polishing processes performed following the filler application resulted in significant improvements in the travertine slabs' aesthetic and physical-mechanical properties. Thanks to the graded abrasive systems and abrasive materials with varying grain sizes used in this stage, surface roughness was gradually reduced, resulting in a uniform shine. As emphasized in the literature [2,6-7], surface smoothness and gloss are among the fundamental parameters that directly affect natural stones' decorative value and usage potential

As a result of the polishing process, a significant increase in the decorative value of travertine surfaces was achieved, resulting in a brighter, more homogeneous, and more aesthetic appearance. Moreover, it was determined that polishing provides a visual benefit and strengthens surface integrity. By reducing microscopic voids and irregularities, the stone becomes more resistant to external influences (e.g., moisture, contamination, surface abrasion). Ultimately, the surface grinding and polishing processes enhanced the travertine slabs' aesthetic integrity and surface durability.

Figure 3.4 Polished surfaces with completed filling

3.4. Strength and Color Properties

Systematic evaluations following the application of the filling mortar revealed significant improvements in the travertine slabs' mechanical and aesthetic properties. The cement-based filler reduced the stone's void ratio, significantly increasing compressive strength and making a structure more resistant to internal stresses. Using nano-additives (particularly nano-boron and nano-calcite) allowed for more effective filling of microcracks and micropores, resulting in a more homogeneous microstructure. This finding is consistent with literature data [17-20] indicating that nano-additives enhance the integrity of cement-based systems by accelerating the nucleation mechanism. Aesthetic colour matching evaluations indicated that the filler material exhibited a harmonious appearance with the natural surface of the travertine. In particular, post-filling polishing achieved a uniform shine, enhancing the surface's decorative value. This result demonstrates that the fillers provide mechanical reinforcement and play an active role in preserving the stone's aesthetic integrity. Minimising colour variations and enhancing surface gloss are considered unique contributions of the study in terms of practical effectiveness and sustainability.

Figure 3.5 filled and polished Marbles

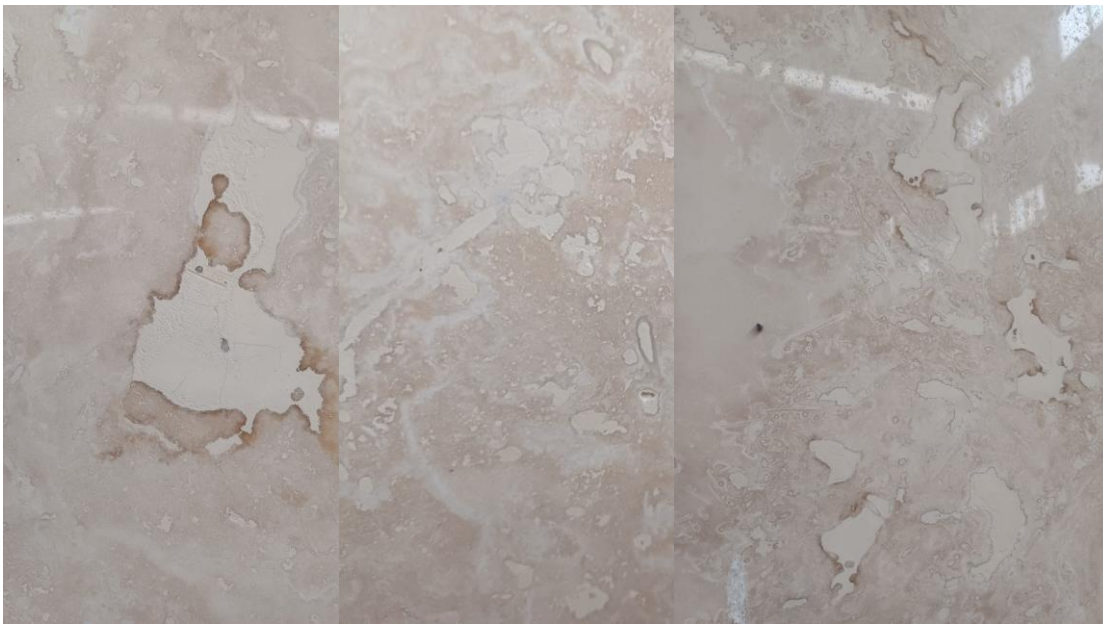

Figure 3.6 Marbles with final filling and polishing processes completed

4. Conclusion

The findings of this study demonstrate that cement-based filling systems with nanomineral additives significantly improve travertine and marble slabs' mechanical and aesthetic aspects. The application process, supported by surface preparation and controlled curing conditions, increased bond strength and limited crack propagation. The synergistic effect of nanoboron and nanocalcite additives enabled the effective filling of microvoids and a homogeneous microstructure. As a result, increased compressive strength, colour integrity, and improved long-term performance were observed. Therefore, this filling system overcomes the limitations of traditional methods and offers a sustainable, durable, and aesthetically superior alternative in the natural stone industry.

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FDM Baskılı PLA ve PLA-CF Malzemelerin Tribolojik Perfomansına Katman Yöneliminin Etkisi

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ÖZET

Bu çalışmada, FDM yöntemi ile üretilen saf polilaktik asit (PLA) ve % 7.5 karbon fiber takviyeli PLA (PLA-CF) numunelerin farklı katman yönelimlerinde (0°, 45° ve 90°) tribolojik performansları sistematik olarak değerlendirilmiştir. Deneyler, 10 N yük, 200 rpm dönme hızı ve 30 dakika süre koşullarında block-on-disc tribometre kullanılarak gerçekleştirilmiştir. Bulgular, PLA numunelerinin daha yüksek ve dalgalı sürtünme katsayısı değerleri sergilediğini (0.52, 0.47 ve 0.44), PLA-CF numunelerinin ise belirgin şekilde daha düşük ve istikrarlı değerler gösterdiğini (0.28, 0.27 ve 0.25) ortaya koymuştur. Aşınma oranı açısından PLA numuneleri yönelime duyarlılık göstermiş; değerler 0°'de 0.0044 g/km iken 90°'de 0.0024 g/km'ye düşmüştür. PLA-CF numuneleri ise tüm yönelimlerde 0.001 g/km'nin altında kalarak üstün aşınma direnci sunmuştur. Elde edilen sonuçlar, karbon fiber takviyesinin ve katman yöneliminin FDM ile üretilen bileşenlerin tribolojik performansını belirleyici biçimde etkilediğini göstermektedir.

Anahtar Kelimeler : Eriyik yığma modelleme, Poliaktik asit, karbon fiber takviyeli PLA, Aşınma, Katman yönelimi

Effect of Layer Orientation On the Tribological Performance of FDM-Printed PLA and PLA-CF Materials

ABSTRACT

This study systematically evaluated the tribological performance of neat polylactic acid (PLA) and 7.5 wt.% carbon fiber-reinforced PLA (PLA-CF) specimens fabricated by fused deposition modeling (FDM) with three distinct layer orientations (0°, 45°, and 90°). Experiments were conducted using a block-on-disc tribometer under a load of 10 N, a rotational speed of 200 rpm, and a duration of 30 minutes. The results revealed that PLA specimens exhibited higher and more fluctuating coefficients of friction, with average values of 0.52, 0.47, and 0.44 for 0°, 45°, and 90°, respectively. In contrast, PLA-CF specimens demonstrated markedly lower and more stable values of 0.28, 0.27, and 0.25. Regarding wear performance, PLA specimens showed orientation-dependent behavior, with wear rates decreasing from 0.0044 g/km at 0° to 0.0024 g/km at 90°. PLA-CF specimens, however, exhibited superior wear resistance across all orientations, with rates consistently below 0.001 g/km. These findings emphasize the crucial role of carbon fiber reinforcement and layer orientation in enhancing the tribological properties of FDM-printed materials.

Keywords: Fused Deposition Modeling (FDM), PLA, PLA-CF, Wear, Layer orientation

1. Introduction

Additive manufacturing (AM) techniques have attracted increasing attention in recent years due to their advantages over conventional production methods, such as lower cost, design flexibility, and rapid prototyping capabilities [1]. Among these techniques, fused deposition modeling (FDM) has become one of the most widely used methods, particularly for polymer-based materials, due to its accessibility and ability to process a broad range of feedstock [2], [3]. However, FDM-printed parts often exhibit inferior mechanical and tribological performance compared to conventionally manufactured ones, mainly due to weak interlayer bonding, porosity, and anisotropy [4]. These limitations restrict the potential use of FDM in engineering applications exposed to wear.

One of the most commonly used materials in FDM is polylactic acid (PLA). PLA is favored for its biodegradability, low cost, and environmentally friendly characteristics [5]. The tensile, flexural, and impact strength of PLA vary significantly with process parameters such as infill density, layer thickness, nozzle temperature, and build orientation [6]. For instance, a higher infill ratio and smaller layer thickness improve both strength and surface quality; however, the intrinsic brittleness and limited wear resistance of PLA restrict its long-term use in engineering applications [7], [8]. To overcome these limitations, carbon fiber reinforced PLA (PLA-CF) has been developed and has gained significant research interest. Carbon fiber addition enhances the stiffness, tensile, and flexural strength of PLA, while also improving its wear resistance [9]. Studies have reported that the inclusion of short carbon fibers can reduce wear rates by several times and lead to significant reductions in the coefficient of friction [10]. Continuous carbon fiber reinforcement has been shown to improve tensile strength by more than 100% [11]. Nevertheless, performance reductions may occur when fibers are not homogeneously distributed within the matrix or when interfacial adhesion is insufficient [12]. Therefore, the optimization of fiber content and process parameters is crucial to achieving the desired performance.

Layer orientation also plays a key role in determining the tribological behavior of FDM-printed polymers. The alignment of deposited layers relative to the sliding direction significantly influences wear and friction. In this study, 0° orientation is defined as perpendicular to the sliding direction. According to the literature, specimens printed at 0° (perpendicular) often exhibit higher wear rates due to direct exposure of layer ends to the contact surface, while fluctuations in the coefficient of friction are also more pronounced [13]. In 45° orientations, interfacial weaknesses and irregular contact areas contribute to increased wear [14]. Conversely, 90° orientations (parallel to the sliding direction) generally provide the lowest wear rates, as continuous filament paths facilitate load transfer and reduce material removal [15]. Although the coefficient of friction is less sensitive to orientation, parallel orientations (90°) often result in lower and more stable values [16]. These findings confirm that FDM-printed parts exhibit pronounced tribological anisotropy.

Despite the significant progress achieved in recent years, research gaps remain concerning the tribological performance of FDM-printed PLA and PLA-CF. In particular, the lack of standardized testing protocols complicates direct comparison across studies [17].

In this context, the present study systematically investigates the tribological performance of neat PLA and 7.5 wt.% carbon fiber reinforced PLA (PLA-CF) fabricated by FDM with different layer orientations (0°: perpendicular to sliding, 45°: diagonal, and 90°: parallel to sliding). Block-on-disc tribometer tests were conducted to measure the coefficient of friction and wear rate. The results provide new insights into the combined influence of material composition and build orientation and are expected to support the optimization of FDM-based composites for wear-critical engineering applications.

2. Materials and Method

2.1. Materials and Model Design

In this study, specimens were produced using two different types of filaments to investigate their tribological performance. Pure polylactic acid (PLA) specimens were fabricated from Elegoo brand PLA filament with a diameter of 1.75 mm. In comparison, 7.5 wt.% carbon fibre-reinforced polylactic acid (PLA-CF) specimens were manufactured from Filameon brand PLA-CF filament with a diameter of 1.75 mm. Properties of PLA and PLA-CF are given in Table 1. The geometrical design of the specimens was carried out using SOLIDWORKS solid modeling software. The block-shaped specimens were modelled with approximate dimensions of 10 × 10 × 4 mm (H x L x W). They were structured to enable a systematic evaluation of the influence of different layer orientations (0°, 45°, and 90°) on tribological properties.

Table 1. Properties of PLA and PLA-CF filaments

Typical value of filament properties	PLA	PLA-CF
Diameter	1.75 mm	1.75 mm
Nozzle temperature	190 – 230 °C	200 – 230 °C
Bed temperature	35 – 60 °C	60 – 85 °C
Tensile strength	38 MPa	55 MPa
Bending strength	72 MPa	80 MPa

***source:** from the manufacturer

2.2. 3D Printing

The three-dimensional models were prepared using Creality Print 6.2 slicing software before fabrication. The specimens were manufactured by the FDM technique employing a Creality K1C 3D printer with a build volume of 220 × 220 × 250 mm. All specimens were produced in a rectangular form with dimensions of 10 × 10 × 4 mm. The printing parameters were kept constant for all specimens. A nozzle with a diameter of 0.4 mm, a layer thickness of 0.15 mm, and an infill density of 100% was employed. The nozzle temperature was set to 200 °C for PLA and 230 °C for PLA-CF, while the build plate temperature was maintained at 50 °C for PLA and 60 °C for PLA-CF. The detailed printing parameters are presented in Table 2.

Table 2. Properties of 3D printing samples of PLA and PLA-CF

3D printer properties	PLA	PLA-CF
Nozzle diameter	0.4 mm	0.4 mm
Nozzle temperature	200 °C	230 °C
Chamber temperature	25 °C	25 °C
Bed temperature	50 °C	60 °C
Layer height	0.15 mm	0.15 mm
Infill density	% 100	% 100
Infill pattern	Rectilinear	Rectilinear
Layer orientation	0°, 45°, 90°	0°, 45°, 90°
Number of wall	2	2

In order to investigate the effect of layer orientation on tribological behavior, the specimens were fabricated in three different orientations: 0° (perpendicular to the sliding direction), 45°, and 90° (parallel to the sliding direction). The schematic representation of the layer orientations is provided in Figure 1.

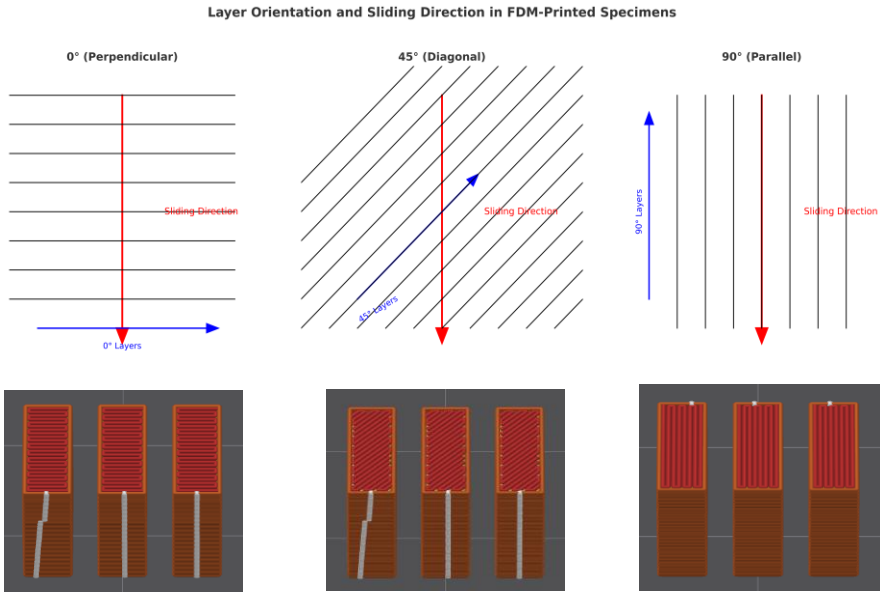

Figure 1. Layer orientations (0°, 45°, and 90°) in FDM-printed PLA and PLA-CF specimens and their relationship with the sliding direction applied during tribometer tests

2.3. Tribological Tests

The tribological behavior of the specimens was examined using a block-on-disc tribometer under dry sliding conditions. Block specimens fabricated with different material types (PLA and PLA-CF) and layer orientations (0°, 45°, and 90°) were tested under a constant normal load of 10 N against a rotating abrasive disc operating at a speed of 200 rpm for a total duration of 30 minutes**.** The image of the tribometer test apparatus is provided in Figure 2. The abrasive disc was made of 440C stainless steel, with a radius of 20 mm and a hardness of 60 HRC.

During the tests, the coefficient of friction (COF) was continuously monitored and recorded. The COF was calculated as the ratio of the measured frictional force (F) to the applied normal load (N) [18]. Each test was repeated three times to ensure repeatability and reliability of the results.

$$\mu = \frac{F}{N} \quad \textbf{(1)}$$

After each test, the specimens were weighed before (m_0) and after (m_f) the experiment using a precision balance with an accuracy of 0.1 mg. The weight loss (Δm) in grams (g) was calculated as follows:

$$\Delta m\ (g) = m_0 - m_f \quad \textbf{(2)}$$

The obtained weight loss values were subsequently used to determine the specific wear rate (WR) per unit sliding distance. The sliding distance L was calculated according to the following equation [19].

$$L = 2\pi r \times n \times t \quad \textbf{(3)}$$

In this study, the sliding distance was calculated as L = 750 m, based on the abrasive disc radius (r = 20 mm), the rotation speed (n = 200 rpm), and the test duration (t = 30 min). The specific wear rate was then determined in grams per kilometer (g/km) using the expression:

$$\mathrm{WR} = \frac{\Delta m}{L} \quad (g/km) \quad \textbf{(4)}$$

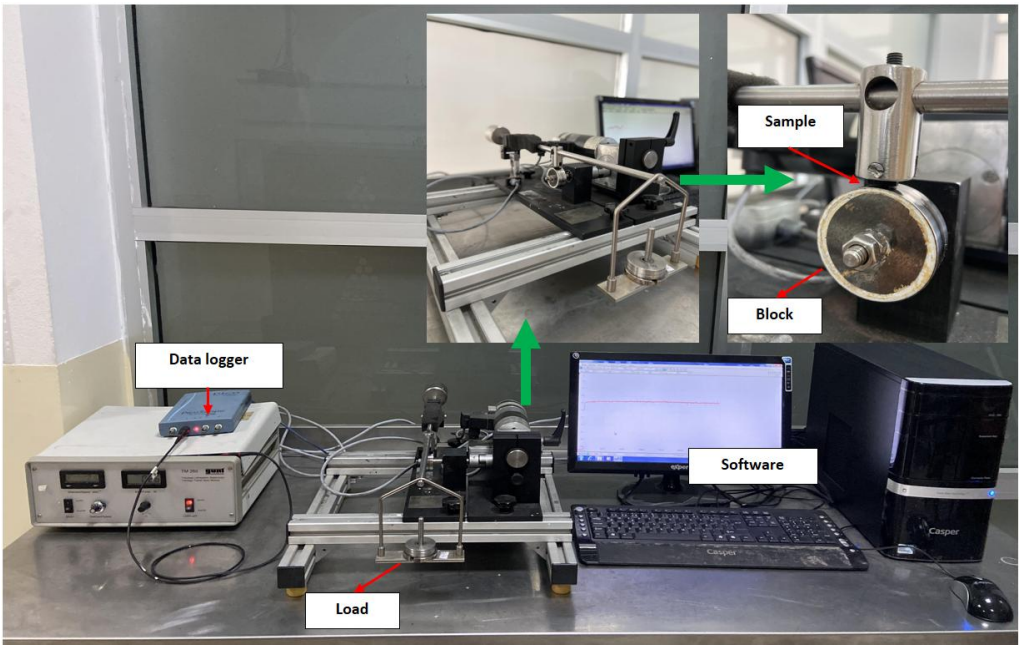

Figure 2. Block on disc tribometer

3. Results and Discussion

3.1. Friction Coefficient

The variation of the COF with time for PLA and PLA-CF specimens fabricated with different layer orientations is presented in Figure 3. The results indicate clear distinctions between the two material groups. PLA specimens exhibited relatively higher COF values with noticeable fluctuations over time, whereas PLA-CF specimens demonstrated lower COF values and a more stable tribological response.

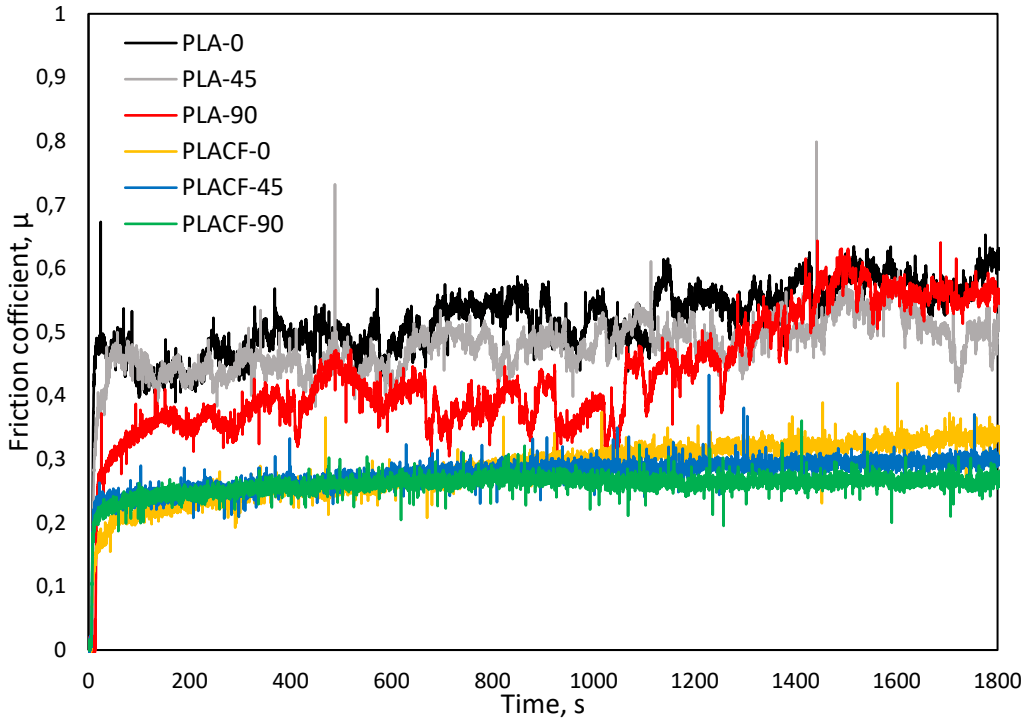

Figure 3. Time-dependent variation of the COF for PLA and PLA-CF specimens produced with different layer orientations (0°, 45°, and 90°).

A detailed examination of Figure 3 reveals that, in all orientations, PLA specimens initially exhibited a rapid increase in COF, followed by irregular fluctuations throughout the test duration. In the 0° orientation, PLA specimens reached an average COF of 0.52 and displayed unstable frictional behavior. At 45°, the average COF was measured as 0.47, although significant fluctuations persisted due to surface roughness and interlayer transitions. In the 90° orientation, the average COF was determined as 0.44, which was attributed to the alignment of the layers parallel to the sliding direction, thereby reducing friction [13][16] . One of the primary reasons for the fluctuating behavior observed in PLA specimens is the detachment of polymeric debris from the surface during sliding, which subsequently enters the interface between the disc and the specimen, forming an irregular third-body layer. The incorporation of such debris into the contact area caused abrupt increases and decreases in the coefficient of friction, leading to a fluctuating trend [20]. Furthermore, a portion of the detached debris adhered back onto the specimen surface, forming a polymeric film layer, which increased the real contact area and consequently induced additional variations in the frictional force [20][21].

In PLA-CF specimens, the beneficial effect of carbon fiber reinforcement on frictional behavior was clearly observed. The presence of carbon fibers provided more stable contact conditions at the surface and significantly reduced the weaknesses of the polymer matrix that typically emerge during wear [22]. In the 0° orientation, PLA-CF specimens exhibited an average COF of 0.28 with a low and stable frictional response. At 45°, an average COF of 0.27 was obtained. In the 90° orientation, PLA-CF specimens demonstrated the lowest COF with an average value of 0.25. These results can be attributed to the synergistic effect of fiber reinforcement and the alignment of layers parallel to the sliding direction. Carbon fibers act as rigid load-bearing phases within the polymer matrix, thereby restricting matrix deformation and limiting wear at the contact interface [23]. The parallel alignment of layers further facilitates load distribution and promotes homogeneous shear stress across the contact surface. As a consequence, both the strengthening effect of the fiber reinforcement and the favorable influence of layer orientation combined to yield a pronounced reduction in the coefficient of friction. Moreover, due to the enhanced wear resistance provided by carbon fibers, less debris was generated from the surface of PLA-CF specimens. As a result, no significant third-body particles entered the interface between the disc and the specimen, ensuring that the COF remained stable and that the tribological response maintained consistent behavior over time.

PLA-CF specimens exhibited lower coefficients of friction compared to PLA specimens across all layer orientations. In the 0° orientation, PLA specimens reached an average COF of 0.52, whereas PLA-CF specimens maintained a lower value of 0.28, corresponding to a reduction of approximately 46%. At 45°, the average COF was 0.47 for PLA and 0.27 for PLA-CF, indicating a decrease of about 43%. In the 90° orientation, PLA specimens showed an average COF of 0.44, while PLA-CF specimens recorded a value of 0.25, again representing a reduction of nearly 43%. The decrease in the coefficient of friction in PLA-CF specimens can be attributed to the reinforcing effect of carbon fibers, which not only increase the stiffness of the polymer matrix but also contribute to the formation of a thin carbon-based transfer film on the surface during sliding, thereby facilitating smoother motion. Layer orientation also demonstrated a notable influence on this behavior. In PLA specimens, higher COF values were observed at 0° and lower values at 90°, which is consistent with the effect of parallel layer alignment reducing resistance to sliding. In PLA-CF specimens, however, the effect of orientation was relatively limited, as the fiber reinforcement ensured consistently low and stable COF values across all orientations.

In summary, PLA specimens exhibited greater sensitivity to orientation, along with fluctuating and unstable frictional responses. In contrast, PLA-CF specimens demonstrated lower COF values, stable time-dependent tribological behavior, and superior performance largely independent of orientation.

3.2. Wear Rate

The wear behavior of PLA and PLA-CF specimens with different layer orientations was evaluated based on the measured mass loss and calculated wear rates after the sliding tests. The results revealed significant differences in wear performance between the two material groups.

For PLA specimens, the mass loss varied depending on the orientation of the layers relative to the sliding direction. As presented in Figure 4, PLA-0 exhibited the highest wear rate of 0.0044 g/km, which

decreased to 0.0030 g/km for PLA-45 and further to 0.0024 g/km for PLA-90. This trend indicates that aligning the layers parallel to the sliding direction reduced material removal and enhanced wear resistance [13] [15] . The underlying reason is that, under parallel orientation, the counter surface travels along continuous filament paths, thereby minimizing micro-junctions at layer ends and reducing fluctuations in contact pressure.

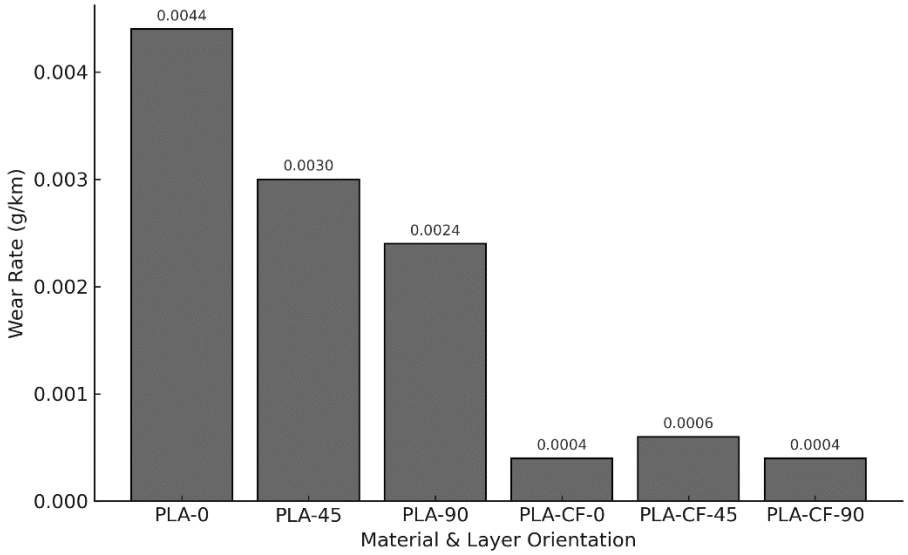

Figure 4. Wear rates of PLA and PLA-CF specimens produced with different layer orientations.

PLA-CF specimens, on the other hand, demonstrated markedly superior wear resistance compared to PLA. In all orientations, the wear rates remained below 0.001 g/km. Notably, PLA-CF-0 and PLA-CF-90 exhibited the lowest wear rates of 0.0004 g/km, clearly highlighting the positive influence of carbon fiber reinforcement on the wear mechanism. Fiber reinforcement restricted surface damage through fiber–matrix interactions during sliding and significantly reduced material loss [24] [25]. In this context, the embedded carbon fibers acted as rigid load-bearing phases within the PLA matrix, distributing applied stresses over a larger volume and thereby limiting wear-induced material removal. PLA-CF-45 specimens showed a wear rate of 0.0006 g/km, which was slightly higher than the other orientations but still considerably lower compared to neat PLA.

Overall, as shown in Figure X, PLA specimens exhibited higher and orientation-dependent wear rates. In contrast, PLA-CF specimens demonstrated low wear rates, with surface damage limited by fiber–matrix interactions and stable tribological behaviour largely unaffected by orientation.

4. Conclusions

In this study, the tribological performance of neat PLA and carbon fiber-reinforced PLA (PLA-CF) specimens manufactured by FDM with different layer orientations (0°, 45°, and 90°) was systematically investigated. The main findings can be summarized as follows:

1. The average coefficient of friction (COF) for PLA specimens was recorded as 0.52 at 0°, 0.47 at 45°, and 0.44 at 90°.
2. The average COF values for PLA-CF specimens were measured as 0.28 at 0°, 0.27 at 45°, and 0.25 at 90°, corresponding to a reduction of approximately 40–46% compared to neat PLA.
3. The wear rate of PLA specimens was determined as 0.0044 g/km at 0°, 0.0030 g/km at 45°, and 0.0024 g/km at 90°.
4. The wear rate of PLA-CF specimens remained below 0.001 g/km in all orientations; 0.0004 g/km was recorded at 0° and 90°, while 0.0006 g/km was observed at 45°.
5. The embedded carbon fibers in PLA-CF specimens acted as rigid load-bearing phases within the polymer matrix, distributing the applied stresses over a larger volume and thereby limiting surface damage and enhancing wear resistance.

6. While PLA specimens exhibited orientation-sensitive, higher, and fluctuating tribological behavior, PLA-CF specimens demonstrated lower friction coefficients, lower wear rates, and more stable tribological performance.

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Alüminotermik Metod İle Metalik Krom Üretimi

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ÖZET

Bu çalışmada, yüksek saflıkta metalik krom üretmek için alüminotermik indirgeme metodu kullanılmıştır. Krom kaynağı olarak krom oksit (Cr_2O_3), indirgeyici olarak ise granül alüminyum kullanılmıştır. Reaksiyon hızlandırıcı olarak sodyum nitrat ($NaNO_3$) ve kromik asit (CrO_3), ateşleme maddesi olarak magnezyum tozu (%99,9 saflıkta) ve cüruf oluşturucu katkı maddesi olarak kalsiyum oksit (CaO) kullanılmıştır. Kontrollü ve sürekli reaksiyonları sağlamak için, farklı formülasyonların spesifik ısı değerleri hesaplanmış ve 2250-4500 J/g aralığındaki değerler deneysel olarak test edilmiştir.

Dört farklı formülasyon, reaksiyon verimi, ürün saflığı ve proses kararlılığına göre değerlendirilmiştir. Üretilen metaller, Endüktif Eşleşmiş Plazma-Optik Emisyon Spektroskopisi (ICP-OES) ve X-ışını Floresansı (XRF) kullanılarak karakterize edilmiştir. Sonuçlar, krom saflıklarının %96 ile %98 arasında olduğunu göstermiştir. Daha yüksek şarj ağırlıkları (>100 kg), daha iyi saflık sağlayarak daha büyük ölçeklerde reaksiyon homojenliğini ve ürün kalitesini artırdı.

Reaksiyondan sonra metal ve cüruf fazları fiziksel olarak ayrıldı. Metalik ürün, standart prosedürler izlenerek analize hazırlandı. Fe, Si ve Al gibi safsızlık elementleri çok düşük seviyelerde bulundu ve bu da malzemenin yüksek saflıktaki uygulamalar için uygunluğunu doğruladı.

Sonuç olarak, geliştirilen alüminotermik proses, yüksek ürün saflığı ve tutarlı performans elde etti. Farklı formülasyonlarda gözlemlenen tekrarlanabilirlik ve ölçeklenebilirlik, yöntemin endüstriyel potansiyelini vurgulamaktadır. Enerji verimliliği, operasyonel kolaylığı ve yüksek kaliteli çıktısıyla bu proses, ileri teknolojik uygulamalar için metalik krom üretimi için umut verici bir yol olarak öne çıkmaktadır.

Anahtar Kelimeler : Metalik krom, SHS, Alüminotermik

Production Of Metallic Chromium By The Aluminothermic Method

ABSTRACT

In this study, aluminothermic reduction was used to produce high-purity metallic chromium. Cr_2O_3 served as the chromium source and granular aluminium as the reductant. Sodium nitrate ($NaNO_3$) and chromic acid (CrO_3) were used as reaction accelerators, magnesium powder (99.9% purity) as the ignition agent, and calcium oxide (CaO) as the slag-forming additive. To ensure controlled and sustained reactions, specific heat values of different formulations were calculated, and those within 2250–4500 J/g were tested experimentally.

Four different formulations were evaluated based on reaction yield, product purity, and process stability. The produced metals were characterized using Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES) and X-ray Fluorescence (XRF). Results showed chromium purities between 96% and 98%. Higher charge weights (>100 kg) led to improved purity, suggesting enhanced reaction uniformity and product quality at larger scales.

After the reaction, metal and slag phases were physically separated. The metallic product was prepared for analysis following standard procedures. Impurity elements such as Fe, Si, and Al were found at very low levels, confirming the material's suitability for high-purity applications.

In conclusion, the developed aluminothermic process achieved high product purity and consistent performance. The reproducibility and scalability observed across different formulations highlight the method's industrial potential. With its energy efficiency, operational simplicity, and high-quality output, the process stands out as a promising route for producing metallic chromium for advanced technological applications.

Keywords: Metallic Chromium, SHS, Aluminothermic

1. Introduction

Chromium, which has become one of the important raw materials of modern industry, possesses advanced physical and chemical properties. In addition to its mechanical strength at high temperatures, metallic chromium is widely used in stainless steel production, aerospace and defence industries, nuclear energy systems, electronic components, and superalloys due to its wear resistance, high hardness, and chemical stability [1,2]. The high purity of metallic chromium used in such applications is of critical importance for the quality and performance of the final product. Considering the current chromium production methods, examples such as carbothermic reduction or vacuum melting have disadvantages including long processing times, high energy consumption, and ecological impacts [3]. In this context, the need for more economical and environmentally friendly alternative production methods is increasing day by day

Within this scope, the Self-propagating High-temperature Synthesis (SHS) method has emerged in recent years as a promising alternative for the production of metals with high melting points, such as metallic chromium, especially due to its advantages of energy efficiency and short reaction time. The SHS method is based on the principle of initiating an exothermic redox reaction, where the high-temperature reaction front propagates spontaneously through the prepared reactive mixture. This method does not require continuous external energy supply, and factors such as short processing time, low equipment costs, and high controllability of product purity make it advantageous in terms of sustainability [4]. Moreover, the controllability of the reaction can be optimized using reaction-promoting additives, igniters, and fluxing agents [5].

In this study, an aluminothermic reduction process aimed at producing high-purity metallic chromium was experimentally performed. The raw materials used in the experiments were selected after extensive research, and the effects of high-purity chromium oxide (Cr_2O_3), sodium nitrate, chromic acid, granulated aluminium, and magnesium were meticulously examined and evaluated in detail. Parameters were optimized to regulate the reaction intensity and efficiency. The physical separation of the resulting product, sample preparation, and characterization processes were conducted at the laboratory scale in accordance with general sampling principles using a systematic approach. The findings obtained from the experimental studies aim to contribute to the development of new process designs for the production of high-purity metallic chromium.

2. Materials and Methods

2.1. Materials

In the experimental studies conducted for the production of metallic chromium, Cr_2O_3 (chromium(III) oxide) was used as the chromium source, while CrO_3 (chromium(VI) oxide) and $NaNO_3$ were employed as accelerators to enhance the reaction kinetics. High-purity granular aluminium was used as the reducing agent. To control the slag formation during the reaction and to efficiently obtain the desired metallic phase, CaO (calcium oxide) was added as a fluxing agent. Additionally, magnesium powder was used as an igniting material to initiate the thermite reaction.

Chemical analyses of all raw materials and additives used in the experiments were performed, and the results, along with the supplier information of the materials, are presented in Table 1.

Table 1. Raw Materials Consumed for Chromium Metal Production

Raw Material	Purity (%)	Purpose of Use	Supplier
Chromium Oxide (Cr_2O_3)	99.42 (XRF) >99 (MSDS)	Chromium source	ACC
Aluminium (Al)	91.47 (XRF) >96 (MSDS)	Reductant	Second-hand Metal Powders
Magnesium (Mg)	97.87 (XRF) >99 (MSDS)	Igniter	Sigma Aldrich
Sodium Nitrate ($NaNO_3$)	99.9 (XRF) >99.5 (MSDS)	Accelerator	BASF
Chromic Acid (CrO_3)	99.9 (XRF) >99.8 (MSDS)	Accelerator	As Kimya
Quicklime (CaO)	>98 (MSDS)	Slag former	Bereket Kimya

2.2. Methods

In this study, the production of metallic chromium was targeted using aluminium, magnesium, and Cr_2O_3 powders, both with and without the addition of $NaNO_3$. In the initial stage, small-scale "dummy" trials were conducted using 40 g mixtures placed in ceramic crucibles and reacted with an external power source. These preliminary experiments served as a guide for determining the optimum reaction conditions and raw material ratios

Different formulations were prepared by the Eti Krom R&D team. After evaluating cost, yield, and product quality, the most suitable formulation was selected, and large-scale experiments were carried out. At this stage, MgO-coated metal crucibles with 99.9% purity and approximately 30 cm in diameter were used. Ensuring that the reactants were dry was established as a fundamental requirement, and Cr_2O_3 was dried at 150 °C when necessary. The dried powders were homogenized in a V-type mixer for 30 minutes and then fed into MgO-lined crucibles. The reaction was initiated by adding a magnesium igniter on top of the mixture and bringing a wire connected to an external power source into contact with the surface. The ignition time ranged from 5 to 10 seconds, and the reaction duration varied between 20 and 180 seconds

After the reaction, the product removed from the crucible was physically separated into metal and slag. The separated metal and slag were first reduced to a particle size of 0–10 mm using a jaw crusher and then ground to below 100 microns. Following the grinding process, the metal samples were sent for ICP-OES analysis, while the slag samples were sent for XRF analysis. The experimental setup for the reduction experiments is presented in Figure 1.

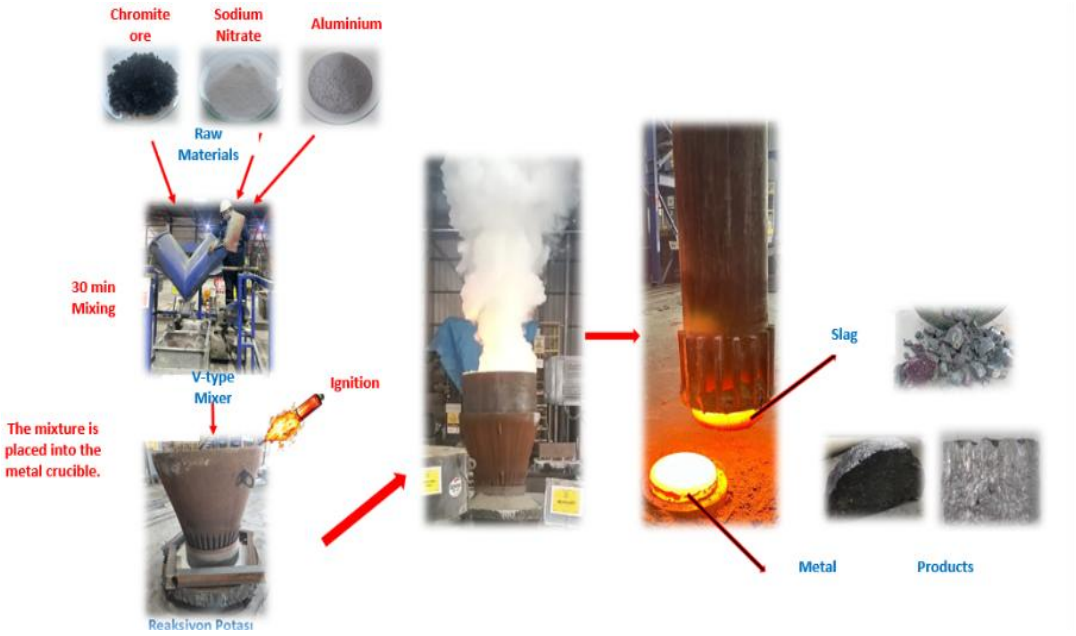


Figure 1. Experimental Setup

2.2.1. Thermodynamic Calculations

Metallothermic reduction is a high-temperature process that involves the reduction of metal oxides by a metal (reducing agent) with a lower free energy. In this study, the objective was to produce metallic chromium by reducing chromium oxide with aluminium powder in the presence of an accelerator ($NaNO_3$)

Such reactions are generally exothermic, meaning they release heat spontaneously without the need for an external energy source. However, for these reactions to proceed safely and in a controlled manner, certain thermal parameters must be considered:

2.2.2. Specific Heat

Specific heat refers to the amount of energy released per gram of mixture per reaction and is a critical parameter for achieving a safe and efficient process. For the reaction to proceed spontaneously, the specific heat must be above 2250 J/g; otherwise, the mixture will not melt. Conversely, if it exceeds 4500 J/g, the reaction may become violent, posing an explosion risk. Therefore, determining the optimal specific heat range is of critical importance.

2.2.3. Adiabatic Temperature

The adiabatic temperature (T_ad) is defined as the theoretical maximum temperature calculated under the assumption that no heat is lost to the surroundings during the reaction. If the T_ad value is above 1527 °C, the reaction can start spontaneously without the need for an external heat source and proceed in a stable manner. Based on the thermodynamic calculations carried out in this study, the main reactions satisfying these conditions are given below:

$$Cr_2O_{3(k)} + 2Al_{(k)} \rightarrow Al_2O_{3\,(k)} + 2Cr_{(k)} \quad (1)$$

The specific heat of the reaction was calculated as 2624 J/g, which falls within the range of 2250–4500 J/g, indicating that the reaction is theoretically feasible. However, experimental studies revealed that this reaction did not initiate without the use of an accelerator such as $NaNO_3$. Therefore, alternative formulations containing accelerators such as $NaNO_3$ and CrO_3 were developed, as shown in Reactions 2 and 3:

$$Cr_2O_3 + 6xNaNO_3 + (10x + 2)Al \rightarrow 3xNa_2O + 3xN_2 + (5x + 1)Al_2O_3 + 2\,Cr\,x \quad (2)$$

(Here, the coefficient x defines the amount of sodium nitrate ($NaNO_3$) to be added to the formulation.)

$$Cr_2O_3 + 0{,}25\ CrO_3 + (2{,}5)Al \rightarrow (1{,}25)Al_2O_3 + 2{,}25\ Cr \quad (3)$$

3. Discussion and Conclusion

The metallothermic reduction process used in the experimental studies is based on the conversion of metal oxides into metals. For this reaction to occur and to obtain metal M1, the metal oxide (M1O) must react with another metal (M2) that has a higher affinity for oxygen. The thermodynamic feasibility of such reactions is evaluated using the Ellingham Diagram. In the Ellingham Diagram, materials located at lower positions have the ability to reduce those above them

In this study, four different formulations with varying specific heat values were designed based on Reaction (4), and these formulations are presented in Table 2.

$$Cr_2O_3 + 6xNaNO_3 + (10x + 2)Al \rightarrow 3xNa_2O + 3xN_2 + (5x + 1)Al_2O_3 + 2\ Cr\ x \quad (4)$$

(Here, the coefficient x defines the amount of sodium nitrate ($NaNO_3$) to be added to the formulation.)

$$Cr_2O_3 + 0{,}25\ CrO_3 + (2{,}5)Al \rightarrow (1{,}25)Al_2O_3 + 2{,}25\ Cr \quad (5)$$

Table 2. Recipe Contents

Recipe Code	Specific Heat (J/g)	(%)
E1N4	4307	$Cr_2O_{3(k)} + 3Al_{(k)} + 0{,}6NaNO_3 \rightarrow 2Cr_{(k)} + 1{,}5Al_2O_{3(k)} + 0{,}3Na_2O + 0{,}3N_2$
E1N6-T1	3006	$Cr_2O_{3(k)} + 2{,}3Al_{(k)} + 0{,}18NaNO_3 + 0{,}33CaO \rightarrow 2Cr_{(k)} + 1{,}15Al_2O_{3(k)} + 0{,}33CaO + 0{,}09Na_2O + 0{,}09N_2$
E1N9	3056	$Cr_2O_{3(k)} + 2{,}2Al_{(k)} + 0{,}12NaNO_3 \rightarrow 2Cr_{(k)} + 1{,}1Al_2O_{3(k)} + 0{,}06Na_2O + 0{,}06N_2$
T1	3625	$Cr_2O_{3(k)} + 0{,}25CrO_{3(k)} + 2{,}5Al_{(k)} \rightarrow 2{,}25Cr_{(k)} + 1{,}25Al_2O_{3(k)}$
E1N9-R1	2845	$Cr_2O_{3(k)} + 2{,}1Al_{(k)} + 0{,}06NaNO_3 \rightarrow 2Cr_{(k)} + 1{,}05Al_2O_{3(k)} + 0{,}03Na_2O + 0{,}03N_2$

In the experimental studies, various formulations with different specific heat values were tested. The E1N4 formulation, with a high specific heat of 4307 J/g, resulted in an intense reaction, which caused difficulties in separating the metal and slag. To control the slag phase, the E1N6-T1 formulation (3006 J/g), containing CaO, was developed; however, the direct addition of CaO to the mixture reduced the reaction yield. Therefore, CaO was applied as a cover, resulting in a more homogeneous product. Alternatively, in the T1 formulation, CrO_3 was used instead of $NaNO_3$, and a similar product yield was achieved; however, due to the high cost of CrO_3, further studies with this formulation were discontinued. Based on the positive results obtained, the E1N9 formulation, with a specific heat of 3056 J/g and without CaO, was taken as a reference, and the E1N9-R1 formulation (2845 J/g), with a lower specific heat, was developed from it.

CONCLUSIONS

In this study, the aluminothermic reduction method was employed to produce high-purity chromium metal, and an extensive experimental process was carried out using different formulations. Due to the low levels of impurities in the obtained chromium products, they could not be characterized using every analytical method; therefore, the metal samples were analysed by ICP-OES, while the slag samples were analysed by XRF. As a result of the experimental work, the specific heat range required for the reaction to proceed in the most efficient manner was determined to be 2900–3000 J/g. Within this range, the E1N9-R1 formulation was found to exhibit the best reaction performance. The analysis results of the metal and slag are presented in Table 3 and Table 4, respectively.

Table 3. ICP-OES Results of Products Obtained with Different Formulations

Recipe Code	Specific Heat (J/g)	Recipe Scales (kg)	(%)			
			Cr	**Fe**	**Si**	**Al**
E1N6-T1	3006	25	93,15	0,75	0,43	5,53
		50	97,00	-	-	-
E1N9	3056	25	97,94	0,66	0,36	0,88
		50	97,33	0,72	0,56	1,27
		100	97,60	0,71	0,16	1,36
T1	3625	25	96,29	0,86	0,39	2,31
		50	96,55	-	-	-
E1N9-R1	2845	100	97,62	0,61	0,099	1,65

Based on the stoichiometric calculations, the theoretical metal/slag ratio was predicted to be 47/53 at 100% yield. However, as a result of the experimental studies, an average of 42% metal by weight was obtained (metal/slag ratio of 42/58). The reaction yield was determined to be 89% by weight. The yield being 89% is considered to be due to factors such as gas release within the process, heat losses, mixture homogeneity, and reaction kinetics.

Table 4. XRF (Munzur-Munteam) Results of Slags for the Recipes

Recipe Code	Specific Heat (J/g)	Recipe Scales (kg)	(%)				
			Cr_2O_3	**Fe_2O_3**	**SiO_2**	**Al_2O_3**	Na_2**O**
E1N4	4307	8	13,6	1,63	0,79	79,36	3,32
E1N6-T1	3006	25	16,88	0,67	0,37	66,56	2,72
T1	3625	50	23,23	2,20	1,98	71,21	-
E1N9-R1	2845	100	13,45	1,23	0,32	81,54	2,27

In conclusion, the E1N9-R1 recipe was found to be successful in terms of reaction stability, product purity, and raw material utilization efficiency, and it holds high potential for integration into advanced industrial applications. Figures 2 and Figure 3 respectively show the X-ray Diffraction (XRD) analysis results of commercially available metallic chromium with 99.9% purity and our laboratory-produced E1N9-R1 sample. Examination of the diffraction pattern reveals the presence of characteristic peaks corresponding to chromium (Cr) in the crystalline structure of the sample. This indicates that chromium is prominently present in the metallic phase after the reaction. The positions and intensities of the peaks suggest a high degree of crystallinity and a significant chromium content within the sample. In conclusion, the E1N9-R1 recipe offers a formulation that has been optimized at both laboratory and pilot scale, enabling the production of high-purity metal and is competitive with commercial products in the industry. The recipe has been found successful in terms of reaction stability, product purity, and raw material utilization efficiency, and it holds high potential for integration into advanced industrial applications. In the upcoming stages, it is recommended to further enhance process efficiency, refine cost analyses, and examine its integration into continuous production systems.

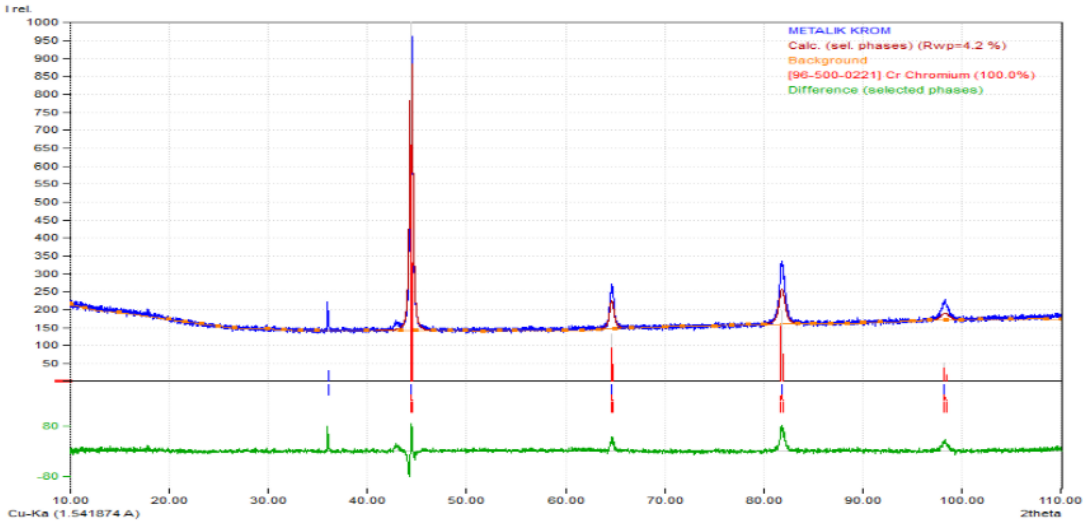
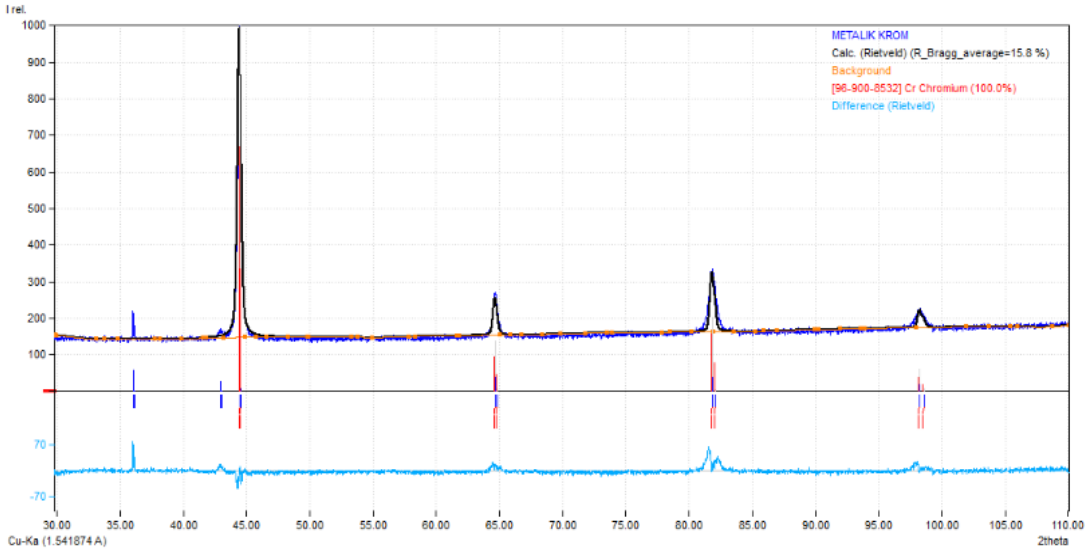


Figure 16. XRD Result of Commercially Available Metallic Chromium Sample with 99.9% Purity



Fi gure 17. E1N9-R1 Metal XRD Result

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Mechanical and Surface Characterization of Glass Fiber Reinforced Polymer Nanocomposites with Hematite and Magnetite

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ABSTRACT

Glass-fiber-reinforced polymer nanocomposites containing hematite (Fe_2O_3) and magnetite (Fe_3O_4) were synthesized and characterized to evaluate the effects of iron oxide fillers on mechanical and physical performance. Polyester-based composites containing fixed amounts of glass fiber and varying hematite or magnetite loadings (0–20 g) were prepared by molding and room-temperature curing. Tensile strength, hardness, contact angle, bulk density, and water absorption tests were conducted to determine structure–property relationships. Increasing Fe-oxide concentration enhanced hardness, hydrophobicity, and density while reducing tensile strength and elongation. Magnetite-filled composites exhibited more pronounced decreases in tensile properties compared to hematite-filled systems. Conversely, water absorption decreased with increasing filler content, indicating reduced porosity and improved compactness. The results show that hematite- and magnetite-reinforced polyester composites offer tunable performance and are suitable for industrial applications requiring enhanced durability and dimensional stability.

Keywords: Polymer composites, Glass fiber, Hematite, Magnetite, Mechanical properties, Surface properties, Polyester matrix

1. Introduction

Glass-fiber-reinforced polymer composites (CTP) have garnered significant attention due to their favorable strength-to-weight ratio, excellent chemical stability, low cost, and versatility across industrial applications (Rajak et al 2021, Kumar et al 2025). They are widely used in the automotive, construction, marine, aerospace, and defense sectors where lightweight and durable materials are essential (Nagaraju et al 2023, Guo et al 2024). Incorporating particulate fillers into polymer matrices allows tailoring properties such as stiffness, fracture toughness, thermal resistance, and surface behavior. Hematite (Fe_2O_3) and magnetite (Fe_3O_4) are iron oxide minerals exhibiting high density, chemical stability, and functional characteristics such as magnetic behavior (for magnetite) and semiconductor properties (for hematite). Their addition to polymer matrices can modify interfacial adhesion, reduce porosity, and enhance mechanical and tribological performance (Kumar e al 2021, Qureshi et al 2022).

Nano- or micro-scale incorporation of Fe oxides in fiber-reinforced composites can alter the load transfer between fiber and matrix, affecting tensile response, hardness, and environmental resistance. Although glass fiber provides high elastic modulus and rigidity, the presence of mineral fillers may influence the composite's composite behavior positively or negatively depending on concentration, dispersion, and interfacial bonding. This study investigates the effects of hematite and magnetite fillers on the mechanical, physical, and surface characteristics of polyester-based glass-fiber composites to better understand their applicability in multifunctional structural materials (Kumar et al 2024, Crespo et al 2014).

2. Materials and Methods

2.1 Materials

Polyester resin (Verpol) was used as the matrix material. The reinforcements were glass fiber, hematite (Fe_2O_3), and magnetite (Fe_3O_4) powders. Hematite was ground using a Refsan jet mill to obtain fine powder suitable for composite preparation. Magnetite powder was obtained commercially. An accelerator was added to promote polymer curing, and a mold-release agent (wax-based) was applied to molds prior to casting.

2.2 Composite Preparation

Polyester resin (9.8 g), accelerator (0.2 g), glass fiber (0.5 g), and varying amounts (0, 5, 10, 15, 20 g) of hematite or magnetite were thoroughly mixed for 7 minutes to ensure homogeneity. The formulations were identified as PH0–PH20 for hematite-filled composites and PM0–PM20 for magnetite-filled composites. The mixtures were poured into molds coated with release agent and cured at 23 °C for 48 hours.

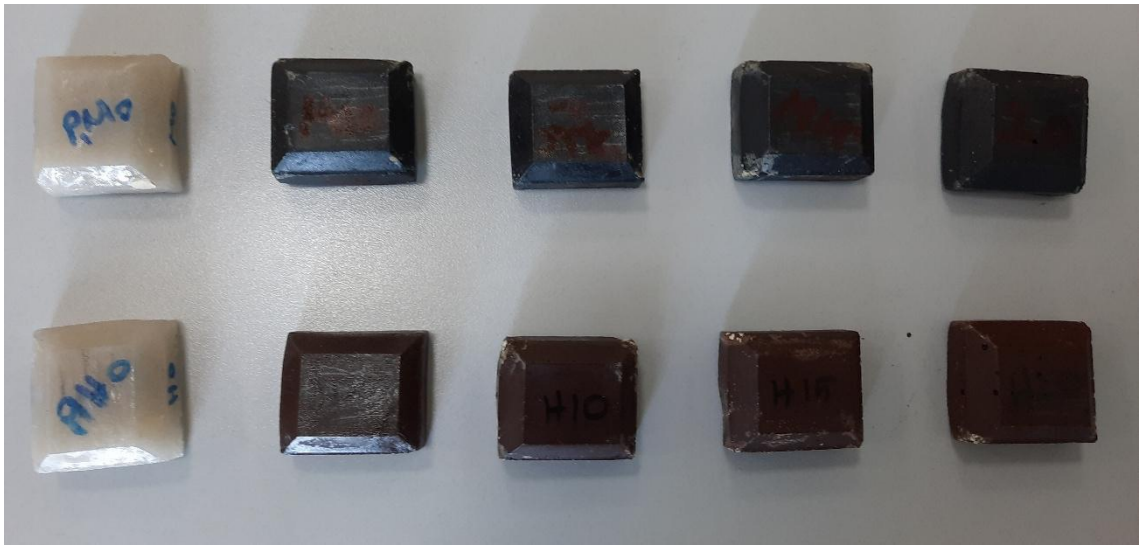

Figure 1. Samples

2.3 Mechanical and Physical Testing

Tensile Strength: A (Test Center) universal testing machine was used to measure elongation and tensile stress until failure.

Contact Angle: Hydrophobicity was evaluated using an Attension ThetaLite TL101 tensiometer.

Hardness: Pencil hardness tests were performed using a Qualitest kit.

Bulk Density: Density was measured using Archimedes' method with an AND brand density device.

Water Absorption: Samples were immersed in water for 48 hours, and water uptake (%) was calculated using mass differences

3. Results and Discussion

3.1 Tensile Properties

Table 1. Tensile strength results of PM samples.

Code	% Elongation	Strength (MPa)	Code	% Elongation	Strength (MPa)
PM_0	14,11	60,45	PH0	14,11	60,45
PM_5	12,35	43,92	PH5	9,81	51,33
PM_{10}	10,28	19,37	PH10	7,72	32,97
PM_{15}	9,45	24,19	PH15	6,39	17,57
PM_{20}	6,39	17,57	PH20	5,25	5,74

The tensile strength and elongation results clearly show that both magnetite- (PM) and hematite-reinforced (PH) polyester composites exhibit decreasing ductility and mechanical strength with increasing filler content, although the severity of deterioration differs between the two oxides. The unfilled polyester samples (PM0/PH0) demonstrate the highest performance, with 14.11% elongation and 60.45 MPa tensile strength, reflecting the continuity and flexibility of the polymer matrix. In the magnetite series, tensile strength declines from 43.92 MPa at PM5 to 19.37 MPa at PM10 and further decreases to 17.57 MPa at PM20, while elongation drops steadily from 12.35% at PM5 to 6.39% at PM20. This pronounced reduction indicates that magnetite particles induce significant stress concentrations and hinder polymer chain mobility. In the hematite series, the reduction in mechanical performance is even more severe. Tensile strength decreases rapidly from 51.33 MPa at PH5 to 32.97 MPa at PH10, and ultimately to just 5.74 MPa at PH20, accompanied by a sharp decline in elongation from 9.81% to 5.25%. Compared to magnetite, hematite leads to greater matrix disruption and weaker interfacial bonding, especially at higher loadings, resulting in reduced load-transfer capability and greater brittleness. Overall, the results demonstrate that increasing amounts of both mineral fillers degrade tensile behavior, but hematite-filled composites (PH series) lose mechanical integrity more dramatically than magnetite-filled composites, indicating poorer compatibility between hematite particles and the polyester matrix. (Gürü et al 2005, Chavan et al 2015).

3.2 Surface Wettability

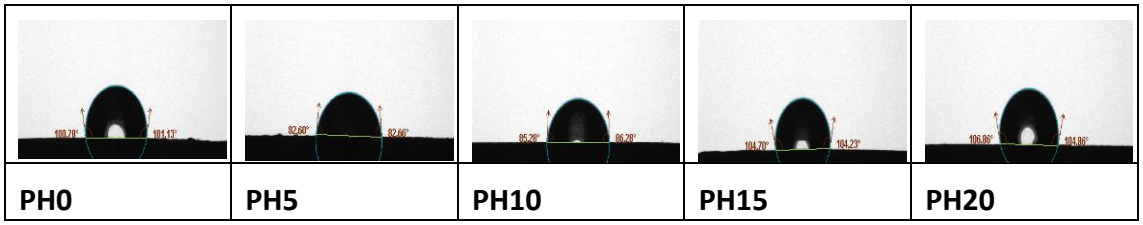

Figure 2. Contact Angle of PH samples

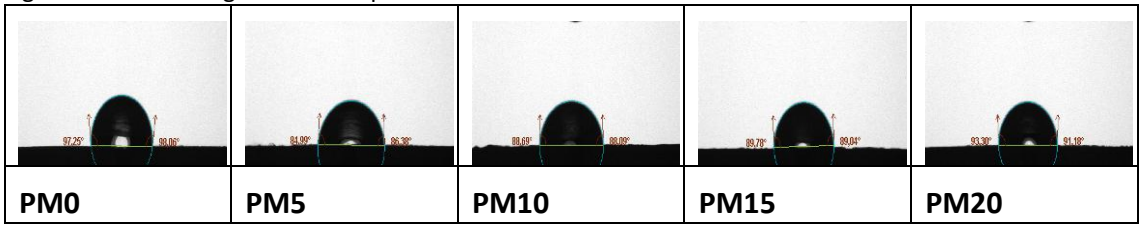

Figure 3. Contact Angle of PM Samples

The contact angle measurements show that both hematite- (PH series) and magnetite-reinforced (PM series) polyester composites exhibit predominantly hydrophobic behavior, although the degree of hydrophobicity varies with mineral type and loading level. In the PH series, contact angles remain consistently high across all compositions, ranging from approximately 100° to 110°, indicating that

hematite additions maintain or slightly enhance surface hydrophobicity. The PH0, PH5, and PH15 samples display angles around 100°–103°, whereas PH10 and PH20 show more pronounced hydrophobicity with values approaching 110°, suggesting that moderate to higher hematite loadings may induce micro-scale surface roughness that reduces surface energy and enhances water repellency. In contrast, the PM series exhibits greater variability and generally lower contact angles, indicating weaker hydrophobic behavior compared to hematite-filled samples. PM0 begins around 97°, but the angles gradually decrease with increasing magnetite content, reaching the lowest values (around 83°–85°) at PM15 and PM20. This trend suggests that magnetite particles disrupt surface uniformity more significantly than hematite, likely creating microvoids or regions with higher surface energy that enhance water spreading. Overall, the results demonstrate that hematite-reinforced composites exhibit better hydrophobic performance and more stable surface characteristics, while magnetite additions tend to reduce hydrophobicity, making the surface more susceptible to wetting as filler concentration increases. This difference is attributed to particle morphology, dispersion quality, and the degree of interfacial compatibility with the polyester matrix.

3.3 Hardness

Table 2. Pencil hardness test result of samples

Samples	Hardness	Samples	Hardness
PM0	4B	PH0	4B
PM5	3B	PH5	2H-H
PM10	2B-3B	PH10	H-F
PM15	3B-4B	PH15	F-HB
PM20	4B	PH20	HB-B

The pencil hardness results show that the incorporation of hematite (PH) and magnetite (PM) particles into the polyester matrix leads to varying degrees of surface hardness modification, reflecting the influence of particle morphology, dispersion quality, and interfacial bonding on the scratch resistance of the composites. In the PM series, hardness begins at 4B for the unfilled sample (PM0) and exhibits a fluctuating trend as magnetite content increases. PM5 shows a modest improvement to 3B, while PM10 demonstrates a reduction to 2B–3B, indicating that partial agglomeration or uneven distribution may weaken surface integrity. Interestingly, PM15 displays an increase to 3B–4B, and PM20 returns to 4B, suggesting that at higher loadings, magnetite particles may fill surface microvoids more effectively or contribute to localized stiffening despite the inherent brittleness they introduce. The PH series, however, demonstrates a more consistent decrease in hardness with increasing hematite content. While PH0 starts at 4B, PH5 drops sharply to 2H–H, indicating a transition toward a harder but more brittle surface characteristic due to hematite's rigid crystal structure. PH10 reaches H–F, PH15 decreases further to F–HB, and PH20 falls to HB–B, revealing a progressive softening effect as the surface becomes increasingly disrupted at higher particle concentrations. Overall, the results indicate that magnetite-filled composites maintain a more stable and generally softer hardness profile, whereas hematite-filled composites exhibit a broader hardness spectrum—initially becoming harder due to particle rigidity but softening again at high filler contents due to surface discontinuity and reduced matrix cohesion. These differences highlight the sensitivity of surface mechanical behavior to mineral type, loading level, and particle–matrix interaction.

3.4 Bulk Density and Water Absorption

Table 3. Bulk density and water absorption results

Code	Bulk Density g/cm^3	% W.A.	Code	Bulk Density g/cm^3	% W.A.
PH0	1,2256	0,58	PM0	1,2101	0,60
PH5	1,3556	0,54	PM5	1,5135	0,42
PH10	1,7842	0,57	PM10	1,8831	0,43
PH15	1,9231	0,31	PM15	2,1249	0,29
PH20	2,1849	0,40	PM20	2,2004	0,31

The bulk density and water absorption results indicate that increasing hematite (PH) and magnetite (PM) content significantly modifies the internal structure and porosity characteristics of the polyester composites. In both series, the unfilled samples (PH0 and PM0) exhibit the lowest densities (1.2256 and 1.2101 g/cm³, respectively) and relatively similar water absorption values (~0.58–0.60%), reflecting the inherent porosity of the pure polymer. As hematite content increases, bulk density rises sharply, reaching 2.1849 g/cm³ at PH20, which is consistent with the higher intrinsic density of hematite and improved particle packing within the matrix. Simultaneously, water absorption decreases overall—from 0.58% in PH0 to 0.40% in PH20—indicating reduced porosity and more compact structural formation at higher hematite loadings; the minimum value is observed at PH15 (0.31%), suggesting optimal densification at this concentration. The magnetite series (PM) shows a similar densification trend, with bulk density increasing from 1.2101 g/cm³ in PM0 to 2.2004 g/cm³ in PM20. Water absorption also decreases consistently with magnetite addition, reaching 0.29% at PM15 and only slightly increasing to 0.31% at PM20. These results confirm that both hematite and magnetite fillers act as effective densification agents, occupying internal voids and limiting pathways for water penetration. However, the magnetite-reinforced composites exhibit slightly lower water absorption values at comparable loadings, which may be attributed to better dispersion or improved matrix–filler compatibility relative to hematite. Overall, the combined trends of increasing density and decreasing water absorption demonstrate that mineral reinforcement—particularly at higher concentrations—enhances the structural compactness and moisture resistance of polyester composites.

4. Conclusion

The mechanical, physical, and wetting behaviors of the hematite- (PH series) and magnetite-reinforced (PM series) polyester composites reveal that the addition of Fe-oxide fillers significantly alters the performance of the polymer matrix, with distinct trends governed by particle morphology, density, and matrix–filler interfacial interactions. Tensile strength and elongation results demonstrate a clear deterioration in ductility and load-bearing capacity as filler concentration increases. The unfilled polymer exhibits the highest performance (σ = 60.45 MPa; ε = 14.11%), reflecting the uninterrupted chain mobility and flexibility of pure polyester. In both PH and PM series, increasing Fe-oxide content restricts matrix continuity and creates stress-concentration sites, leading to reduced elongation and lower tensile strength. Magnetite-filled composites retain moderately higher mechanical performance at low concentrations (PM5: 43.92 MPa), whereas hematite induces a more rapid degradation at higher loadings, dropping sharply to 5.74 MPa at PH20. These observations confirm that hematite particles—likely due to their angular morphology and higher rigidity—cause more severe embrittlement and weaker interfacial bonding compared to magnetite.

Pencil hardness measurements further support the structural changes induced by Fe-oxide inclusion. The PM series exhibits a relatively stable hardness profile (ranging from 2B–4B), suggesting that magnetite's

spherical/rounded particle geometry leads to less aggressive disruption of the surface microstructure. In contrast, the PH samples show an initially harder but progressively softer response (from 2H–H at PH5 to HB–B at PH20). This transition implies that hematite creates a brittle surface at low concentrations but increases surface defects and micro-cracks as loading increases, reducing overall scratch resistance.

Bulk density and water absorption data reveal improved structural compactness with rising filler content for both minerals. As expected due to their high intrinsic densities, the addition of Fe-oxides increases composite density significantly—from ~1.22 g/cm³ at 0 g loading to over 2.18 g/cm³ (PH20) and 2.20 g/cm³ (PM20). Water absorption decreases concurrently, reaching minimum values of 0.31% in PH15 and 0.29% in PM15, indicating reduced porosity and improved packing efficiency. The consistently lower %W.A. values in the PM series suggest better dispersion and a more uniform matrix–filler interface compared to hematite-filled composites.

Contact angle measurements illustrate notable differences in surface wettability between the two filler types. Hematite-filled composites maintain high hydrophobicity across all loadings (≈100–110°), demonstrating that hematite promotes a low-energy, water-repellent surface. In contrast, magnetite-filled samples show decreasing hydrophobicity at higher concentrations, with angles falling to 83–85° in PM15 and PM20. This suggests that magnetite particles generate a more heterogeneous surface containing microvoids or high-energy regions that promote wetting. The superior hydrophobic performance of PH samples may be attributed to hematite's ability to create a more uniformly rough surface topography, consistent with the Cassie–Baxter model of wetting.

Overall, the combined results clearly show that magnetite-reinforced composites retain mechanical performance more effectively but show reduced hydrophobicity, whereas hematite-reinforced composites exhibit greater embrittlement and hardness loss at high loadings but maintain superior water-repellent behavior. These contrasting effects underline the critical importance of mineral selection and filler concentration in tuning the multifunctional properties of Fe-oxide-based polyester composites. The findings also highlight the need for surface modification strategies—such as silane treatment, nano-sizing, or coupling agents—to strengthen interfacial adhesion and overcome the mechanical limitations observed in the current, untreated filler system.

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Investigation of Physical and Mechanical Properties of Boron Mineral Reinforced Polyester Composites

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ABSTRACT

This study investigates the physical and mechanical properties of polymer composites reinforced with boron minerals. Polyester resin was used as the matrix material, while colemanite, ulexite, and tincal, each with an average particle size of 100 µm, were incorporated as reinforcing fillers in varying amounts (0, 5, 10, 15, and 20 g). The prepared mixtures were poured into molds, cured at room temperature, and subjected to a series of tests. Mechanical properties were characterized through hardness and tensile strength measurements, while physical behavior was evaluated by water absorption, porosity, bulk density, and contact angle analyses.

The results showed that increasing boron mineral content generally reduced tensile strength and elongation, while hardness values also tended to decrease with higher reinforcement levels. On the other hand, density values increased for ulexite- and tincal-based composites, whereas water absorption and porosity varied depending on mineral type and content. The maximum density was obtained with 20 g colemanite reinforcement, while the highest water absorption and porosity were observed in tincal-added composites.

Overall, the incorporation of boron minerals influenced the mechanical and surface characteristics of polyester-based composites. These findings highlight the potential of boron-containing fillers in tailoring composite performance for applications in construction, polymer engineering, and advanced material design

Keywords: Polymer composites, glass fiber, hematite, magnetite, mechanical properties, characterization

1. Introduction

Composite materials have gained substantial importance across aerospace, automotive, marine, construction, and defense industries due to their high strength-to-weight ratio, corrosion resistance, design flexibility, and cost-efficiency. Polymers reinforced with mineral fillers, fibers, or particulates can achieve improved mechanical, thermal, and environmental performance compared to unmodified polymers. Polyester-based composites are widely preferred because of their ease of processing, low cost, chemical stability, and ability to incorporate various reinforcements (Shubham and Ray 2024, Bhong et al 2023, Gebrehiwet et al 2023, Oladele et al 2020, Chauhan et al 2021, Clyne and Hull 2019, Gay 2022).

Boron minerals—colemanite, ulexite, and tincal—represent strategically important industrial raw materials thanks to their abundance in Türkiye, high B_2O_3 content, thermal stability, flame-retardant potential, and chemical reactivity (Helvacı 2017, Helvacı 2015). These minerals have been incorporated into polymer matrices to enhance fire resistance, thermal durability, and structural stability. However, their influence on the mechanical and physical properties of polyester composites remains insufficiently explored (Uygunoğlu et al 2015, Akgün 2015, Tanrıkulu and Yaşar 2017).

This study focuses on producing and characterizing polyester composites modified with different concentrations of boron minerals. By evaluating hardness, tensile performance, water absorption, porosity, density, and surface wettability, this work aims to provide detailed insight into how mineral type and concentration affect the structural behavior of polymer composites. Findings will contribute to the development of boron-containing polymeric materials for engineering applications.

2. Materials and Methods

2.1 Materials

Polyester resin (Verpol), accelerator (2 wt%), mold-release wax, and boron minerals (colemanite, ulexite, and tincal) supplied by Eti Maden were used. Colemanite and ulexite were used in powder form; tincal was obtained as rock and ground using a Refsan jet mill to <212 µm.

2.2 Preparation of Composites

Three composite series were produced:

PK series: Polyester + Colemanite

PÜ series: Polyester + Ulexite

PT series: Polyester + Tincal

Figure 1. Composite samples

Minerals were added at 0, 5, 10, 15, and 20 g to 9.8 g polyester resin and 0.2 g accelerator. Each mixture was stirred for 5 minutes to ensure homogeneity and then cast into molds previously coated with wax (Figure references in thesis). Samples were left to cure at room temperature for 24 hours before demolding.

2.3 Mechanical Testing

Hardness

Figure 2. Pencil hardness test

Pencil hardness was measured using a Qualitest pencil hardness set (6H to 6B scale).

Tensile Strength

Figure 3. Tensile strength test

Dogbone-shaped samples were tested using a universal testing machine. Tensile stress (σ), strain (ε), and modulus (E) were calculated using:

2.4 Physical Testing

Water Absorption

Porosity

Bulk Density

Contact Angle

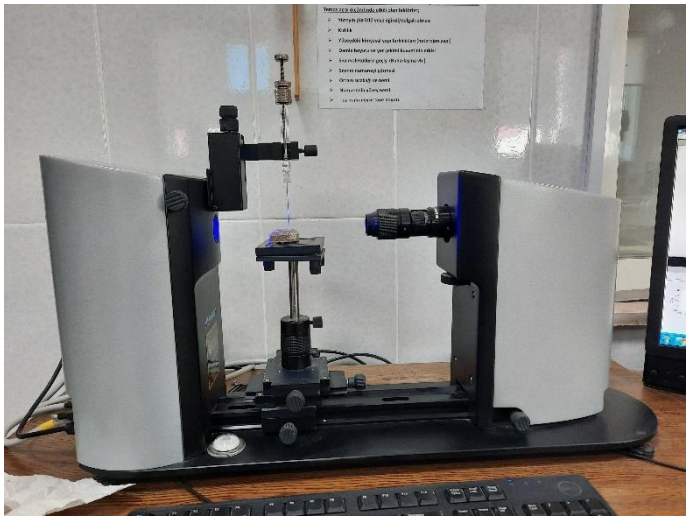

Figure 4. Attension Theta Lite

Sessile drop method using a KSV Attension ThetaLite TL101 optical tensiometer.

3. Results and Discussion

3.1 Hardness

Table 1. Hardness test results.

Code	Hardness	Code	Hardness	Code	Hardness
PK0	4B	PU0	4B	0	4B
PK5	2B-3B	PU5	3B	PT5	2B
PK10	4B	PU10	3B	PT10	2B-3B
PK15	3B	PU15	B	PT15	B-2B
PK20	3B	PU20	B	PT20	HB-B

The pencil hardness results of the boron mineral–reinforced polyester composites show a clear decreasing trend in surface hardness as the mineral content increases, although the magnitude of this decrease varies according to the type of boron mineral used. In the colemanite-reinforced series (PK), the highest hardness values were observed for the unfilled sample (PK0) and the 10 g-filled sample (PK10), both rated at 4B, indicating that low to moderate colemanite addition does not significantly deteriorate surface resistance. However, the hardness decreases to 2B–3B at 5 g and stabilizes around 3B at higher contents (15–20 g), suggesting a moderate softening effect caused by particle–matrix incompatibility. In contrast, the ulexite-reinforced composites (PU) exhibited a more pronounced reduction in hardness, decreasing steadily from 4B in the unfilled sample to B at 15 g and 20 g. This behavior indicates that ulexite particles, due to their more porous and fibrous structure, weaken the surface integrity and increase the composite's susceptibility to scratching. The most significant hardness loss occurred in the tincal-reinforced series (PT), where the hardness dropped from 4B to HB–B at 20 g loading, representing the lowest surface hardness among all groups. The irregular morphology and weaker bonding tendency of tincal particles likely introduce more severe micro-discontinuities within the matrix. Overall, the results demonstrate that

increasing mineral content generally reduces the scratch resistance of polyester composites, with tincal causing the greatest reduction, followed by ulexite, while colemanite exhibits the least adverse effect.

3.2 Tensile Strength

Table 2. Tensile strength test results.

Code	% Elongation	Strength (MPa)	Code	% Elongation	Strength (MPa)	Code	% Elongation	Strength (MPa)
PK0	16,97	81,03	PU0	16,97	81,03	0	16,97	81,03
PK5	12,75	57,12	PU5	10,82	38,88	PT5	7,05	21,15
PK10	8,19	20,4	PU10	7,72	32,97	PT10	5,96	8,26
PK15	7,56	24,01	PU15	5,96	8,26	PT15	10,69	7,23
PK20	5,9	17,32	PU20	3,07	7,03	PT20	5,35	13,43

The tensile strength and elongation results of the boron mineral–reinforced polyester composites clearly indicate that increasing mineral content leads to a substantial reduction in ductility and load-bearing capacity, although the extent varies depending on the type of mineral used. In all three composite groups, the unfilled samples (PK0, PU0, PT0) exhibited the highest tensile strength (81.03 MPa) and elongation (16.97%), reflecting the inherent flexibility and continuity of the pure polyester matrix. Among the colemanite-reinforced composites (PK), tensile strength decreased progressively from 57.12 MPa at 5 g to 17.32 MPa at 20 g, accompanied by a similar reduction in elongation from 12.75% to 5.90%. This trend suggests that increasing colemanite content introduces stress concentrations and weakens matrix continuity. The ulexite-reinforced series (PU) showed an even sharper decline; strength dropped from 38.88 MPa at 5 g to just 7.03 MPa at 20 g, while elongation fell from 10.82% to 3.07%, demonstrating that ulexite's fibrous and porous structure disrupts the polymer network more severely. Tincal-filled composites (PT) displayed the most irregular behavior, with tensile strength decreasing sharply at low contents (21.15 MPa at 5 g; 8.26 MPa at 10 g), followed by partial recovery at higher levels (13.43 MPa at 20 g), while elongation values fluctuated between 5.35% and 10.69%. This inconsistency reflects tincal's larger particle size and heterogeneous morphology, which can both weaken and locally stiffen the matrix depending on dispersion quality. Overall, the results show that all boron minerals reduce tensile performance by limiting polymer chain mobility and introducing interfacial defects, with ulexite causing the most severe degradation, followed by tincal, whereas colemanite provides comparatively more stable mechanical behavior.

3.3 Water Absorption

Table 3. Water absorption test results.

Code	% W. A.	Bulk Density g/cm^3	Code	% W. A.	Bulk Density g/cm^3	Code	% W. A.	Bulk Density g/cm^3
PK0	0,62	1,2497	PU0	0,62	1,2497	PT0	0,62	1,2497
PK5	0,74	1,3961	PU5	0,99	1,3446	PT5	1,31	1,3157
PK10	1,01	1,6381	PU10	0,63	1,4722	PT10	1,51	1,2977
PK15	0,59	1,4299	PU15	0,65	1,5143	PT15	0,85	1,4108
PK20	0,51	1,6505	PU20	0,56	1,5470	PT20	0,59	1,5373

The water absorption and bulk density results demonstrate that boron mineral type and loading significantly influence the microstructural compactness and moisture uptake behavior of the polyester composites. In all series, the unfilled samples (PK0, PU0, PT0) displayed identical baseline values of 0.62% water absorption and 1.2497 g/cm³ density. In the colemanite-reinforced composites (PK), water absorption initially increased from 0.74% at 5 g to a peak of 1.01% at 10 g, then decreased to 0.51% at 20 g. Bulk density, however, showed a general upward trend with increasing colemanite content, reaching the highest density of 1.6505 g/cm³ at 20 g, indicating improved structural packing at higher concentrations. Ulexite-filled composites (PU) exhibited relatively stable and low water absorption values ranging from 0.56% to 0.99%, while bulk density consistently increased from 1.3446 g/cm³ (5 g) to 1.5470 g/cm³ (20 g), suggesting better dispersion and densification of ulexite particles within the polymer matrix. In contrast, tincal-reinforced composites (PT) showed the highest water absorption values among all minerals, peaking at 1.51% at 10 g, which reflects tincal's more irregular morphology and reduced compatibility with polyester. Bulk density in PT samples increased irregularly but ultimately reached 1.5373 g/cm³ at 20 g, indicating partial densification despite higher porosity tendencies. Overall, while increased mineral content generally enhances density by introducing heavier particulate phases, water absorption trends vary depending on particle morphology and interfacial adhesion. Colemanite and ulexite improve structural compactness at higher loadings, whereas tincal tends to generate more voids and moisture pathways, resulting in elevated water uptake compared to the other minerals.

3.4 Contact Angle

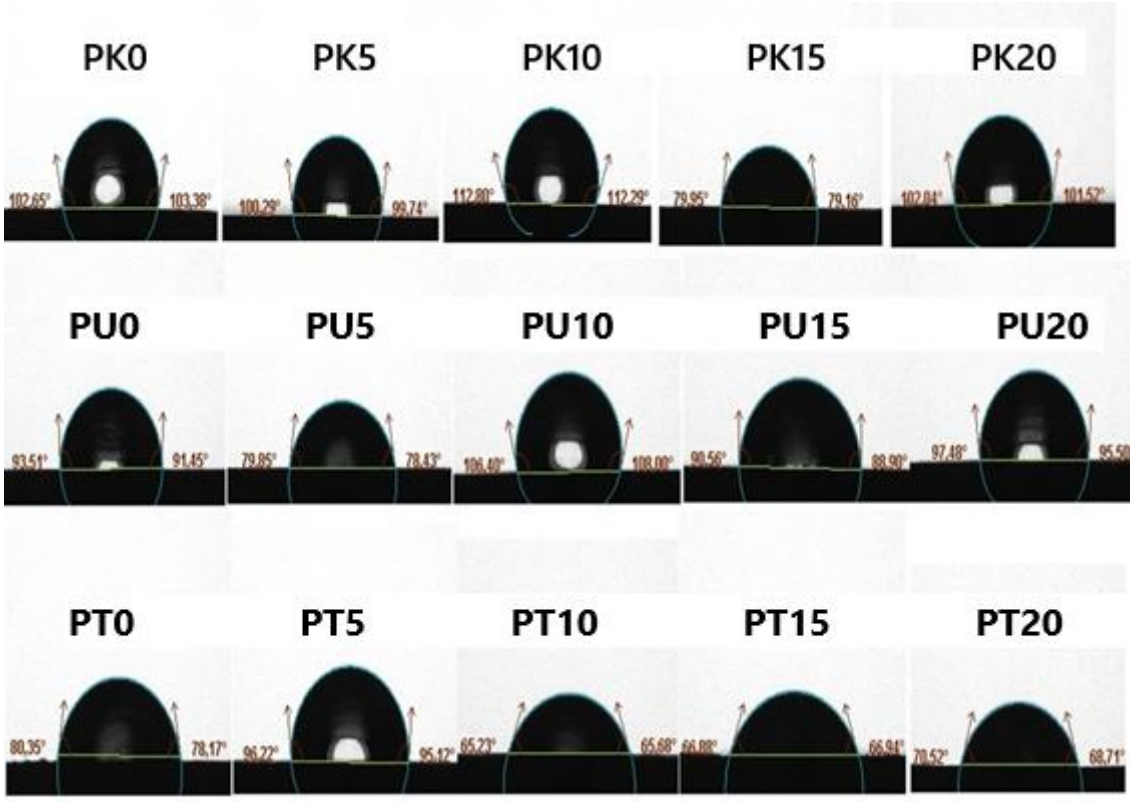

Figure 5. Contact angle results

The contact angle results of the boron mineral–reinforced polyester composites show that mineral type and loading significantly influence surface wettability, leading to distinct hydrophobicity–hydrophilicity behaviors across the PK, PU, and PT series. In the colemanite group (PK), the highest contact angle was observed at 10 g loading (112.54°), indicating a markedly hydrophobic surface, while other PK samples remained relatively stable around 100°–105°, except for PK15, which decreased to 79.55°. This suggests

that moderate colemanite content enhances surface roughness and reduces surface energy, whereas higher loading may disrupt surface uniformity. In the ulexite series (PU), the maximum contact angle occurred at 10 g (107.2°), while lower values were recorded for PU5 (79.14°) and PU0 (93°), reflecting irregular changes likely caused by ulexite's fibrous morphology and variable dispersion within the matrix. The tincal composites (PT) exhibited the lowest overall contact angles, with PT10 showing the minimum value of 65.45°, indicating increased hydrophilicity and suggesting poor interfacial adhesion and surface smoothness compared to the other minerals. Although PT5 demonstrated a relatively higher angle (95.67°), tincal-containing surfaces generally showed reduced hydrophobicity with increasing loading. Overall, the results indicate that colemanite and ulexite can enhance hydrophobicity at moderate concentrations, while tincal reduces contact angle values, likely due to its larger particle size, weaker compatibility with polyester, and tendency to produce microvoids on the surface. These findings highlight the strong influence of mineral morphology and dispersion on surface wettability in boron mineral–reinforced polyester composites.

4. Conclusion

The mechanical and physical characterization results reveal that the addition of boron minerals—colemanite, ulexite, and tincal—significantly alters the structural behavior of polyester composites, with each mineral producing distinct effects based on its morphology, particle size, and interfacial compatibility with the polymer matrix. Pencil hardness measurements showed a general decline in surface hardness with increasing mineral content for all composite groups. While colemanite-filled samples retained relatively higher hardness values, especially at 0 g and 10 g loadings (4B), both ulexite- and tincal-reinforced composites exhibited pronounced softening, reaching as low as HB–B at 20 g tincal. This reduction in hardness is attributed to increased surface discontinuities, microvoid formation, and weaker particle–matrix bonding, which reduce scratch resistance.

Tensile properties followed a similar decreasing trend. The unfilled polyester samples exhibited the highest tensile strength (81.03 MPa) and elongation (16.97%), consistent with the behavior of a continuous and ductile polymer network. Increasing mineral content disrupted this continuity, leading to lower tensile performance. Colemanite composites demonstrated a moderate decline, decreasing to 17.32 MPa at 20 g, whereas ulexite-filled composites showed severe degradation, falling to 7.03 MPa at 20 g. Tincal composites displayed more irregular behavior: tensile strength dropped sharply at low concentrations (8.26 MPa at PT10) and partially recovered at higher loading (13.43 MPa at PT20). These observations reflect the interplay between particle brittleness, resin–particle adhesion, and dispersion quality. Ulexite's fibrous and porous structure likely acts as a preferential crack path, while tincal's larger and irregular particles introduce local stress concentrations that impair tensile load transfer.

The water absorption and bulk density results further support the mechanical data. In general, increasing mineral loading increased composite density because boron minerals possess higher intrinsic densities than polyester. Tincal and ulexite composites showed the clearest density increases, reaching 1.5373 g/cm³ and 1.5470 g/cm³ at 20 g, respectively. Colemanite composites achieved the highest density in the entire study (1.6505 g/cm³ at PK20), indicating effective packing at higher loadings. Water absorption trends varied more strongly with mineral type: tincal-reinforced composites exhibited the highest moisture uptake (1.51% at PT10), suggesting poorer interfacial adhesion and higher porosity. In contrast, colemanite and ulexite composites showed relatively stable and lower water absorption values at higher loadings, indicating better structural compactness.

The contact angle measurements revealed that surface wettability is highly sensitive to both mineral type and concentration. Moderate mineral additions (10 g) of colemanite and ulexite significantly increased hydrophobicity, with PK10 and PU10 exhibiting the highest contact angles (112.54° and 107.2°, respectively). This enhancement is attributed to surface roughness modification and partial reduction of surface energy at optimal filler dispersions. However, further mineral addition reduced hydrophobicity due to increased surface defects and particle agglomeration. Tincal-reinforced composites generally showed the lowest contact angles, especially at PT10 (65.45°), indicating increased hydrophilicity and poor surface integrity compared to the other minerals.

Overall, the combined results indicate that boron mineral reinforcements modify polyester composites through complex physical and interfacial mechanisms. Colemanite demonstrates the most balanced performance, producing moderate reductions in mechanical properties while improving density and hydrophobicity at certain loadings. Ulexite reinforces density but significantly weakens tensile strength and hardness due to its morphology. Tincal exhibits the most inconsistent behavior, producing the highest porosity and water absorption alongside the lowest mechanical properties. These findings highlight that the selection of minerals and loading level are critical in determining the suitability of boron-reinforced polyester composites for engineering applications.

The direct use of boron minerals did not generate significant improvements in mechanical or surface properties due to weak particle–matrix interfacial adhesion. Future work should focus on surface modification techniques such as silane functionalization, nano-sized particle production, ultrasonic dispersion, or hybrid reinforcement systems, which are expected to enhance interfacial bonding and substantially improve the composite performance."

Acknowledgments

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Effect Of Cooling Temperature and Line Speed on The Structural Properties of Medium and High Carbon Steel Wires

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ABSTRACT

One of the most important types of heat treatment to which high carbon steel wires are subjected is patenting. Patenting consists of passing the wire through a furnace with a temperature range of 950-1000 °C. This high temperature treatment produces homogeneous austenite with a coarse grain size. The wires are then rapidly cooled in a lead bath tank to a temperature range of 450 to 570 °C. The cooling process aims to obtain a fine uniform pearlitic phase that will be suitable for plastic deformation in drawing processes. In this study, the effect of cooling temperature (520 and 560 °C) and line speed (40, 50 and 60 m/min) on the structural properties of medium and high carbon steel wires were investigated. The experimental results revealed that mechanical properties of medium and high carbon steel wires were significantly affected by the applied thermo-mechanical treatments. By increasing the cooling temperature, ultimate tensile strength gradually decreased, and ductility improved. Increasing the line speed from 50 m/min to 60 m/min caused a downward trend in mechanical properties. The test results showed that the optimum mechanical properties were obtained for steel wires cooled at 520 °C with a line speed of 50 m/min.

Keywords: Characterization, cooling effect, line speed, steel wire

1. Introduction

High-strength steel wires are extensively utilized across a wide range of industrial sectors due to their exceptional mechanical properties, making them indispensable in many critical applications [1]. Among these, pearlitic steel wires are particularly valued for their remarkable combination of high strength and ductility, which enables them to perform reliably under demanding conditions. These wires are commonly employed in reinforcing car tires, providing the necessary strength and flexibility for safety and durability. They are also integral components in suspension bridge cables, where their tensile strength and fatigue resistance ensure structural stability and longevity. Additionally, pearlitic steel wires are used in the manufacture of high-strength springs, which require excellent elastic properties, as well as in various types of instrumental string wires that demand precise mechanical performance. In the context of renewable energy, these wires contribute to the reinforcement of lightweight wind turbine blades, facilitating cleaner energy production by enhancing blade strength without significantly increasing weight. Furthermore, they are employed as cutting saw wires in the photovoltaic industry, where their strength and precision are crucial for efficient panel production [2]

To optimize the mechanical properties of these pearlitic steel wires, particularly to enhance their drawability, they undergo a specialized two-stage intermediate heat treatment known as the patenting process. This process is critical for refining the microstructure of the steel and improving its plastic deformation capacity. The patenting process begins with heating the steel wire to a temperature above the upper critical temperature (A3), typically above 950 ˚C. This step ensures the transformation of the steel's microstructure into a homogeneous austenite phase characterized by coarse grains [3]. Maintaining this temperature for an adequate period allows the formation of uniform austenite, which is a prerequisite for achieving the desired final microstructure. Following the austenitizing stage, the wire is subjected to a controlled cooling process designed to transform the austenite into a fine lamellar pearlitic structure. This transformation is carefully managed to minimize the formation of proeutectoid ferrite, which can adversely affect mechanical properties. The controlled cooling is often performed in specialized media such as a molten lead bath or a fluidized sand bed, both of which provide precise thermal control to achieve the fine pearlitic microstructure essential for high strength and ductility.

From a metallurgical standpoint, the effectiveness of the patenting process is governed by the principles of isothermal transformation and is typically described using Time-Temperature-Transformation (TTT) diagrams. These diagrams, as illustrated in Fig. 1a and Fig. 1b, are fundamental tools that help determine the optimal pearlite transformation time and the rate at which the austenite phase transforms under specific temperature conditions. The TTT diagrams reveal critical information about the kinetics of phase changes during the heat treatment process. In particular, they highlight the necessity of rapidly cooling the wire from the austenitizing temperature down to below 550 °C, followed by maintaining this temperature for a few seconds. This approach allows the steel to undergo controlled isothermal transformation, resulting in the formation of a fine lamellar pearlite structure that imparts the desired mechanical characteristics to the wire [4]. Overall, the patenting process is essential for producing high-strength steel wires with superior mechanical properties tailored for demanding industrial applications. By carefully controlling heat treatment parameters such as temperature, cooling rate, and holding time, manufacturers can optimize the microstructure and performance of steel wires to meet specific application requirements.

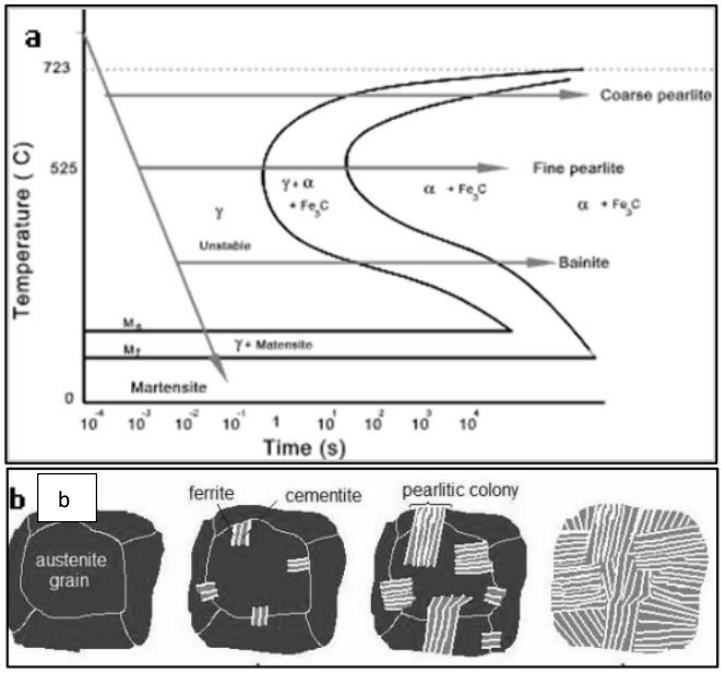

Figure 1. (a) Patenting heat treatment on TTT diagrams and (b) fine pearlite structure [4].

Patenting heat treatment plays a crucial role in enhancing the total drawability of steel wires, which is an important factor for their performance in various applications. Achieving a high elongation ratio—a measure of the wire's ability to stretch without breaking—depends heavily on developing suitable microstructural characteristics within the steel. Although numerous studies have examined the quality

and performance aspects of patented steel wires, there remains a scarcity of quantitative research focused specifically on conditions encountered in industrial production environments. One of the key elements influencing the effectiveness of the patenting heat treatment is the cooling process, which is significantly affected by parameters such as cooling temperature and processing speed. These factors determine the microstructural evolution during transformation and, consequently, the mechanical properties of the finished wire. In this context, the present study aims to systematically investigate the effects of two different cooling temperatures—520 °C and 560 °C—and three distinct process speeds—40, 50, and 60 meters per minute—on the mechanical behavior and microstructure of medium and high carbon steel wires. Beyond the immediate cooling parameters, this study also delves into how variations in chemical composition, as well as the temperature and duration of the transformation process, influence the mechanical properties of wires treated using the lead patenting method. By understanding these relationships, the study seeks to provide deeper insights into optimizing the patenting process to produce steel wires with superior mechanical performance tailored for industrial applications.

2. Material and Method

In this study, medium- and high-carbon steel wire rods with carbon contents of approximately 0.45%, 0.55%, 0.70%, and 0.83% by weight were used. Their detailed chemical compositions and mechanical properties are provided in Table 1 and Table 2, respectively. The wire rods had an initial diameter of 5.50 mm and were subjected to a pickling process to remove iron oxides and other surface impurities. Following pickling, the rods underwent a thorough washing to eliminate any residual acid remaining on the surface. To protect the cleaned rods from re-oxidation and additional contamination, they were then immersed in a phosphate bath. This phosphating step was followed by a borax treatment, which further enhanced the surface condition of the rods. These surface treatments were essential in preparing the rods for the single drawing process by reducing friction and preventing surface defects during deformation.

Table 1. Chemical Composition (wt.%) of Wire Rods.

Materials	C	Mn	Si	P	S	Cr	V	Ni
0.45C	0.499	0.546	0,184	0.011	0.003	0.035	0.002	0.001
0.55C	0.580	0.535	0.168	0.012	0.011	0.030	0.003	0.012
0.70C	0.701	0.543	0.166	0.010	0.005	0.026	0.006	0.026
0.83C	0.841	0.575	0.171	0.015	0.002	0.025	0.004	0.044

Table 2. Mechanical Properties of Wire Rods.

Materials	Tensile Strength, R_m (MPa)	Yield Strength, $R_{p0.2}$ (MPa)	%Elongation, A_{100}
0.45C	860,0	529,7	9,2
0.55C	935,2	575,7	8,6
0.70C	1138,0	752,0	7,4
0.83C	1249,1	805,0	6,7

After surface treatment, the wire rods with an initial diameter of Ø5.5 mm were cold drawn down to a diameter of Ø2 mm. The resulting semi-finished products were then subjected to the patenting heat treatment process. During patenting, the steel wires were heat-treated in a furnace operating at various temperature ranges between 950 °C and 1000 °C, with drawing speeds set at 40, 50, and 60 meters per minute. Upon exiting the furnace, the wires were immediately immersed in a lead bath maintained at temperatures between 520 °C and 560 °C to facilitate controlled cooling and microstructural transformation. The cold drawing process induces strain hardening in the steel wire, which significantly enhances its mechanical properties. This strain hardening leads to increased yield strength ($R_{p0.2}$) and ultimate tensile strength (R_m), as demonstrated by standard tensile testing. However, as the cold drawing progresses, the elongation or ductility of the wire decreases due to the increased hardness and reduced ability to plastically deform. The mechanical properties of the steel wires drawn from 5.5 mm to 2 mm diameter prior to undergoing the patenting heat treatment are summarized in Table 3. The data reveal that the drawing process notably improved the mechanical strength of the wires, with the highest tensile and yield strength values observed in the steel wires containing 0.83% carbon.

Table 3. Mechanical Properties of 2 mm Wires.

Materials	Tensile Strength, R_m (MPa)	Yield Strength, $R_{p0.2}$ (MPa)	% Elongation, A_{100}
0.45C	1579,3	1272,7	1,4
0.55C	1596,7	1328,3	1,6
0.70C	1865,0	1585,3	1,1
0.83C	1990,7	1570,3	1,7

For microstructural analysis, 2 mm wire samples were examined using both a Jeol JSM 6060 scanning electron microscope (SEM) and an Olympus BX41M-LED optical microscope. Prior to imaging, the samples were carefully polished and chemically etched to reveal their microstructures. The chemical etching was performed by immersing the samples in a solution composed of 95 ml of ethanol (C_2H_6O) mixed with 5 ml of nitric acid (HNO_3), providing effective micro-scale etching of the steel surfaces

Mechanical properties were assessed through tensile testing conducted in accordance with the TS EN 6892-1 standard. Tests were performed on a Zwick Z050 universal testing machine with a 5-ton capacity, applying a strain rate of 0.006 s^{-1}. The tensile test samples were prepared with a gauge length of 330 mm to ensure accurate and consistent measurement of the steel wires' mechanical performance.

3. Results and Discussion

3.1. Mechanical Properties

Experiments were carried out on multiple patented steel wires, with their mechanical properties determined either through calculations based on industrial specifications or via direct experimental measurements. For steel wires, patenting heat treatment is essential to achieve higher total drawability. The desired high elongation ratio is attained by developing an appropriate microstructure, specifically a fine lamellar pearlite structure, often referred to as the sorbite phase, which provides a balanced combination of high strength and ductility. The proportion of pearlitic microstructure formed during the patenting process directly influences key mechanical properties such as ultimate tensile strength and reduction in area for the patented wires. The data presented in Table 4 through Table 9, as well as Figures 2, 3, and 4, demonstrate that the heat treatment parameters applied during patenting significantly impact the mechanical properties of steel wires. It is evident that the heat treatment notably affects both the strength properties and percentage elongation of high-carbon steel wires. As the carbon content increases from 0.45% to 0.83%, both tensile and yield strengths show a linear increase, while elongation decreases. This inverse relationship reflects the typical trade-off between strength and ductility, where increased carbon content enhances strength and hardening but reduces the wire's ability to elongate.

Table 4. Tensile Strength at 520°C Cooling Temperature.

Cooling Speed	0.45C	0.55C	0.70C	0.83C
40m/min.	991	1079	1240	1361,2
50m/min.	997,4	1097,8	1245,2	1362,4
60m/min.	925,2	1015	1159	1261,2

Table 5. Tensile Strength at 560°C Cooling Temperature.

Cooling Speed	0.45C	0.55C	0.70C	0.83C
40m/min.	932,8	1032	1181	1347,6
50m/min.	939,6	1048,2	1192,2	1301,4
60m/min.	943	1043,2	1188,6	1293,6

Table 6. Yield Strength at 520°C Cooling Temperature.

Cooling Speed	0.45C	0.55C	0.70C	0. 83C
40m/min.	668,4	733	815,8	914,8
50m/min.	664,4	717,8	830	914,6
60m/min.	623,8	679,2	754,2	857

Table 7. Yield Strength at 560°C Cooling Temperature.

Cooling Speed	0.45C	0.55C	0.70C	0.83C
40m/min.	606	656,8	751,4	870,4
50m/min.	607,4	675,8	761,6	845,4
60m/min.	612,5	675	733,6	819,2

Table 8. % Elongation at 520°C Cooling Temperature.

Cooling Speed	0.45C	0.55C	0.70C	0. 83C
40m/min.	8,3	8,7	7,9	7,7
50m/min.	8,7	8,8	8,1	7,7
60m/min.	8,7	8,1	7,6	7,5

Table 9. % Elongation at 560°C Cooling Temperature.

Cooling Speed	0.45C	0.55C	0.70C	0.83C
40m/min.	9,2	8,9	8,2	7,4
50m/min.	9,3	9,0	8,0	7,8
60m/min.	9,0	8,6	8,3	7,9

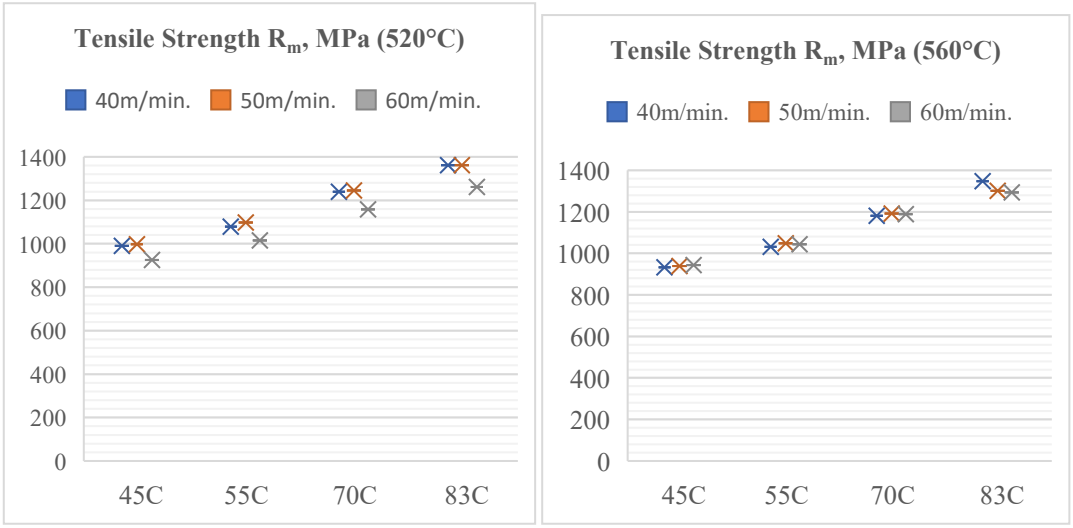

Figure 2. Tensile Strength of 520°C and 560°C Cooling Temperature.

Increasing the cooling temperature from 520°C to 560°C resulted in a reduction in strength values. However, at the higher cooling temperature of 560°C, the steel wires exhibited relatively higher elongation compared to those cooled at 520°C, indicating improved ductility under these conditions. Process speed plays a critical role in the patenting heat treatment, as it directly influences the quenching rate of the wires. The cooling time required to reach the quenching temperature from the austenitizing temperature, as detailed in the experimental setup, is governed by the line speed. Mechanical test results further confirmed that the strength of the steel increases with higher carbon content. Regarding process speed, as the speed increased, the strength initially rose but then showed a tendency to decrease once the line speed exceeded 50 m/min. At the highest processing speed tested, 60 m/min, relatively lower strength values were observed, suggesting that excessively fast processing may adversely affect the heat treatment effectiveness and final mechanical properties.

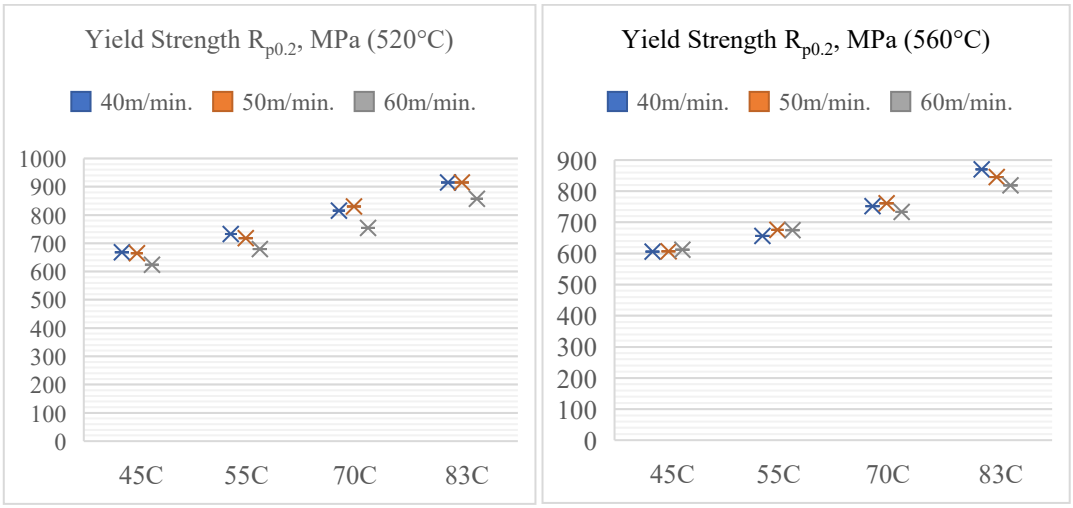

Figure 3. Yield Strength of 520°C and 560°C Cooling Temperature.

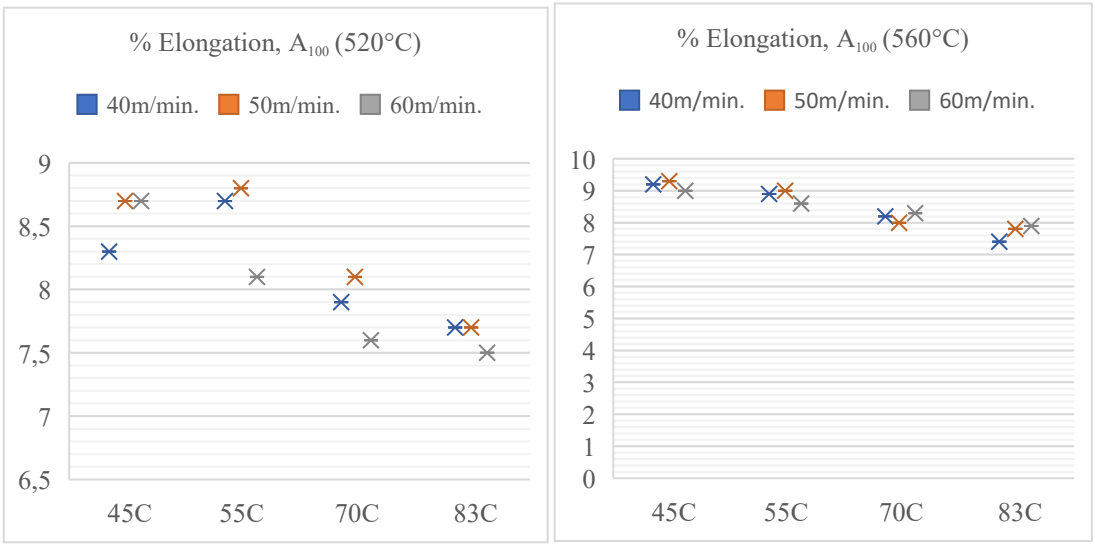

Figure 4. Elongation of 520°C and 560°C Cooling Temperature.

3.2. Microstructural Examinations

The patenting process, which facilitates phase transformation in steel, is fundamental in producing ultra-high strength wires following wire drawing. This process converts the randomly distributed ferrite and cementite present in hot-rolled wire rods into a nanocomposite multilayer structure composed of alternating ferrite and cementite layers, known as pearlite. The effectiveness of this phase transformation during the lead patenting process is primarily influenced by factors such as the steel composition, wire diameter, lead bath temperature, and transformation time [5]. The quenching process in patenting begins with a heating stage, where the steel is austenitized by heating it to a temperature that allows the formation of austenite. This is followed by a controlled cooling phase, which transforms the austenitic matrix into a pearlitic structure. Figure 5 presents optical microscope (OM) images showing the microstructure of the semi-finished steel products after patenting. In Figures 5a and 5b, the microstructures of 0.45% carbon steel cooled at 520ºC and 560ºC exhibit a re-formation of a ferritic and pearlitic matrix that is finer than the original film structure. For the semi-finished products containing 0.83% carbon, grain growth is observed as the cooling temperature increases from 520ºC to 560ºC. Across both carbon contents, there is a noticeable variation in grain size or interlamellar spacing depending on the specific heating and cooling conditions applied. According to the Hall-Petch relationship, a reduction in grain size or interlamellar spacing in pearlite correlates with an increase in strength, suggesting that

finer microstructures resulting from optimized patenting conditions can enhance the mechanical performance of the steel wires [6].

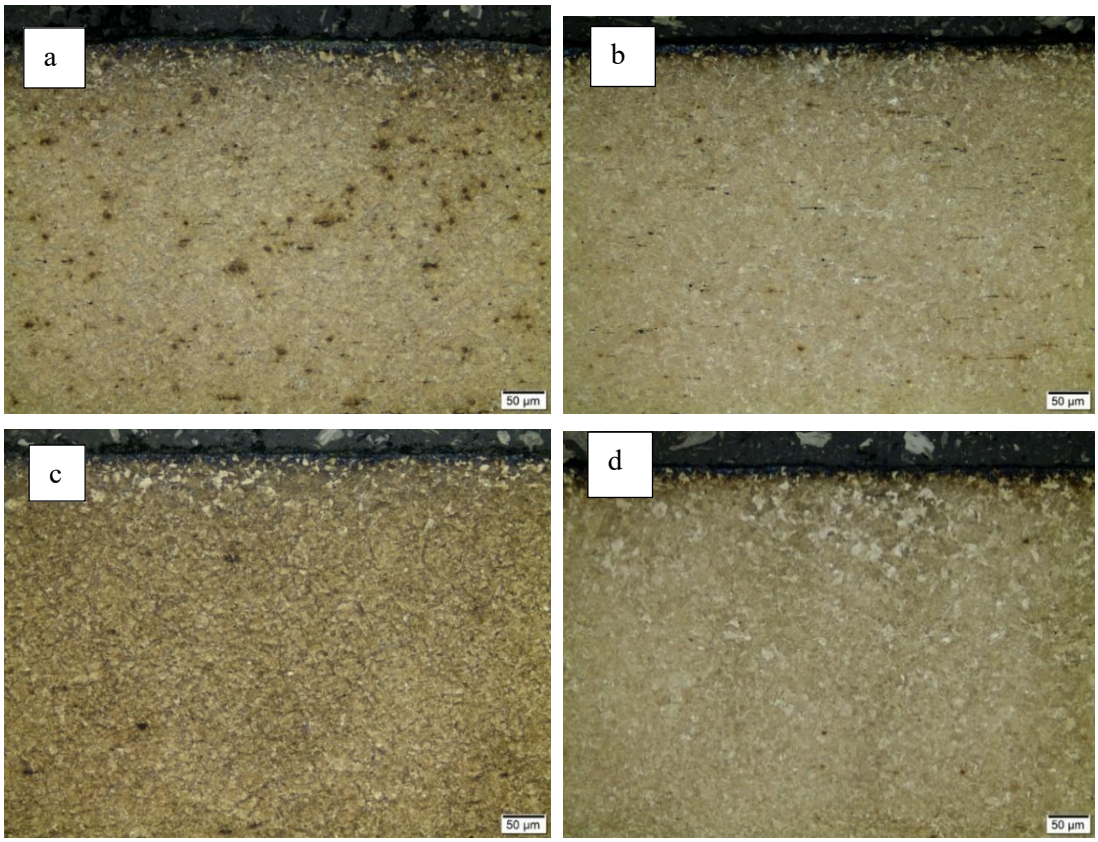

Figure 5. Optical Microstructures of Wires a) 0.45C 520°C 50 m/ min. b) 0.45C 560°C 50 m/ min. c) 0.83C 520°C 50 m/ min. d) 0.83C 560°C 50 m/ min.

Figure 6 presents scanning electron microscope (SEM) micrographs of the steel wires, revealing a microstructure composed of two distinct phases: ferrite and pearlite, as shown in Figures 6a and 6b. Each pearlite colony exhibits its own lamellar orientation, with cementite lamellae appearing as lighter-colored regions and ferrite as darker areas [7]. The patented steel wire, depicted in SEM images in Figures 6c and 6d, displays a typical microstructure widely reported in the literature, where pearlite is the dominant phase. Pearlite consists of a finely mixed structure of ferrite and iron carbide, producing a characteristic "wormy" texture when observed microscopically. The primary metallurgical goal of the patenting process is to tailor these microstructural features to optimize the balance between strength and ductility in the steel wire [8]. Despite variations in carbon content, ferrite precipitation may occur due to segregation effects caused by local cooling rate gradients during the heat treatment. Mechanical testing results further support this observation, showing that higher carbon content correlates with increased strength, primarily because of the greater volume fraction of pearlite formed in the microstructure.

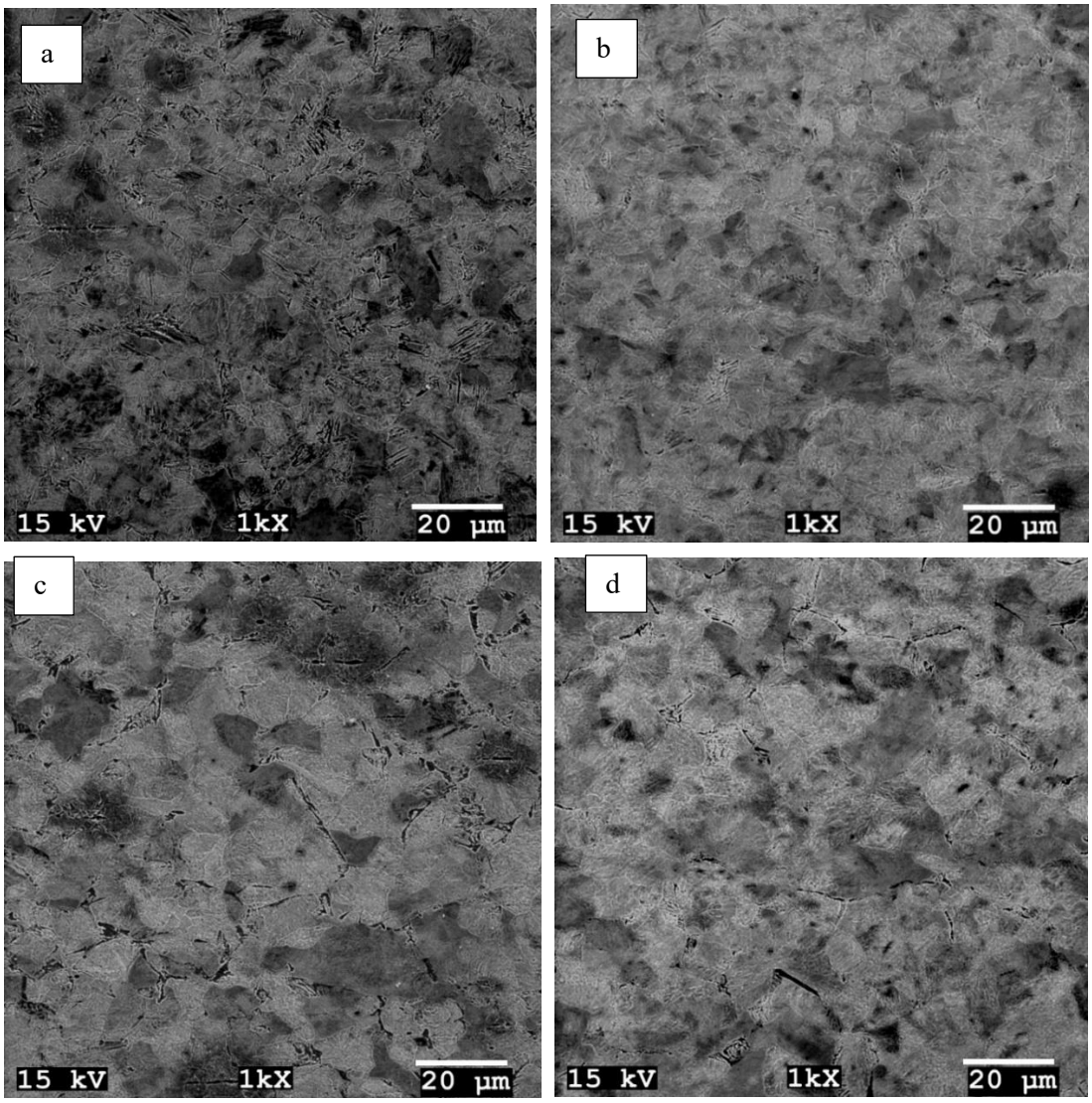

Figure 6. SEM Microstructures of Wires a) 0.45C 520°C 50 m/ min. b) 0.45C 560°C 50 m/ min. c) 0.83C 520°C 50 m/ min. d) 0.83C 560°C 50 m/ min.

4. Conclusions

Patenting is one of the most critical heat treatment processes applied to medium and high-carbon steel wires. The quality and quantity of the pearlitic microstructure formed during patenting are primarily influenced by cooling temperature and transformation time. This study examined the mechanical and microstructural properties of patented wires subjected to varying cooling temperatures (520°C and 560°C) and line speeds (40, 50, and 60 m/min). The patenting heat treatment effectively enhanced both the strength and ductility of the steel wires. As the cooling temperature increased, a gradual reduction in ultimate tensile strength was observed, accompanied by an improvement in ductility. Additionally, increasing the line speed from 50 m/min to 60 m/min resulted in a decline in mechanical properties, suggesting that higher processing speeds negatively affect the wire's microstructural integrity and overall performance. Based on the test results, steel wires cooled at 520°C with a line speed of 50 m/min demonstrated the best balance of strength and ductility, indicating optimal mechanical performance under these conditions.

5. Acknowledgements

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Symposium homepage: https://www.jcharacterization.com

Galvanizleme Parametrelerinin Yüksek Karbonlu Çelik Tellerin Kaplama Performansı ve Mekanik Özelliklerine Etkisi

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ÖZET

Yüksek karbonlu çelik teller, yüksek mukavemet ve elastiklik özellikleri sayesinde yaylık tel, halat ve otomotiv sanayii gibi dinamik yük taşıyan uygulamalarda yaygın olarak kullanılmaktadır. Bu uygulamalarda korozyon direnci büyük önem taşıdığından, çelik tellerin yüzeyine çinko kaplama uygulanması yaygın bir yöntemdir. Bu çalışmada, yüksek karbonlu perlitik çelik tellerin galvaniz kaplama prosesi kapsamında, çinko kaplama parametrelerinin kaplamanın mekanik ve mikroyapısal özelliklerine etkisi incelenmiştir. 5,5 ve 2 mm kalınlığındaki teller belirlenen farklı sıcaklık/hız kombinasyonlarında sıcak daldırma galvanizleme işlemine tabi tutulmuştur. Kaplama sonrası elde edilen tellere özel hadde serileri uygulanarak tel çekme işlemi gerçekleştirilmiştir. Çapları 2 ve 0,70 mm'ye düşürülen çinko kaplı perlitik çelik tellere mekanik testler uygulanmış; ayrıca mikroyapı analizleri gerçekleştirilmiştir. Çalışma kapsamında elde edilen bulgular, banyo sıcaklığı ile hat hızının çinko kaplama kalınlığı ve kaplama-tel arayüzey yapısı üzerindeki etkilerinin mekanik özellikler ile ilişkisini ortaya koymuştur.

Anahtar Kelimeler : Çelik tel, Galvanizleme banyosu sıcaklığı, Hat hızı, Kaplama performansı, Sıcak Daldırma Galvanizleme

Effect Of Galvanizing Parameters on Coating Performance and Mechanical Properties of High Carbon Steel Wires

ABSTRACT

High-carbon steel wires are widely used in applications carrying dynamic loads, such as spring wire, rope, and the automotive industry, due to their high strength and elasticity properties. Since corrosion resistance is of great importance in these applications, zinc coating is a common method applied to the surface of steel wires. In this study, the effect of zinc coating parameters on the mechanical and microstructural properties of the coating was investigated within the scope of the galvanizing process of high-carbon pearlitic steel wires. Wires with thicknesses of 5.5 and 2 mm were subjected to hot-dip galvanizing at different temperature/speed combinations. After coating, the wires were drawn using special rolling series. Mechanical tests were performed on the zinc-coated pearlitic steel wires, whose diameters were reduced to 2 and 0.70 mm; microstructure analyses were also conducted. The findings obtained within the scope of the study revealed the relationship between the effects of bath temperature and line speed on zinc coating thickness and coating-wire interface structure and mechanical properties.

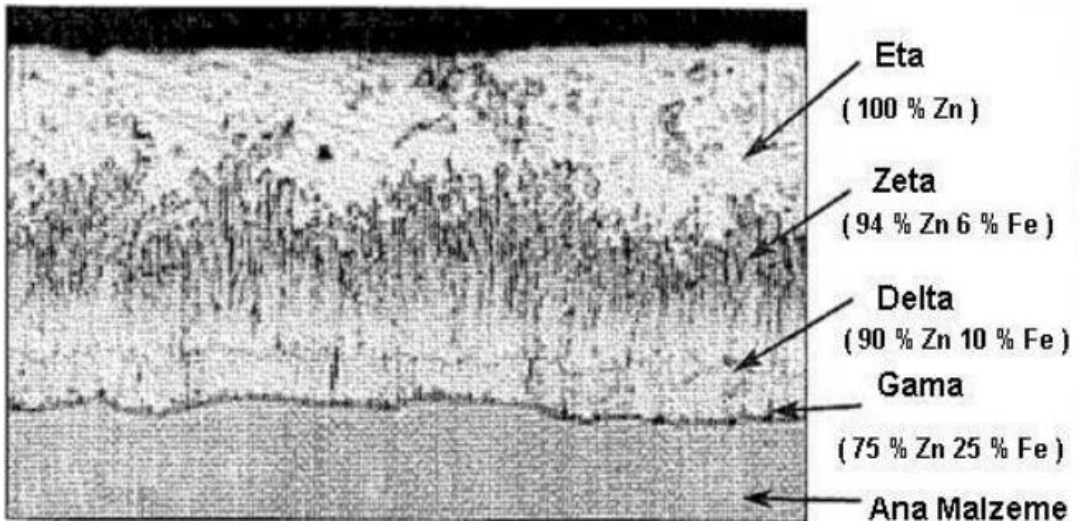
Keywords: Steel wire, Galvanizing bath temperature, Line speed, Coating performance, Hot Dip Galvanizing

1. Giriş

Yüksek karbonlu, perlitik yapıya sahip çelik teller; yüksek mukavemet ve elastiklikleri nedeniyle yaylık tel, halat ve otomotiv sektörleri gibi dinamik yüklere maruz kalan uygulamalarda yaygın şekilde

kullanılmaktadır. Bu bağlamda, korozyon direnci kritik bir parametre olarak öne çıkmaktadır. Atmosferik etkiler nedeniyle oluşabilecek yüzey hasarlarını önlemek ve ürün ömrünü uzatmak amacıyla sıcak daldırma galvanizleme (Hot-Dip Galvanizing, HDG) yöntemi tercih edilmektedir. Bu yöntemde tel, sürekli üretim hattında yüzeyi koruyucu bir çinko tabakası kazanmak üzerine, belirli sıcaklıkta (genellikle 440–470 °C) çinko banyosundan geçirilmektedir. Kaplamanın kalınlığı, mikro-yapısı ve dayanımı, doğrudan banyo sıcaklığı ve telin geçiş hızı (hat hızı) gibi parametrelere bağlıdır [1],[2].

Sıcak daldırma galvanizleme işlemi sırasında çelik ve çinko arasında Şekil 1.'de görüldüğü gibi Fe–Zn intermetalik fazları (ζ, δ, Γ ve η) oluşmakta; bu fazların dağılımı ve morfolojisi, sıcaklığa ve kaplama süresine göre değişim göstermektedir [1],[3]. Sıcaklığın 450–480 °C arasında olması, genellikle kompakt ζ tabakasının oluşumunu desteklerken; 500 °C ve üzeri sıcaklıklarda δ tabakası baskın hale gelmekte ve kaplamanın kalınlığı artmaktadır [1].



Şekil 1. Galvaniz kaplama katmanları.

Bununla birlikte, sıcak daldırma galvanizleme işlemi yüksek karbonlu ve yüksek mukavemetli çeliklerde mekanik özellikleri etkileyebilmektedir. Milan ve arkadaşları, yüksek mukavemetli (460–1250 MPa) çeliklerde sıcak daldırma galvanizleme sonrası akma dayanımında %18 ve çekme dayanımında %13 azalmalar gözlemlemiştir [4]. Yüksek sıcaklık, çeliğin yapıdaki sertlik ve dayanımını olumsuz etkileyebilmektedir. Öte yandan, karbonlu çeliklerde mekanik özellikler sabit kalabilmekte ya da iyileşebilmekte, uzama parametresi genellikle değişmemekte, ancak tokluk ölçümleri azalma gösterebilmektedir [5].

5,5 mm ve 2 mm kalınlığındaki teller belirlenen farklı sıcaklık (440°C ve 460°C) ve hız (80DV, 100DV, 120DV) kombinasyonlarında sıcak daldırma galvanizleme işlemine tabi tutulmuştur. Kaplama sonrası elde edilen numunelere özel hadde serileri uygulanarak tel çekme işlemi gerçekleştirilmiştir. Tel çekme işlemi sonrası çapları 2 mm ve 0.70 mm'ye düşürülen çinko kaplı perlitik çelik tellere çekme testi, ZABA testi (çinko miktarı tayini), torsiyon testi ve sarma testi gibi mekanik değerlendirmeler uygulanmış; ayrıca optik mikroskopi ve taramalı elektron mikroskobu (SEM) teknikleriyle mikroyapı analizleri gerçekleştirilmiştir.

2. Malzemeler ve Yöntem

Bu çalışmada kullanılan deney numuneleri, yüksek karbonlu perlitik çelik filmaşinlerden hazırlanmıştır. Filmaşinler endüstriyel ölçekte sıcak haddeleme yöntemi ile üretilmiş olup, deneysel galvanizleme sürecine alınmadan önce bir dizi yüzey hazırlama ve ısıl işlem basamağına tabi tutulmuştur.

2.1. Yüzey Hazırlama İşlemleri

Tel yüzeylerinde sıcak haddeleme ve depolama sırasında oluşan oksit tabakalarının ve pasın giderilmesi amacıyla Şekil 2.'deki yüzey temizleme hattında hidroklorik asit (HCl) çözeltisi kullanılarak kimyasal yüzey temizleme işlemi yapılmıştır. Asidik dekapaj işlemi sırasında banyo konsantrasyonu, serbest asit miktarı ve demir iyonu içeriği titrasyon yöntemiyle kontrol edilmiş, işlem süresi ise hidrojen gevrekleşmesi riskini en aza indirecek şekilde optimize edilmiştir. Temizleme sonrası numuneler bol su ile durulanarak asit kalıntılarından tamamen arındırılmıştır. Ardından teller, yüzeyde ince bir film oluşturarak galvaniz banyosunda ıslanabilirliği artırmak amacıyla fosfat kaplamaya tabi tutulmuş ve üzerine boraks tabakası uygulanmıştır. Bu adımlar sayesinde hem kaplamanın homojenliği hem de sonraki tel çekme işleminde kalıplarla olan sürtünmenin azaltılması hedeflenmiştir.

Şekil 2. Yüzey temizleme hattı.

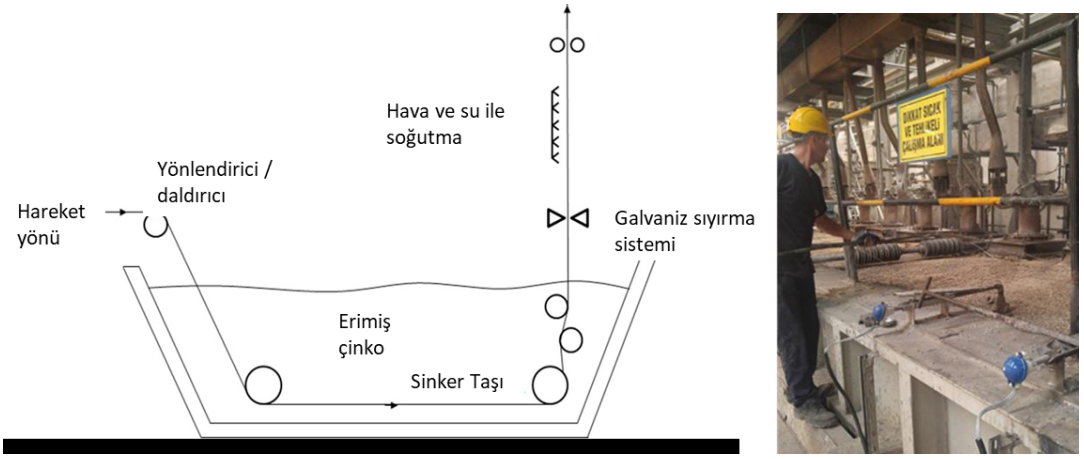
2.2. Patentleme Isıl İşlemi

Yüzey hazırlığı tamamlanan teller, mikro yapının istenen özelliklere getirilmesi amacıyla Şekil 3.'de görülen hattan patentleme ısıl işlemine tabi tutulmuştur. Bu işlemde teller önce östenitleme sıcaklığına kadar ısıtılmış, ardından kontrollü koşullarda perlit dönüşüm sıcaklığına kadar soğutulmuştur. Bu ısıl işlem sonucunda, telin mikroyapısında ince lamelli ve homojen bir perlit yapısı elde edilerek hem mukavemet hem de süneklik özellikleri dengelenmiştir. Ayrıca patentleme işlemi, haddeleme sırasında meydana gelen sertleşmenin giderilmesine de katkı sağlamıştır. İşlem sonrasında yüzeyde yeniden oluşan tufaller ikinci bir asidik temizleme ile giderilmiş, ardından tekrar fosfat ve boraks kaplama uygulanmıştır.

Şekil 3. Patentleme hattı.

2.3. Sıcak Daldırma Galvanizleme

Hazırlanan teller, %99,99 saflıkta çinko içeren Şekil 4.'de görülen sıcak daldırma galvaniz banyosuna daldırılarak kaplanmıştır. Galvanizleme sırasında banyo sıcaklıkları iki farklı seviyede (440 °C ve 460 °C) belirlenmiş, telin hattan geçiş hızları ise üç farklı seviyede (80 DV, 100 DV ve 120 DV) değiştirilerek deneysel parametreler oluşturulmuştur. Bu değişkenler sayesinde daldırma süresi kontrol edilmiş ve çinko kaplama tabakasının kalınlığı ile intermetalik faz oluşumunun parametrelere bağlı olarak nasıl değiştiği incelenmiştir. Banyo sıcaklığı hassas termokupllarla sürekli izlenmiş, yüzeyde oluşan cüruflar periyodik temizleme ile uzaklaştırılmıştır. Teller banyo çıkışında hava bıçakları ile fazla çinkodan arındırılmış ve böylece kaplama kalınlığının homojenliği sağlanmıştır.



Şekil 4. Galvanizleme hattı.

2.4. Tel Çekme İşlemi

Galvaniz kaplama sonrası teller, kuru tel çekme makinesinde Şekil 5.'de verilmiş olan çok kademeli hadde serilerinden ayrı ayrı geçirilerek çapları sırasıyla 5.5 mm'den 2.0 mm'ye ve 2.0 mm'den 0.70 mm'ye düşürülmüştür. Çekme sırasında kullanılan kalıplar düzenli olarak temizlenmiş ve çekme hızları kaplama tabakasının zarar görmesini engelleyecek şekilde ayarlanmıştır. Fosfat ve boraks kaplamalarının sağladığı kaygan yüzey etkisi sayesinde çekme sırasında sürtünme minimum seviyede tutulmuş, kaplamanın soyulması veya çatlaması önlenmiştir.

SERİ VERİLDİĞİNDE KESİT KÜÇÜLMESİ MİKTARININ VE FARKLARININ HESAPLANMASI

HADDE NO	ÇAP (MM)	KESİT DÜŞMESİ (%)
GİRİŞ	5,50	
1	4,79	24,13
2	4,20	23,13
3	3,71	22,13
4	3,29	21,13
5	2,94	20,13
6	2,65	19,13
7	2,39	18,13
8	2,18	17,13
9	2,00	16,13
21	AVE	20,13

FİİLİ HADDE SERİSİNİN DEĞERLENDİRİLMESİ

KONTROL PARAMETRELERİ	
HADDE SAYISI	UYGUN
GİRİŞ ÇAPI	UYGUN
MAKSİMUM KESİT KÜÇÜLMESİ	UYGUN
MİNİMUM KESİT KÜÇÜLMESİ	UYGUN
KESİT DÜŞME MİKTARLARI	UYGUN

NOTLAR: KONTROL PARAMETRELERİNİN TAMAMI KARŞISINDA UYGUN NOTU OLMALIDIR. AKSİ HALDE FİİLİ HADDE SERİSİ YENİDEN GÖZDEN GEÇİRİLMELİ VEYA ÖNERİLEN HADDE SERİSİ İÇİN *DEFHES 01* SAYFASINDAKİ HESAPLAMA TABLOSU KULLANILMALIDIR.

SERİ VERİLDİĞİNDE KESİT KÜÇÜLMESİ MİKTARININ VE FARKLARININ HESAPLANMASI

HADDE NO	ÇAP (MM)	KESİT DÜŞMESİ (%)
GİRİŞ	2,00	
1	1,76	22,56
2	1,56	21,44
3	1,39	20,61
4	1,24	20,42
5	1,11	19,87
6	1,00	18,84
7	0,91	17,19
8	0,83	16,81
9	0,76	16,16
10	0,70	15,17
21	AVE	18,90

FİİLİ HADDE SERİSİNİN DEĞERLENDİRİLMESİ

KONTROL PARAMETRELERİ	
HADDE SAYISI	UYGUN
GİRİŞ ÇAPI	UYGUN
MAKSİMUM KESİT KÜÇÜLMESİ	UYGUN
MİNİMUM KESİT KÜÇÜLMESİ	UYGUN
KESİT DÜŞME MİKTARLARI	UYGUN

NOTLAR: KONTROL PARAMETRELERİNİN TAMAMI KARŞISINDA UYGUN NOTU OLMALIDIR. AKSİ HALDE FİİLİ HADDE SERİSİ YENİDEN GÖZDEN GEÇİRİLMELİ VEYA ÖNERİLEN HADDE SERİSİ İÇİN *DEFHES 01* SAYFASINDAKİ HESAPLAMA TABLOSU KULLANILMALIDIR.

Şekil 5. 5.50 ve 2.0mm ilk çapa uygulanan hadde serileri.

2.5. Mekanik Testler

Kaplama sonrası mekanik özelliklerin belirlenmesi amacıyla çekme, torsiyon ve sarma testleri gerçekleştirilmiştir. Çekme deneyleri, Raagen ETM-50-S1 model 5 ton kapasiteli üniversal test makinesi ile yapılmış; numuneler standartlara uygun ölçü boyunda hazırlanarak uygun çenelerle bağlanmıştır. Testler sırasında kuvvet–uzama eğrileri kaydedilmiş ve akma dayanımı, çekme dayanımı ile kopma uzaması hesaplanmıştır. Torsiyon testinde teller kendi eksenleri etrafında burulmaya tabi tutulmuş ve kopma meydana gelene kadar döndürülerek tur sayısı belirlenmiştir. Sarma testinde ise teller belirli mandrel çaplarında sarılmış, kaplama bütünlüğü stereo mikroskop altında incelenerek çatlak, soyulma veya kaplama süreksizlikleri değerlendirilmiştir.

2.6. Kaplama Miktarı ve Kalınlık Ölçümleri

Galvaniz kaplama miktarı, ZABA yöntemi ile belirlenmiştir. Bu yöntem kapsamında kaplamalı teller tartıldıktan sonra çinko tabakası asidik çözelti ile çözdürülmüş, tekrar tartım yapılarak kütle farkından birim yüzey alanına karşılık gelen çinko miktarı hesaplanmıştır. Kaplama kalınlığı ise hem gravimetrik yöntemle elde edilen veriler hem de metalografik kesitlerin optik mikroskop ve SEM incelemeleri ile belirlenmiştir. Numuneler epoksi reçine içerisine gömülerek zımpara ve parlatma işlemleriyle hazırlanmış, kesit yüzeylerinden alınan ölçümler ile kaplama kalınlığı farklı bölgelerde ortalama değer ve standart sapma hesaplanarak raporlanmıştır.

2.7. Mikroyapısal Karakterizasyon

Galvanizleme sonrası 5,50 ve 2 mm ilk çapa sahip tellerin kaplama tabakalarının mikroyapısal analizi için taramalı elektron mikroskobu (SEM) kullanılmıştır. SEM görüntüleri kaplama–çelik arayüzeyinde oluşan Fe–Zn intermetalik fazlarının morfolojisini ve tabaka yapısını detaylı olarak değerlendirmek amacıyla kullanılmıştır. Ayrıca enerji dağılımlı X-ışını spektroskopisi (EDS) ile elementel analizler yapılmış, faz sınırları Zn ve Fe dağılımları üzerinden doğrulanmıştır.

3. Sonuçlar ve Tartışma

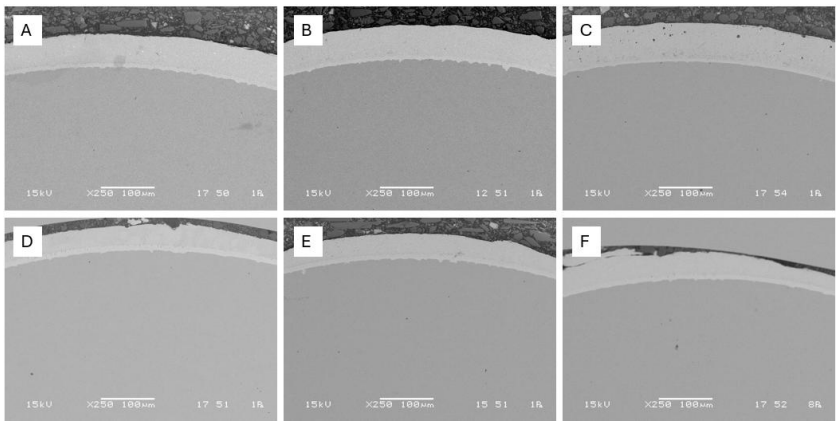
3.1. SEM ve EDS Sonuçları

Galvanizleme işleminden elde edilen kaplama tabakasının morfolojik özelliklerini ve çelik–çinko arayüzeyinde oluşan intermetalik fazların dağılımını belirlemek amacıyla taramalı elektron mikroskobu (SEM) ve enerji dağılımlı spektroskopi (EDS) analizleri gerçekleştirilmiştir. Analizler, yüksek çözünürlüklü görüntüleme ve elementel haritalama imkânı sağlayan SEM-EDS cihazı kullanılarak Sakarya Üniversitesi Merkez Araştırma Laboratuvarı bünyesinde yapılmıştır. Bu kapsamda, 2.00 mm ve 5.50 mm çaplı teller üzerinde farklı galvanizleme koşullarının kaplama kalınlığı, faz oluşumu ve kimyasal kompozisyon üzerindeki etkileri detaylı olarak incelenmiştir.

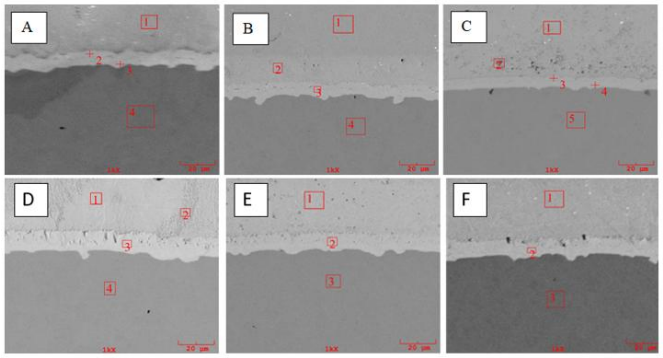
Galvaniz kaplama işleminin çelik tel yüzeyinde oluşturduğu mikroyapının ve kaplama bütünlüğünün değerlendirilmesi amacıyla Taramalı Elektron Mikroskobu (SEM) analizi uygulanmıştır. SEM, yüksek çözünürlükte görüntüleme kapasitesi sayesinde hem yüzey morfolojisini hem de kesit yapısını detaylı bir şekilde gözlemleme olanağı sağlamaktadır. Bu analizde, galvanizle kaplanmış numunelerin yüzey ve enine kesit görüntüleri elde edilerek; çinko tabakasının kalınlığı, sürekliliği, tabaka sınırları, oluşan intermetalik fazlar ve olası kusurlar (çatlaklar, boşluklar, soyulmalar vb.) incelenmiştir. Yüzey görüntülerinde çinko taneciklerinin dağılımı ve homojenliği; kesit görüntülerinde ise çinko tabakasının alt tabaka çeliğe yapışma durumu, kalınlık farkları ve mikroyapısal sürekliliği analiz edilmiştir. Ayrıca kaplama tabakası ile ana metal arasında oluşan intermetalik bölgelerin varlığı ve bu bölgelerin yapısal bütünlüğe etkileri de değerlendirilmiştir.

Şekil 6 ve 7.'De görüldüğü üzere tüm numunelerde dış yüzeyde tespit edilen çinko konsantrasyonları oldukça yüksek olup A–C serisinde yüzey[1] için %93,05–%98,19 (80–120 DV aralığı), D–F serisinde ise %93,80–%95,95 aralığındadır; orta[2] ve alt[3] noktalarda da Zn oranları görece yüksek seyretmekte (A–C

orta ~%90,01–%96,75; alt ~%87,37–%91,99; D–F orta ~%90,44–%94,86; alt ~%86,55–%89,50), çelik substrat noktalarında ise Zn çok düşük (%1–%2 civarı) tespit edilmiştir. Bu veriler, kaplamanın yüzeye yakın bölgelerinde hâkim fazın Zn-ce zengin (metalik veya çok Zn içeren intermetalik karışım) bir yapı olduğunu; alt tabaka ölçümlerinin ise intermetalik zon ile substrat arasındaki geçişe işaret ettiğini göstermektedir. Sayısal kalınlıklarla birleştirildiğinde 440 °C koşullarında toplam kaplama kalınlıkları A: 63,3 µm, B: 64,2 µm, C: 72,8 µm iken δ-katmanları sırasıyla 9,73; 10; 12,8 µm olarak ölçülmüş; buna karşılık 460 °C'de toplam kaplama kalınlıkları (D: 46–47,2 µm, E: 47,3–50,3 µm, F: 30,7–54,9 µm olarak ölçülen heterojen aralık) daha ince olmasına rağmen δ-katman kalınlıkları (D:10; E:12,8; F:12,2 µm) 440 °C'ye kıyasla eşit veya daha büyük çıkmıştır. Bu durum, işlem sıcaklığı arttıkça Fe–Zn difüzyon kinetiğinin hızlanması sonucu intermetalik (δ vb.) tabakaların göreli olarak büyüdüğünü ve toplam kaplama içindeki paylarının arttığını; sonuç olarak 460 °C'de toplam kaplamanın inceleşmesine rağmen intermetalik katmanın daha belirgin hale gelmesine yol açtığını desteklemektedir. Daldırma hızı (DV) etkisi ise sıcaklığa bağlı olarak farklı davranmıştır: 440 °C'de DV arttıkça (80→120 DV) toplam kaplama ve yüzey Zn oranında artış (A→C: 63,3→72,8 µm; yüzey Zn ~%93→%98) ve δ-katmanda kalınlaşma (9,73→12,8 µm) gözlenirken, 460 °C'de yüksek hız (120 DV, F) örneğinde belirgin heterojenlik ve kalınlık dalgalanmaları (30,7–54,9 µm aralığı) ortaya çıkmıştır; bu da yüksek sıcaklık-yüksek hız kombinasyonunun ıslanma/bağlanma davranışını bozarak düzensiz kaplamalara neden olduğunu göstermektedir.



Şekil 6. Ø2.00 mm galvaniz kaplı çelik tel SEM görüntüleri. A) 440°C 80DV, B) 440°C 100DV, C) 440°C 120DV, D) 463°C 80DV, E) 463°C 100DV, F) 463°C 120DV.



A,B,C Çinko Konsantrasyonu (%wt)			
	80DV	**100DV**	**120DV**
Yüzey [1]	93,053	97,26	98,19
Orta [2]	90,010	96,75	90,37
Alt[3]	87,367	91,99	90,013*
Çelik[4]	1,425	1,055	1,183

D,E,F Çinko Konsantrasyonu (%wt)			
	80DV	**100DV**	**120DV**
Yüzey [1]	95,946	96,082	93,798
Orta [2]	90,444	94,856	90,259
Alt[3]	86,550	89,501	88,003
Çelik[4]	2,093	1,532	1,240

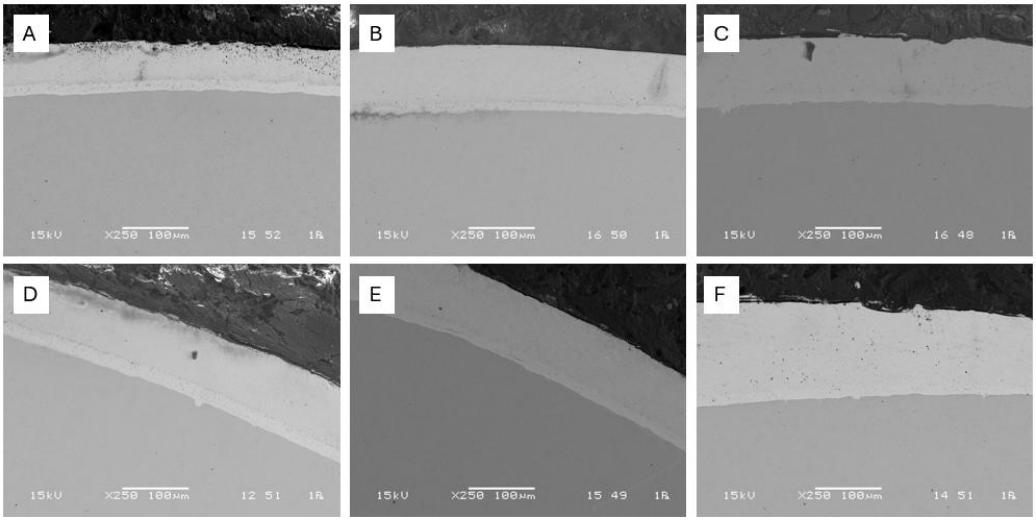
Şekil 7. Ø2,00 mm için EDS görüntüleri ve Çinko konsantrasyon sonuçları A) 440°C 80DV, B) 440°C 100DV, C) 440°C 120DV, D) 463°C 80DV, E) 463°C 100DV, F) 463°C 120DV.

Şekil 8 ve 9.'da görüldüğü üzere 5,50 mm çapa sahip galvaniz kaplanmış çelik tellerin SEM ve EDS analizleri, kaplama özellikleri ve yapıların belirlenmesinde önemli veriler sunmaktadır. Tüm numunelerde, dış yüzeyde tespit edilen çinko konsantrasyonları oldukça yüksek olup, A–C serisinde yüzey [1] için %90,27–%96,95 (80–120 DV aralığı), D–F serisinde ise %83,12–%91,87 aralığındadır. Orta [2] ve alt [3] noktalarda da çinko oranları görece yüksek seyretmekte; A–C serisinde orta ~%85,29–%87,76; alt ~%82,11–%84,18; D–F serisinde ise orta ~%81,08–%89,36; alt ~%79,24–%86,81 arasında değişmektedir. Çelik substrat noktalarında ise çinko oranı çok düşük (%2,37–%3,72 civarı) tespit edilmiştir. Bu veriler, galvaniz

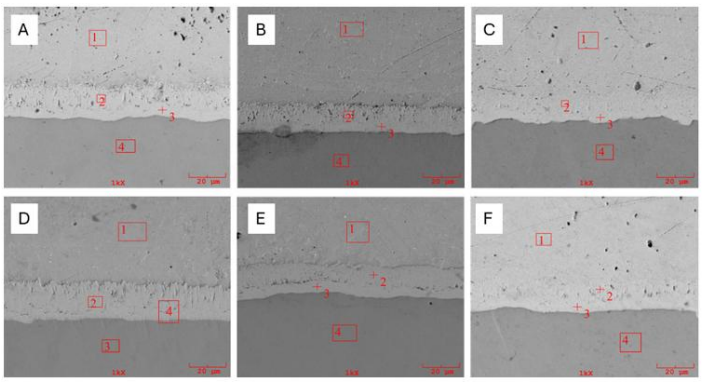
kaplamanın yüzeye yakın bölgelerinde çinko açısından zengin bir yapı oluşturduğunu, ancak alt katmanların intermetalik faz ile çelik substrat arasındaki geçiş bölgesi olduğunu göstermektedir.

SEM ve EDS verileriyle birleştirildiğinde, 440°C koşullarında toplam kaplama kalınlıkları A: 63,3 µm, B: 64,2 µm, C: 72,8 µm iken, delta (δ) katmanlarının kalınlıkları sırasıyla 15,2 µm, 13,6 µm, 13,6 µm olarak ölçülmüştür. Buna karşılık, 460°C'de toplam kaplama kalınlıkları D: 46–47,2 µm, E: 47,3–50,3 µm, F: 30,7–54,9 µm arasında değişen heterojen aralıklarla daha ince olmasına rağmen δ katman kalınlıkları D: 17,3 µm, E: 21,1 µm, F: 13,1 µm gibi değerlerle 440°C'ye kıyasla eşit veya daha büyük çıkmıştır. Bu durum, işlem sıcaklığının artmasının Fe–Zn difüzyon kinetiğini hızlandırarak intermetalik fazların (özellikle δ tabakası) daha belirgin hale gelmesine yol açtığını göstermektedir. 460°C'de daha ince toplam kaplama olmasına rağmen, intermetalik katman daha belirgin bir şekilde ortaya çıkmıştır.

Hattan geçiş hızı (DV) etkisi ise sıcaklığa bağlı olarak farklı bir davranış sergilemiştir. 440°C'de, hız arttıkça (80→120 DV) toplam kaplama kalınlığı ve yüzeydeki çinko oranı artış göstermiştir (A→C: 63,3→72,8 µm; yüzey çinko ~%90,27→%96,95). Ayrıca δ katman kalınlıkları da (9,73→13,6 µm) artmıştır. Ancak, 460°C'de yüksek hızda (120 DV, F) heterojenlik ve kalınlık dalgalanmaları gözlemlenmiştir (30,7–54,9 µm aralığı), bu da yüksek sıcaklık ve yüksek hız kombinasyonunun ıslanma ve bağlanma davranışını bozarak düzensiz kaplamalara neden olduğunu göstermektedir. EDS analizleri, alt katmanlarda da yüksek çinko konsantrasyonları (%79,24–%86,81) göstermektedir; bu durum, EDS noktalarının intermetalik ve metalik faz karışımını algılamasından kaynaklanmaktadır.



Şekil 8. Ø5.50 mm galvaniz kaplı çelik tel SEM görüntüleri. A) 440°C 80DV, B) 440°C 100DV, C) 440°C 120DV, D) 463°C 80DV, E) 463°C 100DV, F) 463°C 120DV.



A,B,C Çinko Konsantrasyonu (%wt)			
	80DV	**100DV**	**120DV**
Yüzey [1]	90,265	96,946	96,527
Orta [2]	85,290	87,763	93,451
Alt[3]	82,113	84,179	86,815
Çelik[4]	2,367	2,649	1,330

D,E,F Çinko Konsantrasyonu (%wt)			
	80DV	**100DV**	**120DV**
Yüzey [1]	83,128	98,446	91,865
Orta [2]	81,087	91,893	87,743
Alt[3]	79,246	89,480	83,083
Çelik[4]	3,729	2,827	0,893

Şekil 9. Ø5,50 mm için EDS görüntüleri ve Çinko konsantrasyon sonuçları A) 440°C 80DV, B) 440°C 100DV, C) 440°C 120DV, D) 463°C 80DV, E) 463°C 100DV, F) 463°C 120DV.

3.2. Çekme Testi Sonuçları

Tel çekme öncesi ve sonrası yapılan çekme testi sonuçları, işlem sıcaklığı ve daldırma hızının (DV) çelik tellerin mekanik özellikleri üzerinde önemli bir etkisi olduğunu ortaya koymaktadır.

Tablo 1.'de tel çekme öncesi 5,50mm çap için çekme testi sonuçları paylaşılmıştır. 440°C koşulunda, daldırma hızı arttıkça akma mukavemeti önce artmakta (80 DV: 788 MPa, 100 DV: 853 MPa), ancak 120 DV hızında azalmaktadır (771 MPa). Kopma mukavemeti ise 80 DV'de 1341 MPa, 100 DV'de 1332 MPa, 120 DV'de ise 1353 MPa'ya çıkarak hız arttıkça değişkenlik göstermektedir. Bu durum, daldırma hızının başlangıçta akma mukavemetini artırdığı ancak daha yüksek hızlarda bu etkinin zayıfladığı ve kopma mukavemetinin artmaya devam ettiği görülmektedir. 460°C koşulunda ise akma mukavemeti 80 DV'de 856 MPa'dan 120 DV'de 918 MPa'ya kadar yükselirken, kopma mukavemeti 80 DV'de 1334 MPa, 100 DV'de 1333 MPa, 120 DV'de ise 1298 MPa'ya düşmektedir. Bu, sıcaklık arttıkça akma mukavemetinin yükseldiğini ancak kopma mukavemetinin yüksek hızlarda azaldığını göstermektedir.

Tablo 1. Tel çekme öncesi Ø5,50 mm için 440°C ve 460°C'deki çekme testi sonuçları.

Çekme Testi (440°C)			
Çap (5,50 mm)	Hız (DV)		
	80	100	120
Akma Mukavemeti (MPa)	788	853	771
Kopma Mukavemeti (MPa)	1341	1332	1353

Çekme Testi (460°C)			
Çap (5,50 mm)	Hız (DV)		
	80	100	120
Akma Mukavemeti (MPa)	856	768	918
Kopma Mukavemeti (MPa)	1334	1333	1298

Tablo 2.'de tel çekme sonrası 2,00 mm çap için çekme testi sonuçları paylaşılmıştır. 440°C koşulunda akma mukavemeti belirgin bir artış göstermiştir (80 DV: 1807 MPa, 100 DV: 1945 MPa, 120 DV: 1716 MPa), aynı şekilde kopma mukavemeti de artmış ve 80 DV'de 2063 MPa, 100 DV'de 2103 MPa, 120 DV'de ise 2008 MPa'ya yükselmiştir. 460°C koşulunda ise akma mukavemeti 80 DV'de 1840 MPa, 100 DV'de 1700 MPa, 120 DV'de 1687 MPa'ya çıkarken, kopma mukavemeti 80 DV'de 2109 MPa, 100 DV'de 2126 MPa, 120 DV'de ise 2109 MPa olarak ölçülmüştür. Tel çekme işlemi, özellikle yüksek hızda yapılan işlemlerde kopma mukavemetini artırırken, akma mukavemetinin de genellikle arttığını göstermektedir. Bu sonuçlar, sıcaklık ve daldırma hızının telin mekanik özellikleri üzerinde kritik bir rol oynadığını ve bu parametrelerin optimize edilmesinin, özellikle kopma mukavemetini iyileştirmede önemli olduğunu ortaya koymaktadır.

Tablo 2. Tel çekme sonrası 2,00 mm çap için 440°C ve 460°C'deki çekme testi sonuçları.

Çekme Testi (440°C)			
Çap (2,00 mm)	Hız (DV)		
	80	100	120
Akma Mukavemeti (MPa)	1807	1945	1716
Kopma Mukavemeti (MPa)	2063	2103	2008

Çekme Testi (460°C)			
Çap (2,00 mm)	Hız (DV)		
	80	100	120
Akma Mukavemeti (MPa)	1840	1700	1687
Kopma Mukavemeti (MPa)	2109	2126	2109

Tablo 3.'de tel çekme öncesi 2,00 mm çap için çekme testi sonuçları paylaşılmıştır. 440°C koşulunda, daldırma hızının artmasıyla akma mukavemeti önce artmakta (80 DV: 829 MPa, 100 DV: 851 MPa), ancak 120 DV hızında 793 MPa'ya düşmektedir. Kopma mukavemeti ise 80 DV'de 1041 MPa, 100 DV'de 1062 MPa, 120 DV'de ise 1002 MPa'ya azalmaktadır. 460°C koşulunda ise, akma mukavemeti 80 DV'de 820,33 MPa, 100 DV'de 871 MPa, 120 DV'de ise 804 MPa'ya yükselmektedir; kopma mukavemeti ise 80 DV'de 1047 MPa, 100 DV'de 1011,66 MPa, 120 DV'de ise 969,33 MPa'ya düşmektedir.

Tablo 3. Tel çekme öncesi 2,00 mm çap için 440°C ve 460°C'deki çekme testi sonuçları.

Çekme Testi (440°C)			
Çap (2,00 mm)	Hız (DV)		
	80	100	120
Akma Mukavemeti (MPa)	829	851	793
Kopma Mukavemeti (MPa)	1041	1062	1002

Çekme Testi (460°C)			
Çap (2,00 mm)	Hız (DV)		
	80	100	120
Akma Mukavemeti (MPa)	820,33	871	804
Kopma Mukavemeti (MPa)	1047	1011,66	969,33

Tablo 4.'de tel çekme sonrası 0,70 mm çap için çekme testi sonuçları paylaşılmıştır. Tel çekme sonrasında, özellikle 440°C koşulunda akma mukavemeti belirgin bir şekilde artmış; 80 DV'de 1748 MPa, 100 DV'de 1748 MPa, 120 DV'de ise 1692 MPa'ya çıkmıştır. Kopma mukavemeti de 80 DV'de 2121 MPa, 100 DV'de 2176 MPa, 120 DV'de ise 2176 MPa'ya yükselmiştir. 460°C koşulunda ise, akma mukavemeti 80 DV'de 1716 MPa, 100 DV'de 1670 MPa, 120 DV'de ise 1712 MPa'ya çıkarken, kopma mukavemeti 80 DV'de 2111 MPa, 100 DV'de 2075 MPa, 120 DV'de ise 2085 MPa olarak ölçülmüştür.

Tablo 4. Tel çekme sonrası 0,70 mm çap için 440°C ve 460°C'deki çekme testi sonuçları.

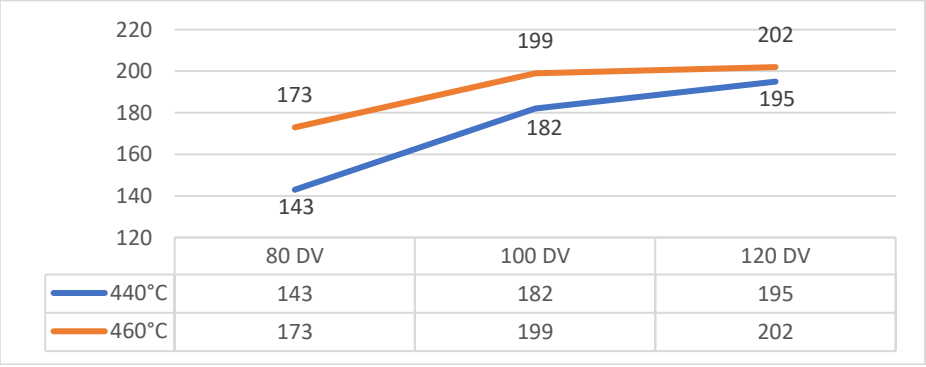
Çekme Testi (440°C)			
Çap (0,70 mm)	Hız (DV)		
	80	100	120
Akma Mukavemeti (MPa)	1748	1748	1692
Kopma Mukavemeti (MPa)	2121	2176	2176

Çekme Testi (460°C)			
Çap (0,70 mm)	Hız (DV)		
	80	100	120
Akma Mukavemeti (MPa)	1716	1670	1712
Kopma Mukavemeti (MPa)	2111	2075	2085

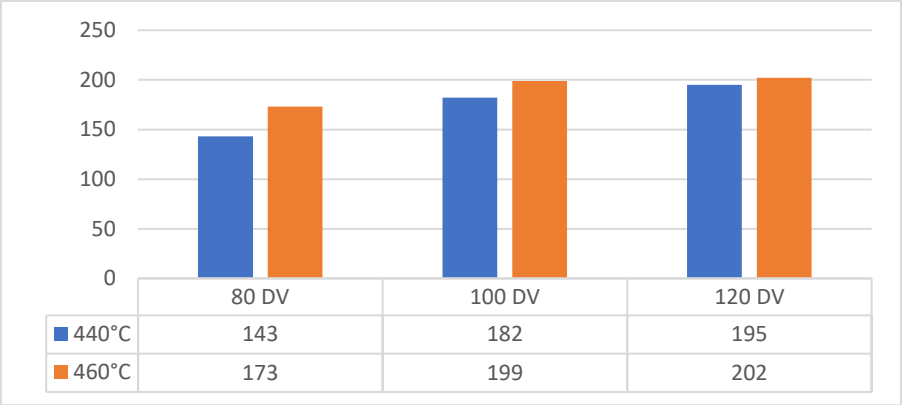
Bu veriler, tel çekme işleminin akma ve kopma mukavemetini artırdığı, özellikle yüksek sıcaklık ve daldırma hızının kopma mukavemetini iyileştirdiği, ancak daldırma hızının aşırı artmasının akma mukavemetini olumsuz etkileyebileceğini göstermektedir.

3.3. ZABA ve Torsiyon Testi Sonuçları

Tel çekme sonrası galvaniz kaplı tellerin ZABA ve torsiyon test sonuçları incelendiğinde hem tel çapının hem de galvanizleme parametrelerinin kaplama kalınlığı ve mekanik performans üzerinde belirleyici etkiler gösterdiği görülmektedir. Şekil 10.'da Ø2,00 mm çapa çekilmiş tellerde ZABA test sonuçları, banyo sıcaklığının artışı ile kaplama miktarında belirgin bir yükselme göstermiştir. Özellikle 440 °C'de 143 g/m² olan kaplama miktarı, 460 °C'de 173 g/m²'ye çıkmış ve hız artışı ile birlikte 202 g/m² seviyesine ulaşmıştır. Bu durum, yüksek sıcaklıklarda çinko difüzyonunun daha etkin gerçekleştiğini ve tel yüzeyinde daha yoğun bir kaplama tabakasının oluştuğunu ortaya koymaktadır. Şekil 11.'de görüldüğü üzere aynı tellerin torsiyon testlerinde de benzer bir eğilim gözlenmiş; daha yüksek sıcaklıklarda kaplamanın sürekliliği artarak telin dönme dayanımını olumlu etkilemiştir.

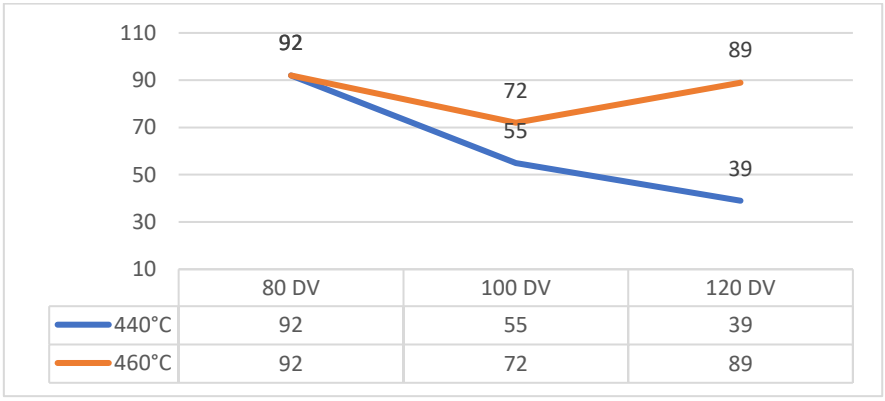


Şekil 10. Tel çekme sonrası Ø2,00 mm için ZABA testi sonuçları.

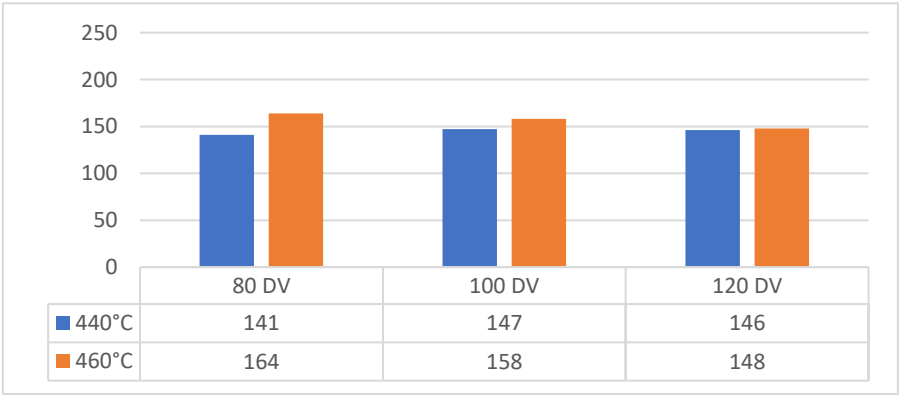


Şekil 11. Tel çekme sonrası Ø2,00 mm için torsiyon testi sonuçları.

Şekil 12.'de Ø0,70 mm çapa çekilmiş tellerde ZABA test sonuçları verilmiştir. Ø2,00 mm çapa göre daha düşük kaplama değerleri göstermiştir. İnce çaplı tellerde tel yüzey alanının artmasına bağlı olarak kaplamanın çekme işlemi sırasında daha fazla zorlandığı ve dolayısıyla 440 °C'de 92 g/m²'den 39 g/m²'ye düşen bir azalma eğilimi sergilediği görülmektedir. Ancak 460 °C'de kaplama miktarının 72–89 g/m² aralığında kalması, daha yüksek sıcaklığın ince çaplı tellerde kaplama bütünlüğünü korumada nispeten avantaj sağladığını göstermektedir. Şekil 13.'de verilen Ø0,70 mm tellerin torsiyon test sonuçları da bu eğilimi desteklemekte; düşük kaplama değerlerine rağmen 460 °C'de elde edilen tellerin dönme dayanımlarının 440 °C'ye kıyasla daha yüksek olduğu görülmektedir.



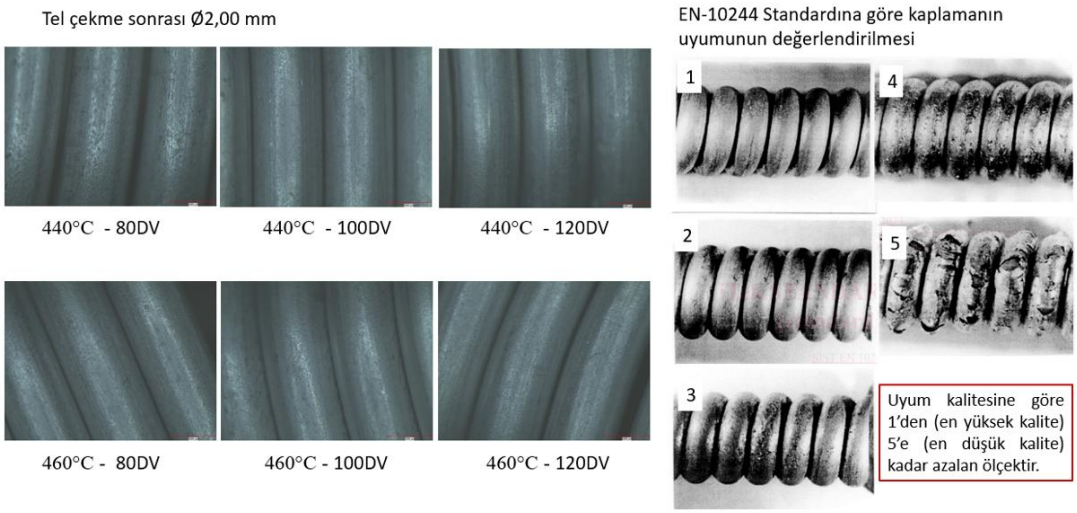
Şekil 12. Tel çekme sonrası Ø0,70 mm için ZABA testi sonuçları.



Şekil 13. Tel çekme sonrası Ø0,70 mm için torsiyon testi sonuçları.

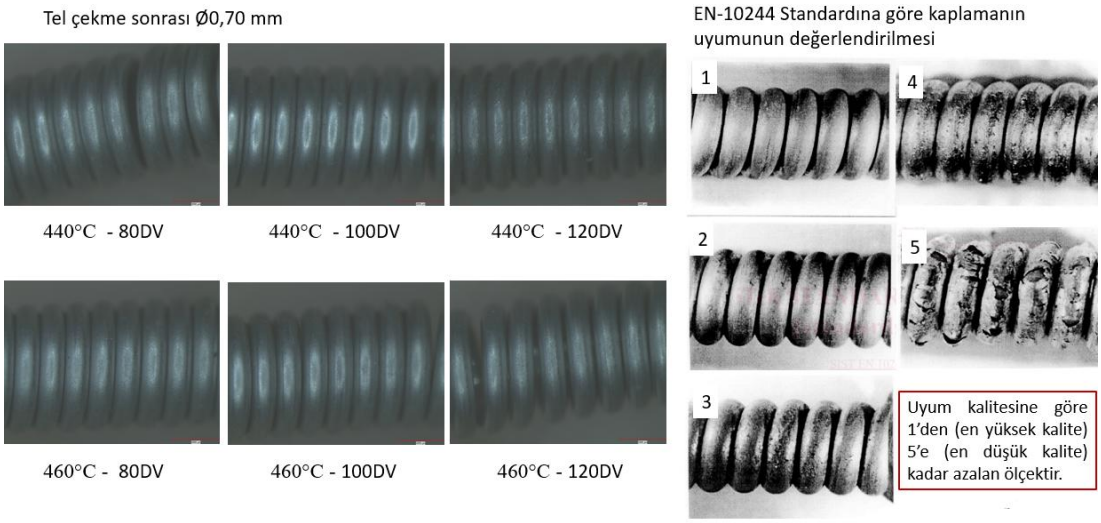
3.4. Sarma Testi Sonuçları

Şekil 14.'da verilen sarma testi sonrası elde edilen stereo mikroskop görüntüleri, kaplamanın çekme ve deformasyon etkileri altındaki sürekliliğini ve EN-10244 standardına göre uyum kalitesini ortaya koymaktadır. Ø2,00 mm çaplı tellerde 440 °C ve 460 °C sıcaklıklarda farklı hızlarda galvanizleme sonrası gözlemler, kaplamanın bütünlüğünün sıcaklık ve hız parametrelerine duyarlı olduğunu göstermektedir. 440 °C'de elde edilen kaplamalarda, özellikle 80 DV hızında kısmen homojenlik sağlansa da yüzeyde yer yer ince çizgilenmeler ve süreksizlikler gözlenmiştir. Hız artışıyla birlikte (100–120 DV) kaplama daha düzgün bir dağılım göstermekte, ancak bazı bölgelerde mikroskobik yüzey hataları belirginleşmektedir. 460 °C'de ise çinko tabakasının daha yoğun ve süreklilik gösterdiği, 80–100 DV hızlarında homojen bir kaplama yüzeyinin oluştuğu, 120 DV'de ise yüzeyin nispeten daha kompakt ve düzgün olduğu görülmektedir. EN-10244 standardı ile karşılaştırıldığında, 460 °C'de 100–120 DV hızlarında elde edilen kaplamaların 1. ve 2. kalite seviyelerine daha yakın olduğu, 440 °C'de ise kaplama bütünlüğünün 2. ve 3. kalite düzeyine karşılık geldiği söylenebilir. Bu sonuçlar, galvanizleme sıcaklığının artırılmasının kaplama uyum kalitesini iyileştirdiğini ve tel çekme sonrası sarma testinde kaplamanın deformasyona karşı daha dayanıklı hale geldiğini göstermektedir.



Şekil 14. Tel çekme sonrası Ø2,00 mm için sarma testi sonuçları.

Şekil 15.'de, sıcak daldırma galvaniz kaplaması uygulanmış çelik tellerin, tel çekme işlemi sonrası (Ø2,00 mm'den Ø0,70 mm'ye) sarma testi performansları değerlendirilmiştir. Galvanizleme işlemi, 440 °C ve 460 °C sıcaklıklarında, sırasıyla 80, 100 ve 120 DV hızlarında gerçekleştirilmiş ve numuneler EN-10244 standardına göre uyum kalitesi açısından sınıflandırılmıştır. Stereo mikroskop ile elde edilen görüntüler, özellikle tel yüzeyinde kaplamanın tel çekme sonrası homojenliğini ve tutunma kalitesini ortaya koymaktadır. 440 °C'de yapılan galvanizleme işlemlerinde, artan DV hızı ile birlikte kaplama uyumunun kademeli olarak bozulduğu; 120DV'de gözle görülür şekilde homojenliğin azaldığı gözlemlenmiştir. Buna karşın, 460 °C sıcaklıkta elde edilen görüntüler, özellikle 100DV hızında, EN-10244 standardına göre 1. ve 2. kaliteye yakın bir kaplama uyumu göstermektedir. Bu bulgular, yüksek sıcaklık ve uygun hat hızlarının galvaniz kaplamanın tel çekme sonrası mekanik deformasyonlara karşı direncini artırabileceğini ortaya koymaktadır.



Şekil 15. Tel çekme sonrası Ø0,70 mm için sarma testi sonuçları.

4.SONUÇ

SEM ve EDS görüntüleri galvaniz banyosunun sıcaklığı ve hat hızının Fe ve Zn'nin birbiri içerisinde olan difüzyonunu doğrudan etkilediğini göstermiştir. Sıcaklığın artması ile 80 ve 100DV'de Fe-Zn intermetalik bağı artarken, 120DV'de azalmıştır. Bunun sebebi sıcaklığın artması ile banyo viskozitesinin düşmesi ve buna ek olarak hattan geçişin hızlı olması kaplamanın yüzeye tutunmasını zorlaştırmıştır.

Çekme testi sonuçlarına göre tüm çaplarda akma ve kopma mukavemeti açısından 440°C banyo sıcaklığında 100DV hız optimum sonuç verirken, banyo sıcaklığının 460°C'ye çıkarılması ile 80DV hız ile optimum sonuç elde edilmiştir.

ZABA (çinko kaplama kütle testi) sonuçlarına göre banyo sıcaklığının artması ile aynı hat hızında çinko kaplama kütlesinin arttığı görülmüştür.

Torsiyon testi sonuçlarına göre her iki son çap içinde sıcaklık artışı ile aynı hat hızlarında artış gözlemlenmiştir.

Sarma testi incelemelerinde yapılan kaplamanın kalitesi EN 10244 standardına göre tüm sıcaklık ve hızlarda kaliteye uyduğu gözlemlenmiştir.

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Achieving Maximum Strength By Optimizing The Equivalent Elastic Modulus Of Multilayer Steel Ropes Through Complex Parameter Design

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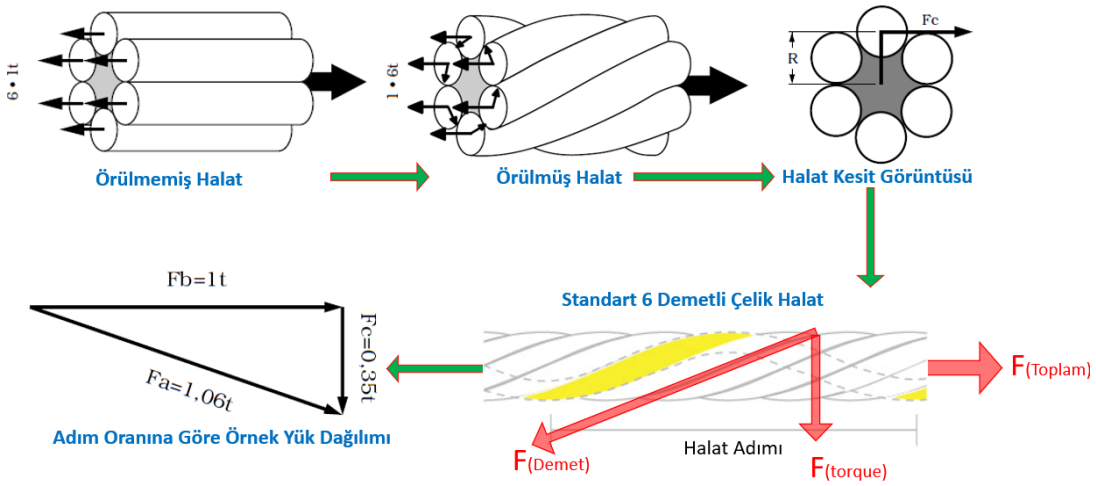
ABSTRACT

Wire ropes are materials used for load lifting and handling in industries such as construction, port operations, mining, elevators, forestry, and more. The specifications required of a steel wire rope vary depending on the industry in which it is used. Due to their design, conventional steel wire ropes tend to rotate depending on the lifting height. To prevent the inherent rotation of conventional wire ropes, multilayer rotation-resistant ropes have been developed for lifting applications over 80 meters. Rotation resistance is achieved when the layers are braided in opposite directions. However, due to their multi-layered structure and 35-strand configuration under load, there may be losses in breaking strength and service life compared to standard 6- or 8-strand ropes. In this study, the optimum equivalent elastic modulus for rotation-resistant ropes will be investigated. The equivalent elastic modulus of the rope will be calculated based on the load sharing among the strands, wires, and helix angles, as well as the elastic modulus and lengths of the wires. A new rope design with maximized strength will be created by ensuring that all the wires share the load equally at an equivalent load capacity. The multi-strand wire rope has a multilayer structure with left-hand lay in the core strands and right-hand lay in the outer strands. The outer layer consists of a total of 96 wires forming 16 strands. The steel core consists of 133 wires forming 19 strands arranged in two different layers. An increase of up to 15% in tensile strength compared to conventional 35x7 rotation-resistant ropes is expected to be achieved. Testing will be carried out under laboratory conditions, and the elastic modulus of the rope will be calculated and verified both theoretically and experimentally.

Keywords: Elastic Modulus, Equivalent elastic modulus, Steel wire, Steel wire rope, Multilayer steel wire rope, perfection

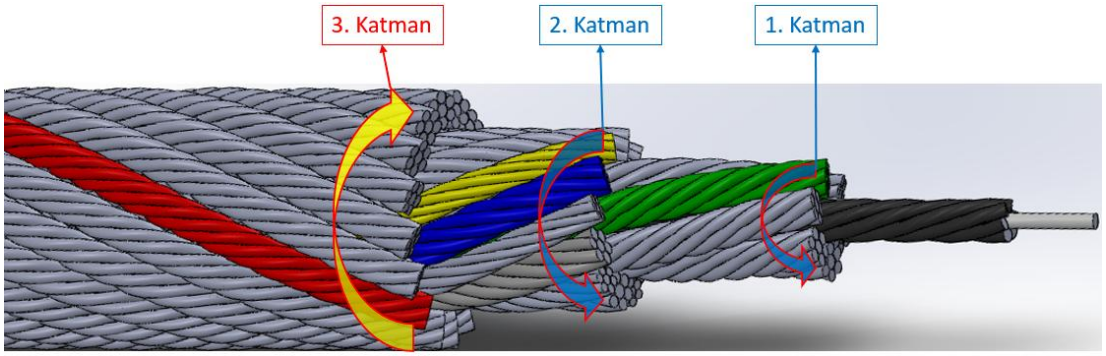
1. Giriş

Çelik halatlar; çok telli demetlerin (strand) helisel olarak örülmesiyle oluşan, yük taşıma ve hareket iletimi görevlerinde yaygın kullanılan esnek taşıyıcılardır. Kaldırma ve çekme sistemleri (kule vinç, mobil vinç, portal vinç), teleferik vinç sistemleri, denizcilik ve maden endüstrisi başlıca uygulama alanlarıdır. Özellikle 60 m ve üzeri kaldırma mesafelerinde halat, yük altında örüm yönünün tersine bir dönme momentine maruz kalır. Bu durum, açma yönünde döndürme kuvveti nedeniyle hasar riskini artırır ve servis performansını düşürür.

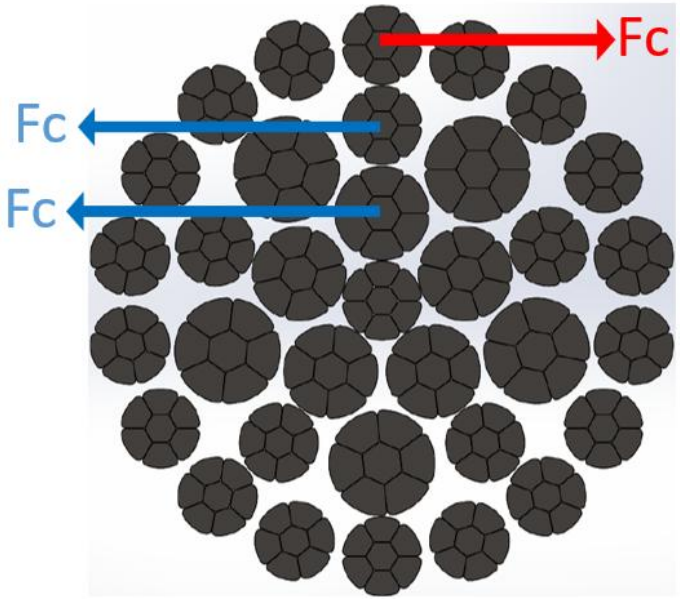


Şekil 1. Standart 6 demetli halatta yük altında dönme-tork davranışı

Dönme dirençli (rotation-resistant) halatlar, bu dönme momentini iç ve dış katmanların zıt örüm yönleri sayesinde, karşı tork üretip dengeleyecek biçimde tasarlanır. Tasarımda katman sayısı, sarım yönü ve adım (pitch) belirleyici parametrelerdir.



Şekil 2. Dönme dirençli halatların iç ve dış katmanların örüm yönleri 3D gösterimi



Şekil 3. Çok Katmanlı Halatta Yük Altında Demet Katmanlarının Moment Davranışı

Bu çalışmanın odağı eşdeğer elastik modül (***E_{eq}***)'dür. Çelik halat, düz bir çubuğa göre daha düşük eksenel rijitlik gösterir. Çünkü her tel helisel yol izler ve yükün bir kısmı kayma/şekil değiştirme sebebi ile kayba neden olur. Özellikle çok-demetli ve çok-katmanlı tasarımlarda ***E_{eq}***, yük paylaşımı (***N-payı***) dengesizliğinden etkilenir. İç katmanlar aşırı yük alırsa halatın toplam elastik modülü düşer, kopma yükü düşer ve yan etki olarak yorulma ömür performansı kısalır. Dolayısıyla çok-demetli halatlarda ***E_{eq}***'in yükseltilmesi yalnızca elastik uzama davranışını iyileştirmekle kalmaz; kopma yükünün artmasına, yorulma ve dönme performansı üzerinde de artı etkiler sağlar

Bu bildiride; 35×7 çok-katmanlı halat özelinde, tel ve demet helis açılarını (***α, α'***), tel elastisite modüllerini (***E_i***), tel kesit alanlarını (***A_i***) ve katman/kompozisyon sayısını içeren bir matematiksel model ile ***E_{eq}***'in nasıl yükseltilebileceğini analitik olarak hesaplıyoruz. İki senaryo kıyaslanmıştır: (***i***) alan-orantılı yük paylaşımı ve (***ii***) üniform paylaşım. Modelden elde edilen optimum ***α'*** değerleri, sınırlı sayıda numuneyle deneysel prosedür içinde sınanmış ve sonuçlar kuram–deney tutarlılığı açısından tartışılmıştır.

2. Kuramsal Çerçeve ve Hesap Yöntemi

2.1. Geometri ve temel tanımlar

- **Tel helis açısı: *α***
- **Demet (strand) helis açısı: *α'***
- **Adım oranı:** $k = \dfrac{\text{helis adımı}}{\text{çevresel yol}}$

  Çoğu tasarımda **α** ve **α'**, bilinen ***k*** üzerinden yaklaşık olarak;

  $$\alpha \simeq \arccos\left(\frac{1}{k_{\text{wire}}}\right), \qquad \alpha' \simeq \arccos\left(\frac{1}{k_{\text{strand}}}\right)$$

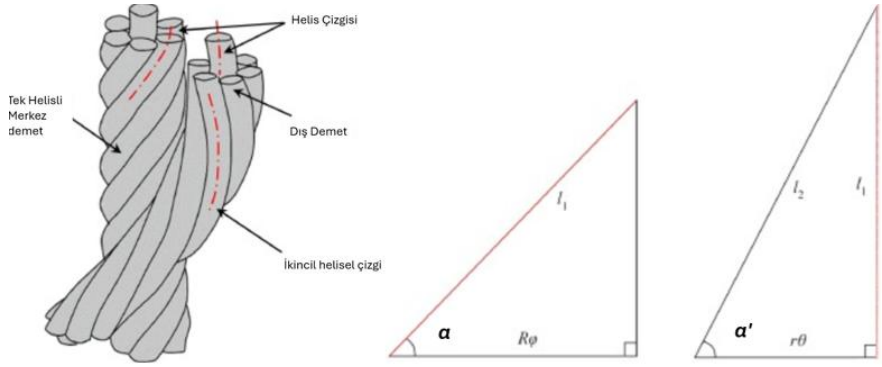
  ile hesaplanabilir (Bu, halat pratiklerinde kullanılan trigonometrik yaklaşımdır)
- **Tel kesit alanı**: $A_i = \frac{\pi d_i^2}{4}$
- **Tel elastisite modülü**: ***E_i*** (Üretim çeliği, tel çekme prosesi, hadde serisi, toplam redüksiyon oranı ve karbon/alaşım içeriğine bağlı olarak telden tele az da olsa değişebilir).

2.2. Helis nedeniyle rijitlik azalışı: indirgeme fonksiyonu

Eksenel yük altında tel/demet eksenleri halat ekseniyle açı yapar; bu nedenle etkin eksenel rijitlik, helis açısı arttıkça düşer. Bunu modellemek için, tel/demet ölçeğinde indirgeme fonksiyonu ***f(ϑ)*** tanımlanır. Klasik ilk yaklaşım ***$f(\vartheta)=\cos^2\vartheta$*** olsa da, helisel sistemlerde kayma uyumluluğu önemlidir. Bu yüzden G kayma modülünü içeren aşağıdaki ifade kullanılır (Hesaplamalarda verimli ve kararlı sonuç vermiştir):

$$f(\theta) = \frac{\cos^2\theta}{1 + \frac{E}{G}\tan^2\theta}, \qquad G = \frac{E}{2(1+\nu)}\ (\nu \approx 0.30) \ \Rightarrow\ \frac{E}{G} \approx 2.6.$$

Bu faktör tel ölçeğinde ***f(α)***, demet ölçeğinde ***f(α')*** olarak ayrı ayrı uygulanır; çok-katmanlı halatlarda bu iki etken, çarpan gibi davranır. Bu form, tel/demet eksenine paralel–dik bileşenlerdeki uzama ve kayma uyumunu birleştiren pragmatik bir indirgeme kuralıdır; literatürdeki tel-halat rijitlik modelleriyle (Costello; Knapp; Leech) tutarlı bir düşük-üst sınır davranışı sergiler.



*Şekil 4. Birincil helisel çizgi (**α'**) ve ikincil helisel çizginin **(α)** çelik halat uzay geometrisindeki açısal genişlemesinin gösterimi*

2.3. Eşdeğer elastik modül E_{eq}

Halatın toplam metalik alanı, $A_\Sigma = \sum_i A_i$ iken, **t**el bazlı pay, (eksenel rijitlik payı):

$$K_i = E_i\, A_i\, f(\alpha_i)\, f(\alpha'_j),$$

burada ***i*** tele, ***j*** demete aittir.

Halat eksenel eşdeğer modülü:

$$E_{eq} = \frac{\sum_i K_i}{\sum_i A_i} = \frac{\sum_i E_i A_i\, f(\alpha_i)\, f(\alpha'_j)}{A_\Sigma}$$

Bu ifade, tüm katmanlar/topolojiler için geçerlidir; tellerin elastisite modülleri farklıysa (ör. farklı tel mukavemet sınıfları, farklı C içeriğine sahip teller), doğal olarak E_{eq} buna duyarlı olur.

2.4. Yük paylaşımı ve N-payı

Uzama altındaki yük dağılımı (N-payı) her tel için,

$$N_i \;\propto\; E_i A_i\, f(\alpha_i)\, f(\alpha'_j),$$

Katman ***j*** için toplam pay:

$$N_j = \sum_{i \in j} N_i, \qquad \widehat{N}_j = \frac{N_j}{\sum_\ell N_\ell}$$

Buradan iki hedef senaryosu tanımlarız:

- Alan-orantılı yük paylaşımı: $\widehat{N}_j^\star = \dfrac{A_j}{\sum_\ell A_\ell}$
- Tam üniform: $\widehat{N}_j^\star = \dfrac{1}{L}$ (katman sayısı L)

Problem: α'$_j$ **açılarını,** $\widehat{N}_j \to \widehat{N}_j^\star$ olacak şekilde seçmek (tel ***αi*** ve E_i, A_i sabit kabul edilir). Tel ölçeğindeki α_i çoğunlukla telin demetteki örüm geometrisiyle belirlenmiştir;

2.5. α'_j için çözüm (invers tasarım)

Katman j için; $\widehat{N}_j \propto B_j\, f(\alpha'_j), \qquad B_j := \sum_{i\in j} E_i A_i\, f(\alpha_i)$

olduğundan, hedefe ulaşmak için;

$f(\alpha'_j) \;\propto\; \dfrac{\widehat{N}^{\star}_j}{b_j}, \qquad b_j := \dfrac{B_j}{\sum_\ell B_\ell}$ formülü kullanılır

Burada $f(\cdot)$ monoton olduğu için α'_j tekil bulunur. Pratikte demet açısı θ, θ∈[0°,40°] aralığında kabul edilir,

$$f(\alpha'_j) = \frac{\widehat{N}^{\star}_j}{b_j} \;\Rightarrow\; \alpha'_j$$

sayısal olarak elde edilir. Böylece her katman için "gerekli $\Delta\alpha'_j$ doğrudan çıkar.

Mühendislik kısıtları: Pratikte uygulanabilir ve üretilebilir adım oranları, tel ve demetin eğilme-bükülme altında burulma riski, temas yüzeylerinin sürtünme ile yer değiştirmesi ve tork faktörünün (Feyrer) bozulmamasıdır. Bu yüzden alan-orantılı hedef genelde daha uygulanabilir, tam homojen yük paylaşımlı hedef -payı çoğu zaman pratikte uygulanabilir değildir. (sayısal sonuçlar da bunu doğrulamıştır).

2.6. Literatür ve kurgu

- **Tork momenti ve tork faktörü:** Feyrer'in moment ve tork faktörü denklemleri (tasarım aşamasında dönme direncinin nicel öngörüsü ve gereksinimi).
- **Çok katman/zıt örüm yönleri ile dönme direnci:** Proje raporları ve saha açıklamaları (katman sayısı, sarım yönü, adım uzunluğu belirleyici).
- **Performans çıktılar:** Kopma yükü ve halat elastisite modülünde artış, tork direncini korumak.

2.7. Bu çalışmada uygulanan hesap akışı (özet)

1. **Girdi**: Katman/demet listesi; her tel için d_i, E_i; tel ve demet adım oranlarından α_i, α'_j; tel sayıları ve yerleşim (metalik alan).
2. **Tel düzeyi indirgeme**: $f(\alpha_i)$ ile $E_i A_i$ katkılarını projekte et.
3. **Deme t düzeyi indirgeme**: Katman j için $B_j = \sum_{i\in j} E_i A_i f(\alpha_i)$ ve mevcut $f(\alpha'_j)$.
4. **Mevcut N-payı**: $\widehat{N}_j \propto B_j f(\alpha'_j)$; normalize et.
5. **Hedef belirle**: (a) alan-orantılı $\widehat{N}^{\star}_j = A_j / \sum A$; (b) üniform $1/L$.
6. **İnvers çözüm**: $f(\alpha'_j) = \widehat{N}^{\star}_j / b_j$ için α'_j çöz; üretilebilir aralığa **projeksiyon** yap.
7. **Eşdeğer modül**:

$$E_{eq} = \frac{\sum_i E_i A_i\, f(\alpha_i)\, f(\alpha'_j)}{\sum_i A_i}$$

Çok demetli (3 katmanlı) halatların, dış katmanların demet açısını küçülterek, iç katmanda ise büyüterek (tork dengesini korumak kaydıyla) Eşdeğer Elastik modülün arttırılabileceği yukarıdaki formülle tespit edilmiştir.

Özet teknik sonuç: 35×7 halatın veri seti üzerinde yaptığımız üniform model (kayma uyumluluğu dahil) ile alan-orantılı yük paylaşımı hedeflendiğinde E_{eq} anlamlı şekilde yükseliyor; tam üniform hedef ise genelde üretim/tork dengesi kısıtları nedeniyle optimum koşulda ve pratikte uygulanabilir değildir.

3. Deneysel Prosedür

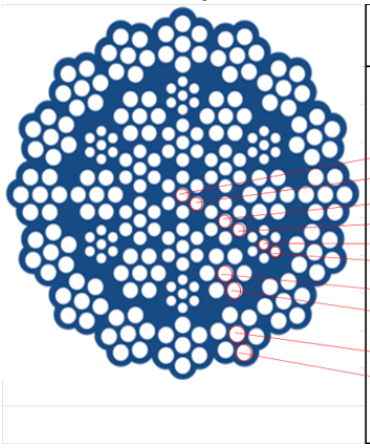
Bu çalışmada teorik olarak geliştirilen eşdeğer elastik modül ***(E_{eq})*** hesaplama yöntemi, sınırlı sayıda pratik test ile doğrulanmıştır. (sebebi ise demet açı değişimi, adım değişimi sonrası her bir parametre için halat tasarımı gereksinimi olmasıdır) Testlerin amacı, tel ve demet helis açılarının ***(E_{eq})*** ve kopma yükü üzerindeki etkisini deneysel olarak gözlemlemek ve kuramsal hesaplarla karşılaştırmaktır.

Numune üretimi:

Tablo 1. Deneme halatının tasarım parametreleri

1	Halat Çapı	[mm]	**16**
2	Halat Çap toleransı	[-%/+%]	**-0/+5**
3	Halat kompozisyonu ISO 17893/ EN12385-2		**35x7**
4	Öz kompozisyon		**19x7**
5	Dış demet tel dizilimi		**18x(1+6)**
6	Tel Mukavemet Sınıfı	[N/mm2]	**2160**
7	Minimum kopma yükü	[kN]	**200**
8	Halat yönü		**Sağ Çapraz**
9	Tel kimyasal kompozisyonu		**0,83C yaylık tel**
10	Halat birim ağırlık	[kg/m]	**1.226**
11	Halat tel kaplaması EN 10264-2	(U/AB/B)	**B**
12	Standart		**EN 12385-4**

Şekil 5. Deneme halatının tasarım parametre çıktıları, tel mukavemetleri, tel ve demet uzunlukları



Halat uzunluğu (m)	Demet tanımı	demetteki Tel tanımı	Tel çapı (mm)	Tel Mukavemeti (Mpa)	Akma mukavemeti (Mpa)	Akma Uzaması (%)	Tel Ei değerleri (Gpa)	Demet boy katsayısı	Demet uzunluğu (m)	demetteki Tel tanımı	demetteki tel boy katsayısı	Demet sayısı (adet)	Demet çapı (mm)	Demet adım uzunluğu (mm)
100	merkez demet	merkez tel	1.00	2158.20	1622.00	0.30	223.00	1	100	merkez tel	1	1	2.72	19.0
	merkez demet	dış tel	0.86	2462.31	2040.00	0.31	229.00	1	100	dış tel	1.046			
	1. katman demet	merkez tel	0.96	2177.82	1635.00	0.29	225.00	1.0231	102.31	merkez tel	1	6	2.52	22.7
	1. katman demet	dış tel	0.90	2315.16	1955.00	0.27	226.00	1.0231	102.31	dış tel	1.0275			
	2. katman ince demet	merkez tel	0.74	2354.40	1975.00	0.26	224.00	1.0777	107.77	merkez tel	1	6	1.92	23.3
	2. katman ince demet	dış tel	0.68	2246.49	1900.00	0.28	222.00	1.0777	107.77	dış tel	1.0275			
	2. katman kalın demet	merkez tel	1.00	2305.35	1948.00	0.29	222.00	1.0681	106.81	merkez tel	1	6	2.59	17.3
	2. katman kalın demet	dış tel	0.92	2266.11	1925.00	0.29	221.00	1.0681	106.81	dış tel	1.0275			
	3. katman demet	merkez tel	0.96	2177.82	1633.00	0.29	224.00	1.0807	108.07	merkez tel	1	16	2.50	22.5
	3. katman demet	dış tel	0.88	2403.45	1988.00	0.26	228.00	1.0807	108.07	dış tel	1.0275			

İki farklı demet helis açısı ***(α')*** seçildi:

1. Mevcut tasarım: Standart uygun adım oranı (yaklaşık 28–30° dış demet örüm açısında).
2. Optimum tasarım: Matematiksel modelle belirlenen alan-orantılı yük paylaşımına karşılık gelen adım oranı (yaklaşık 23–25° dış demet örüm açısında).

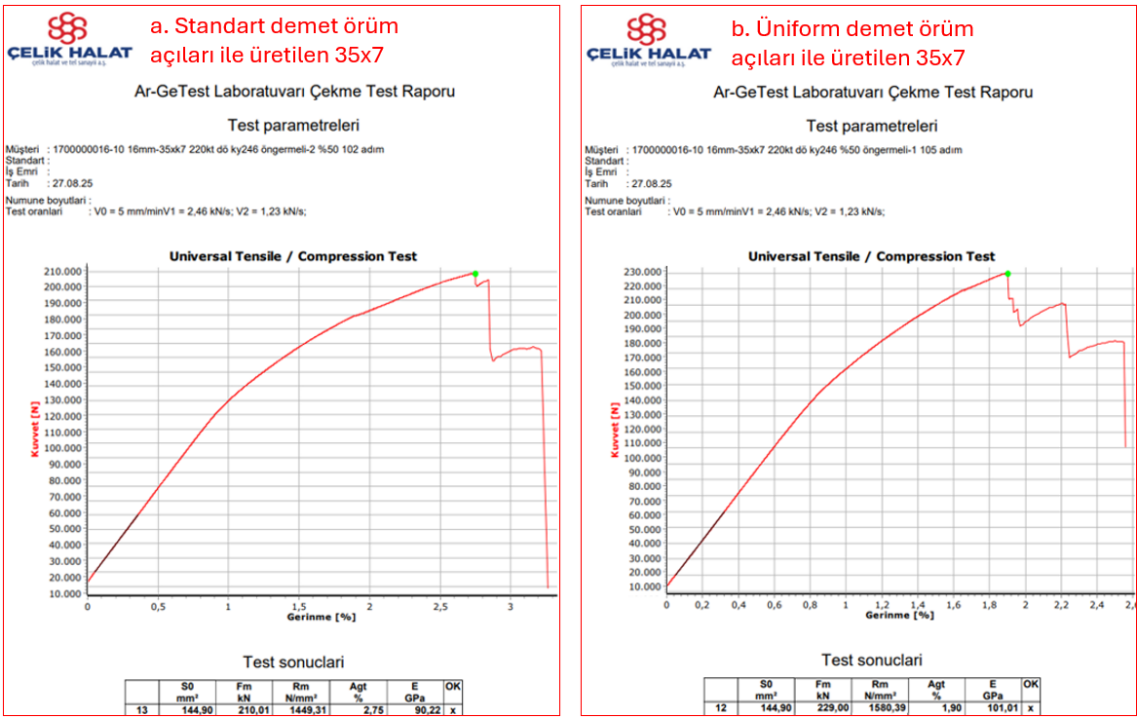
Test koşulları:

Tüm çekme testleri, TS EN ISO 6892-1 ve TS EN 12385-1+A1 standartlarına uygun olarak RAAGEN 100 tonluk hidrolik çekme test makinesi kullanılarak gerçekleştirilmiştir. Test sonuçlarının tutarlılığını ve güvenilirliğini sağlamak için halat numuneleri ISO 3108 gerekliliklerine göre hazırlanmıştır. Her bir tel gerilme seviyesi için tek bir uzama testi gerçekleştirilmiştir. Uzama testlerinin tamamlanmasının ardından, aynı numuneler çekme kopma testlerine tabi tutulmuştur. Uzama prosedürü, her halatın minimum kopma yükünün (MBL) %5 ile %50'i arasında 10 kez döngüsel olarak yüklenmesini içermektedir. Bu döngüsel süreç, nihai testten önce yapısal gerilmenin stabilize olmasını sağlamıştır. Tüm testler sırasında, kaymayı önlemek ve doğru kuvvet uygulamasını sağlamak için 280 barlık sabit bir kavrama basıncı korunmuştur.

- **Cihaz:** Çekme test cihazı, 1000 kN kapasiteli, video ekstansometre uzama ölçer ile,
- **Ölçülen parametreler:**

- Elastik bölgedeki eğimden hesaplanan E_{eq}
- Gerçek Kopma yükü (ABL) (kN)
- Uzama yüzdesi (%$\Delta L/L_o$)

Yorulma testleri ve torsiyon testleri bu aşamada yapılmamış, yalnızca statik elastik modül ölçümü uygulanmıştır.



Şekil 6. Deneme üretimi test grafikleri a.) Standart 35x7 b.) Üniform 35x7

4. Sonuçlar ve Değerlendirme

4.1. Teorik ve deneysel E_{eq} karşılaştırması

Teorik modelden elde edilen değerler:

- Mevcut tasarım: E_{eq}≈127.8 GPa
- Alan-orantılı hedef: E_{eq}≈191.0 (Pratikte uygulanabilir değil)
- Üniform hedef: E_{eq}≈137.3

Deneysel test sonuçları:

- Mevcut tasarım (dış demet açısı 28-30°): E_{eq}≈90±3
- Üniform tasarım (dış demet açısı 23-25°): E_{eq}≈101±4 GPa

Karşılaştırma: Deneysel sonuçlar ile teorik model aynı trendi göstermektedir: ilk 2 katmandaki demet açılarının arttırılması ve en dış 3. Katmandaki demet açısının düşürülmesi ile E_{eq} yükselmiştir. Teorik artış öngörüsü (%+7,4) deneyselde %+12 düzeyinde gerçekleşmiştir. Farkın nedeni:

- Tel–tel temasındaki sürtünme kayıpları
- Tellerin ve demetlerin yük aktarımındaki geri farkı sebebiyle uyumsuzluk
- Modelde göz ardı edilen tel helisleri

4.2. Kopma yükü ve uzama davranışı

- **Gerçek Kopma yükü (ABL):** İki tasarım arasında test sonuçlarına göre mukavemette %9 fark gözlenmiştir. Bu farkın, farklı açılardaki örümün yük paylaşımını (N-Payı) üniform paylaştırması sebebiyle olduğu tespit edilmiştir. Yük paylaşımı homojenliği arttırılmıştır.
- **% Uzama (%ΔL/L_o):** Optimum açılı tasarımda elastik modülün yükselmesi ile uzama eğrisi daha dikleşmiş, elastik bölgede daha rijit davranış sergilenmiştir.

4.3. Yorum ve mühendislik çıkarımları

- Deneysel sonuçlar, demet helis açılarının halatın E_{eq} değerinde kritik rol oynadığını doğrulamıştır.
- Matematiksel model, eğilimleri doğru tahmin etmiştir; fakat mutlak değerlerde pratik kayıplar nedeniyle farklar vardır.
- Alan-orantılı yük paylaşımı hedefi, pratikte en uygulanabilir optimizasyon yöntemi olarak öne çıkmıştır. Tam üniform yük dağılımı ise üretim kısıtları (adım oranı, eğilme sonucu kuş gözü riski) nedeniyle tercih edilebilir değildir.
- Daha ileri testler (yorulma ömrü, torsiyon) yapıldığında, E_{eq}'teki artışın dolaylı olarak ömrü uzatma ve dönme davranışını iyileştirme potansiyeli doğrulanabilir.

5. Sonuç

Bu çalışmada, 3 katmanlı 35×7 çok demetli çelik halatların eşdeğer elastik modülünün E_{eq}artırılması için matematiksel modelleme ve deneysel doğrulama gerçekleştirilmiştir. Başlıca sonuçlar şu şekilde özetlenebilir:

1. Matematiksel model: Tel ve demet helis açıları (α, α'), tel elastisite modülü (E_i) ve kesit alanı (A_i) parametrelerini içeren model ile E_{eq} analitik olarak hesaplanmıştır. Kayma uyumluluğu faktörü dahil edilerek teorik değerlerin gerçekçi şekilde sınırlandığı görülmüştür.

2. Yük paylaşımı (N-payı): Mevcut tasarımda yük dağılımı katmanlar arasında dengesizdir. Alan-orantılı hedefleme ile E_{eq}'in teorik olarak %49'a varan artış gösterebileceği hesaplanmıştır. Üniform paylaşım ise pratik üretim metotlarına uygun olarak tasarlanmış ve ürünün kullanımında performansa negatif etkisi olmamasına dikkat edilmiştir.

3. Deneysel doğrulama: İki farklı örüm açısı ile üretilen numuneler üzerinde yapılan çekme testleri, teorik modelin öngördüğü eğilimi doğrulamıştır. Deneysel olarak E_{eq}'de %12–13 seviyesinde artış kaydedilmiştir. Bu fark, tel-tel sürtünmesi, çekme testinde çenede kayma kayıpları ve mikro-geometri etkilerinden kaynaklanmaktadır.

4. Mühendislik çıkarımı: Eşdeğer elastik modülün artırılması ile, çelik halatlarda daha rijit elastik davranış, dengeli yük paylaşımı sayesinde kopma yükünde **%9** artış, Halat elastik modülünde ise **%12** artış sağlandığı tespit edilmiştir.

5. Sonuç olarak, birincil demet helis açılarının ve ikincil tel helis açılarının optimizasyonu, çok-katmanlı halatların mekanik davranışında kritik bir tasarım parametresidir. İlerleyen çalışmalarda FEM tabanlı analizler ve yorulma testleri ile modelin daha kapsamlı doğrulanması hedeflenmektedir.

6. Teşekkür

Bu çalışmanın yürütülmesine olanak sağlayan **Çelik Halat ve Tel Sanayii A.Ş. Ar-Ge Merkezi**'ne teşekkür ederiz. Deneysel testlerin gerçekleştirilmesinde kullanılan çekme test cihazı ve laboratuvar altyapısı, **Çelik Halat Ar-Ge Teknoloji Laboratuvarı** tarafından sağlanmıştır. Ayrıca, daha önce yürütülen ulusal ve kurumsal Ar-Ge projelerinde (örn. *2021-0031 ve 2022-0036 kodlu proje çalışmaları*) elde edilen bilgi birikimi ve altyapı bu bildirinin hazırlanmasında önemli rol oynamıştır.

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Fren Balatalarında Bor Katkı Maddelerinin Rolü ve Tribolojik Performansa Etkisi

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ÖZET

Fren balataları, araçların güvenli yavaşlama ve durmasında temel rol oynayan, yüksek sıcaklık ve sürtünmeye dayanıklı malzemelerdir. Geçmişte mekanik avantajları nedeniyle kullanılan asbest, sağlık ve çevre riskleri sebebiyle yasaklanmış; yerini metalik, yarı metalik ve seramik katkılı alternatifler almıştır. Günümüzde çevre dostu, sürdürülebilir ve yerli kaynaklı katkıların kullanımı ön plana çıkmaktadır.

Bu çalışmada, Türkiye'de zengin rezervlere sahip bor minerali olan üleksit fren balatalarında katkı maddesi olarak araştırılmıştır. Geleneksel katkılara alternatif olarak %10 oranında ilave edilen üleksitin sürtünme stabilitesi, maliyet ve çevresel faydaları değerlendirilmiştir. Numuneler üzerinde yoğunluk tayini, kül oranı, compressibility, kopma dayanımı, Chase ve dinamometre testleri yapılmıştır. TGA analizinde %5,4 kütle kaybı gözlenmiş, Chase testinde G sınıfı sürtünme katsayısı elde edilmiştir. Sonuçlar, üleksitin hem mekanik performansı desteklediğini hem de sürdürülebilir yerli katkı potansiyeli sunduğunu göstermektedir.

Anahtar Kelimeler : Fren Balatası, Üleksit, Triboloji, Sürdürülebilirlik

The Role of Boron Additives in Brake Pads and Their Effect on Tribological Performance

ABSTRACT

Brake pads are essential components that ensure safe vehicle deceleration and stopping, engineered to endure high temperatures and frictional loads. Historically, asbestos was widely used due to its favorable mechanical properties, but it was banned because of severe health and environmental hazards. Metallic, semi-metallic, and ceramic-based alternatives have since replaced it. Today, the development of eco-friendly, sustainable, and locally sourced additives has gained priority.

This study investigates the use of ulexite, a boron mineral abundantly available in Turkey, as an additive in brake pad formulations. Ulexite was incorporated at a 10% ratio to evaluate its influence on friction stability, cost efficiency, and environmental benefits. Produced samples underwent density determination, ash content, compressibility, shear strength, Chase, and dynamometer tests. Thermogravimetric analysis (TGA) revealed an 5.4% mass loss, hile the Chase test confirmed a G-class friction coefficient. The findings indicate that ulexite not only enhances mechanical and tribological performance but also provides advantages in sustainability and local resource utilization.

Keywords: Brake Pad, Ulexite, Tribology, Sustainability

1. Introduction

Brake pads are critical components for automotive safety. By applying frictional force to the brake disc, they convert kinetic energy into heat energy, enabling the vehicle to decelerate and stop. To perform this function reliably, brake pads must withstand high temperatures, maintain a stable coefficient of friction, exhibit low wear rates, and be environmentally safe (Blau, 2001).

Brake pads generally consist of four main components: reinforcing materials (fibers), binding agents (such as phenolic resins), fillers, and friction modifiers (Öztürk et al., 2015). The proportion and distribution of these components directly determine the tribological properties, mechanical strength, and service life of the brake pad.

In the past, asbestos-based brake pads were widely used due to their superior mechanical and thermal properties. Asbestos offers advantages such as high tensile strength, non-flammability, low thermal expansion, and electrical stability (Ravikiran et al., 2017). However, since asbestos fibers are respirable, they pose serious health risks, leading many countries to ban its use, which in turn directed the industry toward the development of metallic, semi-metallic, and ceramic-based alternatives (Eriksson & Jacobson, 2000). Although metallic and semi-metallic pads provide high strength, they suffer from issues such as noise, excessive disc wear, and brake dust generation (Bijwe, 2019). Ceramic additives, on the other hand, stand out with their low wear rate, quiet operation, thermal stability, and environmentally friendly characteristics, making them one of the most widely preferred materials today (Blau, 2015).

In recent years, boron minerals have attracted considerable attention within the scope of sustainable material research. Turkey holds approximately 65% of the world's boron reserves, and this strategic advantage makes the use of boron compounds in the automotive industry highly appealing (General Directorate of Eti Mining Operations, 2023). The literature reports that boron additives stabilize the coefficient of friction over a wide temperature range, reduce both pad and disc wear, and enhance tribological performance (Öztürk & Demir, 2016; Hwang et al., 2013).

For instance, Sugözü et al. produced brake pads containing 4–12% ulexite and borax and found that increasing the additive ratio improved friction stability (Sugözü et al., 2018). Başar and his team manufactured pads reinforced with colemanite and borax using the hot-pressing method and reported that the most stable coefficient of friction was achieved at a 4% additive ratio (Başar et al., 2020). More recent studies have shown that nano-sized boron additives further improve tribological performance, particularly by enhancing wear resistance (Sugözü et al., 2021).

The advantages of boron additives are not limited to performance alone. They also provide significant benefits in terms of health and the environment by reducing harmful dust and noise generation, thus offering quieter, cleaner, and more sustainable braking (Blau, 2015). In this respect, boron minerals align with the automotive industry's current goals of achieving both high performance and environmental sustainability.

This study focuses on the use of ulexite, a mineral abundantly available in Turkey, as an additive in brake pad formulations. The aim is to contribute to the development of environmentally friendly brake pads with high tribological performance based on local resources, while also offering sustainable solutions from economic, environmental, and technological perspectives. In this context, brake pads containing 10% ulexite were produced using the hot-pressing method. Following mixing, pressing, and curing processes, the obtained specimens were subjected to chemical tests (acetone extraction, ash content, moisture content, and density) and physical tests (shear strength, compressibility, Chase friction test, and dynamometer analyses). In addition, thermogravimetric analysis (TGA) was carried out to investigate the degradation behavior at high temperatures.

2. Materials and Methods

2.1. Materials Used

Studies have demonstrated that the type, particle size, shape, and amount of the materials forming the composite directly influence its friction and wear properties. Accordingly, when designing the composite content, the properties of the materials and findings from previous studies were taken into consideration. The composite composition and material characteristics are presented in Table 1.

Table 1. Composite components and material properties

Material	**Type**
Phenolic resin	*Binder*
Steel shavings	*Metallic chips*
Graphite	*Solid lubricant*
Powder cashew	*Friction modifier*
Barite	*Space filler*
Ulexite	*Reinforcement*

In this study, three main groups of components were selected for brake pad production in order to optimize tribological performance:

Binder, phenolic resin with thermoset properties was preferred due to its ability to provide high mechanical strength and thermal stability.

Fillers, barium sulfate ($BaSO_4$) and calcium carbonate ($CaCO_3$) were incorporated to increase the density of the brake pad and to contribute to friction stability.

Friction modifiers, materials such as graphite, steel powder, and cashew powder were used to maintain a stable coefficient of friction and ensure uniform heat distribution during operation.

In addition to these, ulexite ($Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O$), which is abundant in Turkey, was selected as an additive. Ulexite was supplied with a particle size of 45 µm and incorporated into the mixture at a ratio of 10%. In this way, a strategy based on the utilization of local resources was adopted, while also aiming to achieve environmental sustainability.

2.2. Sample Preparation

Approximately 10 different powders were used in the preparation of the brake pad specimens. As an alternative additive, 10% ulexite was incorporated. The composition of the ulexite-reinforced brake pad is presented in Table 2.

Table 2. Brake pad composition

Material	**Weight Ratio (%)**
Phenolic resin	*8-12*
Vermikülit	*2-5*
Graphite	*10-12*
Powder cashew	*8-10*
Barite	*8-10*
Fiber	*2-5*
Metal sulfide	*5-7*
Steel powder	*22-30*
Mica powder	*6-8*
Ulexite	*10*

The brake pad components were mixed in a high-speed mixer for 5 minutes to achieve a homogeneous mixture. The mixtures were then poured into cleaned and preheated molds, followed by the application of the hot-pressing method. As shown in Table 3, the pressing process was carried out at 150 °C under a pressure of 120 bar for 8 minutes. After pressing, the specimens were subjected to a curing process at 200 °C for 7 hours with a gradual temperature increase to ensure the complete stabilization of the internal structure. The resulting composites were cut and prepared in accordance with the dimensions required for the subsequent tests.

Table 3. Production parameters of composites

	Time (min)	**Pressure (bar)**	**Temperature (°C)**
Mixing	*5*	*-*	*-*
Hot molding	*8*	*120*	*150*
Curing	*360*	*-*	*Gradual, 200*

The brake pad specimen produced after the curing process is shown in Figure 1.

Figure 1. Ulexite-reinforced brake pad

2.3. Chemical Tests

The characterization tests conducted on the samples are summarized below;

Density determination, measured according to ASTM D792 standard, based on the buoyancy principle in water.

Moisture content and ash content, calculated through drying at 105 °C and combustion at 600 °C.

Acetone extraction, performed using a Soxhlet apparatus to investigate the solubility of phenolic resin.

These tests are critical not only for evaluating the fundamental chemical composition of the brake pads but also for assessing the stability of the binder phase.

2.4. Mechanical and Tribological Tests

2.4.1. Shear Strength Test

The shear strength of the specimens was measured in accordance with the ASTM D638 standard using the shear strength device shown in Figure 2.

Figure 2. Shear strength device

2.4.2. Compressibility Test

The compressibility test is a mechanical test conducted to examine the elastic and plastic deformations of brake pads and other composite materials under load. Compressibility tests are performed at room temperature and elevated temperature in accordance with ISO 6310 and SAE J2468 standards using the compressibility test device shown in Figure 3. The specimens are subjected to a stepwise pressure of 80 bar at 23 ± 5 °C and 400 ± 10 °C, and this procedure is repeated three times. According to the obtained results, the compressibility value should be ≤ 2% at 23 ± 5 °C and ≤ 5% at 400 ± 10 °C (Chan & Stachowiak, 2004).

Figure 3. Compressibility test device

2.4.3. Friction and Wear Test

The friction and wear tests applied to the brake pad specimens were carried out using Chase and dynamometer-type devices, as shown in Figures 4 and 5, in accordance with SAE J661 and SAE J2522

standards. The Chase test, based on the SAE J661 standard, was used to evaluate the coefficient of friction and wear behavior. The dynamometer test, based on the SAE J2522 standard, simulated real driving conditions to comprehensively assess friction stability, wear rate, and the effects of temperature.

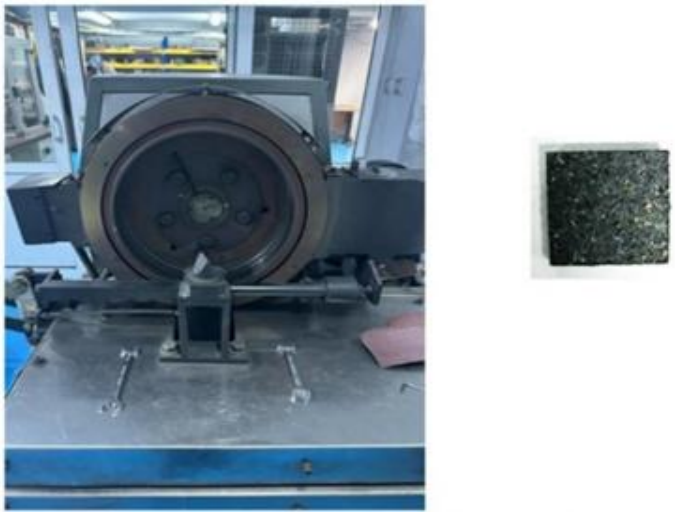


Figure 4. Chase test device and test specimen

The Chase test is carried out with a brake pad specimen cut to dimensions of 25.4 × 25.4 × 40 mm, which is pressed against a rotating disc system. While the disc rotates at specific speeds, controlled pressure is applied to the specimen. The disc speed is set to approximately 400 rpm, with an applied pressure of about 1 MPa, and the temperature is increased up to ~400 °C. Under these conditions, the coefficient of friction is measured as cold μ and hot μ.

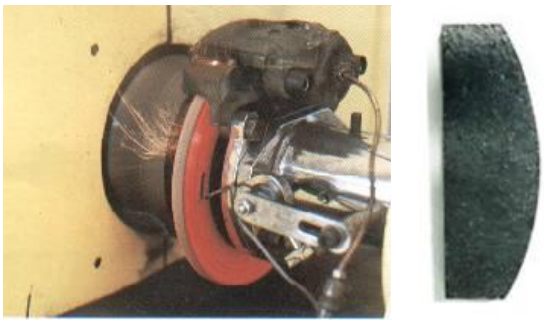


Figure 5. Dynamometer test device and test specimen

The dynamometer test is the laboratory simulation of the actual vehicle braking system (disc, pad, and caliper). The brake disc is rotated by a high-powered electric motor, while the brake pad applies pressure through a hydraulic system. The test specimens, produced in the actual dimensions of vehicle brake pads, are mounted onto the dynamometer system. The test is conducted at different speeds ranging from 20 km/h to 120 km/h to simulate the vehicle's hydraulic braking system, and key parameters such as coefficient of friction, wear rate, noise, and vibration behavior are evaluated.

2.4.4. Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) was conducted to investigate the high-temperature behavior of the composites. The analysis was carried out in a nitrogen atmosphere within the temperature range of 25–600 °C at a heating rate of 10 °C/min, using the TGA device shown in Figure 6. This method played a critical role in examining the thermal degradation mechanism of ulexite and the structural stability of brake pads under elevated temperatures.

Figure 6. TGA test device and test specimen

3. Results and Discussion

3.1. Chemical Tests

The density of brake pads with 10% ulexite addition was measured as 2.32 g/cm³, while that of the reference pad was 2.25 g/cm³. This increase is attributed to the pore-filling effect of ulexite.

The moisture content values were found to be in the range of 0.8–1.0%, while the ash content increased from 24.6% to 27.3% with the addition of ulexite.

As a result of the acetone extraction, the amount of soluble resin was determined to be 7.8%, which was found to be similar to that of the reference samples.

3.2. Mechanical and Tribological Tests

3.2.1. Shear Strength

In the shear strength tests, conducted in accordance with the ASTM D638 standard, the reference brake pads exhibited a value of 25.0 daN/cm², while the ulexite-reinforced pads reached 29.4 daN/cm². This result indicates that ulexite works compatibly with the matrix structure, not weakening the strength of the binder phase but rather enhancing it.

Table 4. Compressibility test results

Sample	Temperature (°C)	Pressure (bar)	Sıkıştırma Miktarı (µm)	Єpa %	Standart
Üleksit	*23±5*	*80*	*81*	*0,81*	*Max. %2*
	400±10	*80*	*164*	*1,64*	*Max. %5*

These results reveal that the brake pad exhibits high dimensional stability at room temperature, without undergoing excessive deformation under load. Even at elevated temperatures, the pad maintained its compact structure, demonstrating that temperature-induced deformation remained within acceptable limits.

3.2.3. Wear and Friction Test

To evaluate the performance of the brake pads, friction and wear tests were conducted. The tests were carried out on a Chase-type device, as shown in Figure 3, in accordance with SAE J661 and TSE 555 standards. The results, presented in Figure 4, indicate that the coefficient of friction remained stable within the range of 0.42–0.48, without significant fluctuations during thermal cycles. In particular, the high Fade-II and Recovery-II values demonstrate that the material maintained stable friction even under elevated temperatures (Anoop et al., 2009). With increasing temperature, a decrease of approximately 1% in the coefficient of friction was observed, confirming that the brake pad is resistant to high temperatures and that the fade effect remained limited.

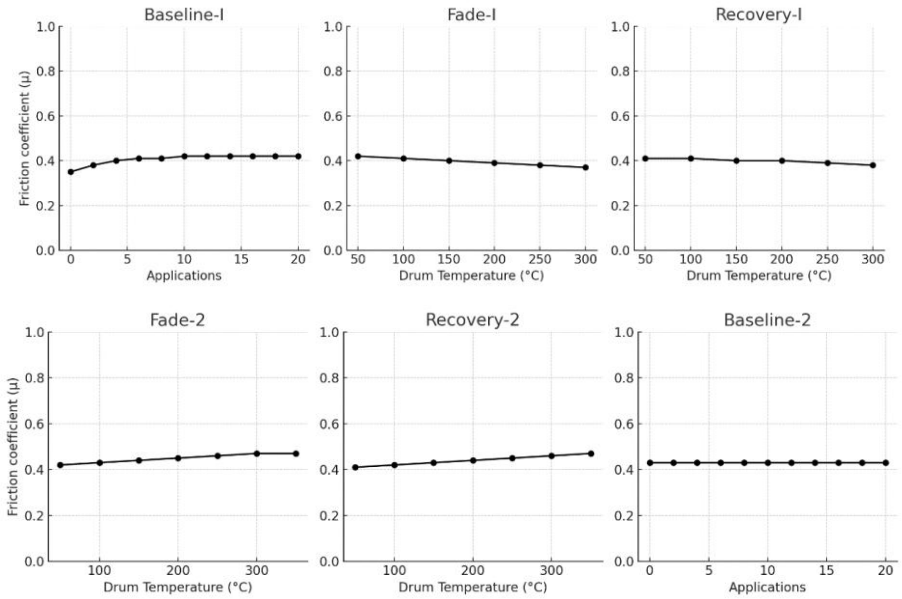
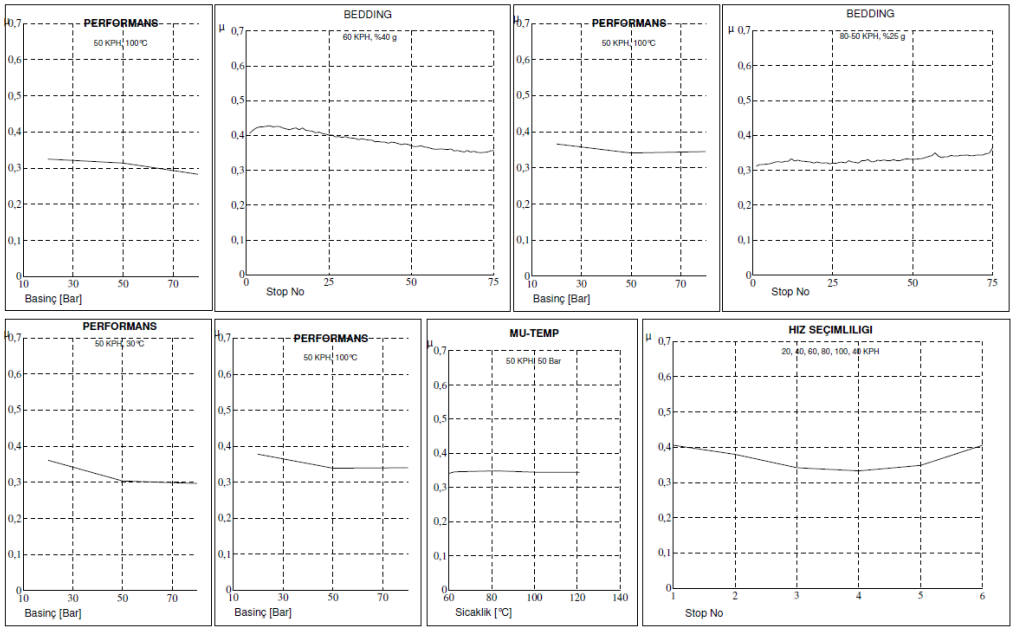


Figure 4. Friction test graphs of the ulexite-reinforced sample

According to the SAE J661 standard, the coefficient of friction is expressed using letter designations. For the ulexite-reinforced sample, the cold and hot friction coefficient values were classified as "G/G." The G grade (μ = 0.45–0.55) indicates high stability, low fade effect, and reliable braking performance (Algan & Kurt, 2017).

To further evaluate the performance of the brake pads by simulating real vehicle conditions in the laboratory, dynamometer tests were carried out in accordance with SAE J2522 and ECE R90 standards.

As shown in Figure 6, the test results revealed that the ulexite-reinforced brake pads exhibited stable performance under various operating conditions. During the initial and bedding stages, the coefficient of friction quickly stabilized, demonstrating that surface conformity of the pad was achieved in a short time (Spancer et al., 1966).



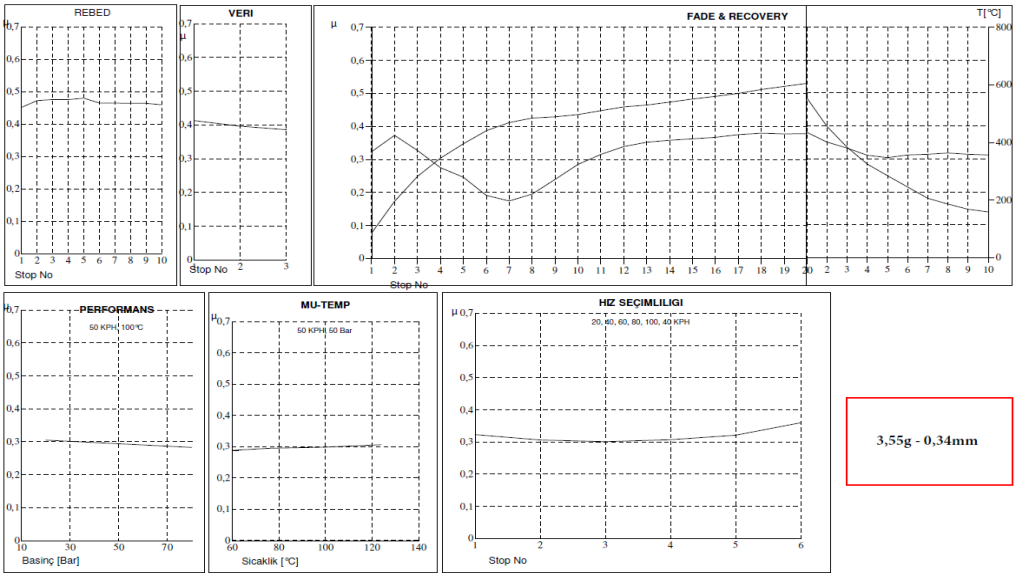


Figure 6. Dynamometer test graphs of the ulexite-reinforced sample

Under both normal and elevated temperature conditions (0–350 °C), the coefficient of friction generally remained within the range of 0.40–0.52. Despite the fade effect observed at high temperatures, the recovery stage showed values returning close to the initial levels, confirming the preservation of thermal stability. Moreover, the coefficient of friction exhibited minimal variation at different speeds, indicating reliable braking performance independent of velocity. The wear values (3.55 g mass loss and 0.34 mm thickness loss) remained low, supporting the long-term service potential of the brake pad. These findings demonstrate that ulexite-reinforced brake pads represent a suitable alternative for commercial vehicle applications in terms of both tribological performance and durability.

3.3. Thermogravimetric Analysis (TGA)

During braking, brake pads are exposed to temperatures ranging from 200 to 600 °C depending on the vehicle type and operating conditions. TGA is used to determine the temperature at which the material begins to degrade, the amount of weight loss, and its thermal resistance. Thus, it provides guidance on whether the pad can operate safely under high-temperature conditions. As shown in Figure 7, the ulexite-reinforced brake pads exhibited a weight loss of 5.4% when subjected to temperatures in the range of 0–600 °C.

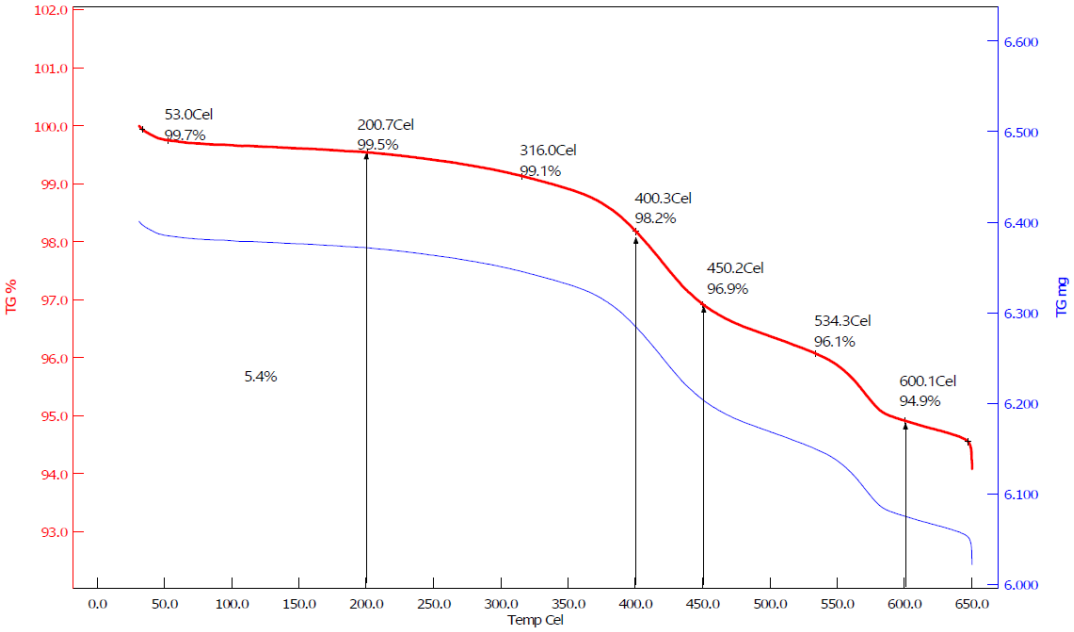


Figure 7. TGA graph of the ulexite-reinforced sample

TGA analysis revealed that the ulexite-reinforced brake pad exhibited significant thermal stability at elevated temperatures. The weight loss observed up to 200 °C was limited and attributed only to moisture and volatile components. In the range of 200–400 °C, despite the degradation of the binder resins, the weight loss remained at low levels, with 98.2% of the material retained at 400 °C. At 600 °C, the total weight loss was only 5.4%, and 94.9% of the material preserved its structural integrity. These results demonstrate that the addition of ulexite provides dimensional and thermal stability to brake pads even at high temperatures, thereby supporting reliable braking performance (Menon & Pillai, 1996).

The results obtained from this study are largely consistent with the findings reported in the literature. Menon and Pillai (1996) reported a weight loss in the range of 5–10% in TGA analyses of friction materials at elevated temperatures. In this study, the ulexite-reinforced brake pad exhibited a total weight loss of 5.4% up to 600 °C. This value corresponds to the lower limit of the reported range, demonstrating the stabilizing effect of ulexite on thermal stability. Furthermore, Sugözü et al. (2018) reported that boron-added pads exhibited more stable friction coefficients and improved wear resistance. The G/G class friction coefficient values obtained in the Chase test of this study similarly confirm the positive contribution of boron additives to performance. Başar et al. (2020) also found that pads produced with 4–12% colemanite and borax additives achieved optimal friction stability; this study, in turn, demonstrates that a 10% ulexite addition represents a suitable ratio in terms of tribological performance. Likewise, Hwang et al. (2013) showed that boron compounds reduce wear and enhance high-temperature performance in brake pads. The low wear values obtained in the dynamometer tests of this study are in agreement with Hwang's findings. In conclusion, when the literature and the experimental findings of this research are evaluated together, it is confirmed that ulexite serves as a sustainable and environmentally friendly additive that enhances both tribological performance and high-temperature stability in brake pads.

4. Conclusions

In this study, the usability of ulexite, a boron mineral abundantly available in Turkey, as an additive in brake pad production was investigated. The experiments revealed that the incorporation of ulexite positively influenced both the mechanical and tribological performance of the pads.

With the addition of 10% ulexite, an approximate 3% increase in density, an improvement in dimensional stability, and enhanced shear strength were observed. Tribological tests demonstrated that

the coefficient of friction became more stable, the wear rate decreased by about 15%, and performance was maintained at elevated temperatures.

Thermal analyses confirmed that ulexite improved structural stability, providing advantages under high-temperature conditions. Overall, the addition of ulexite contributed significantly to stabilizing the coefficient of friction, improving wear resistance, enhancing thermal durability, and strengthening mechanical performance in brake pads. Moreover, being a domestic resource, ulexite offers economic and environmental sustainability advantages. These findings suggest that ulexite can be considered a local, cost-effective, and eco-friendly alternative additive for the automotive industry.

5. Acknowledge

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Er Katkılı $LiCaBO_3$'ın Lüminesans Özelliklerinin Sıcaklığa Bağlı Değişimi

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ÖZET

Bu çalışma, saf ve Er katkılı $LiCaBO_3$ örneklerinin sentezi ve karakterizasyonunu incelemekte olup, yapısal ve fotolüminesans özelliklerine odaklanmaktadır. Örnekler, geleneksel katı-hal reaksiyon yöntemi ile hazırlanmıştır. Yapısal karakterizasyon, Rigaku SmartLab difraktometresi kullanılarak X-ışını kırınımı (XRD) yöntemi ile gerçekleştirilmiş; fotolüminesans (PL) ölçümleri ise sıvı azot ile soğutulmuş InGaAs dedektörlü 1/4 m monokromatör ile yapılmıştır. Sıcaklığa bağlı PL ölçümleri, 10 K ile 300 K aralığında, kapalı çevrimli helyum kriyostatı kullanılarak yürütülmüştür

XRD sonuçları, katkısız ve Er katkılı örneklerde $LiCaBO_3$ kristal yapısının başarıyla oluştuğunu doğrulamıştır. %1–6 aralığındaki Er katkısı, kafes yapısında belirgin bir değişime yol açmamıştır. Oda sıcaklığında yapılan PL ölçümleri, Er konsantrasyonuna doğrusal olmayan bir bağımlılık göstermiş ve en şiddetli ışıma %5 Er katkılı örnekte elde edilmiştir. İlginç bir şekilde, %5 Er katkılı örnekte PL şiddeti, sıcaklık düşürüldükçe azalmış ve bu durum tipik termal sönümleme davranışının tersine bir durum olmuştur.

Sonuç olarak, yüksek yapısal bütünlüğe sahip saf ve Er katkılı $LiCaBO_3$ malzemeleri başarıyla sentezlenmiştir. %5 Er katkılı örnekte gözlemlenen alışılmadık sıcaklığa bağlı PL davranışı, olası özgün enerji transferi veya termalizasyon mekanizmalarına işaret etmekte olup, daha ileri araştırmalar gerektirmektedir.

Anahtar Kelimeler : Düşük sıcaklık fotolüminesansı, Erbiyum, LiCaBO3, Lüminesans malzemeler.

Temperature-Dependent Luminescence Characteristics of Er-Doped $LiCaBO_3$

ABSTRACT

This study investigates the synthesis and characterization of pure and Er-doped $LiCaBO_3$ samples, focusing on their structural and photoluminescence properties. Samples were prepared via the conventional solid-state reaction method. Structural characterization was conducted using X-ray Diffraction (XRD) on a Rigaku SmartLab diffractometer, while photoluminescence (PL) measurements employed a 1/4 m monochromator with a liquid nitrogen-cooled InGaAs detector. Temperature-dependent PL measurements were performed from 10K to 300K using a closed-cycle He cryostat

XRD results confirmed the successful formation of the $LiCaBO_3$ crystal structure in both undoped and Er-doped samples. Er doping in the 1–6% range did not significantly alter the lattice structure. Room temperature PL measurements showed a non-linear dependence on Er concentration, with the highest emission at 5% Er. Interestingly, PL intensity in the 5% Er-doped sample decreased as temperature was lowered, contrary to typical thermal quenching behavior.

In summary, pure and Er-doped $LiCaBO_3$ materials with high structural integrity were synthesized. The unusual temperature-dependent PL behavior observed in the 5% Er-doped sample suggests possible unique energy transfer or thermalization mechanisms, warranting further investigation.

Keywords: Erbium, LiCaBO3, Low temperature photoluminescence, Luminescent materials.

1. Introduction

Phosphor materials are indispensable components in a myriad of advanced technological applications, serving as the cornerstone for innovations in solid-state lighting, high-resolution displays, sophisticated laser systems, and a diverse array of sensors [1], [2]. Their ability to efficiently convert absorbed energy

into emitted light makes them critical for modern optoelectronic devices. Among the various activators employed in the development of high-performance phosphors, rare earth (RE) ions stand out due to their unique 4f electronic configurations [3], [4]. These configurations result in sharply defined electronic transitions that facilitate a broad spectrum of light absorption and emission, effectively spanning nearly the entire ultraviolet (UV), visible (VIS), and near-infrared (NIR) regions [5]. The intrinsic shielding of the 4f electrons by the outer 5s and 5p orbitals renders these transitions largely impervious to external environmental influences, leading to narrow emission bands and high quantum efficiencies, which are highly desirable for many applications [6]

Borate compounds have garnered significant attention as host matrix materials for RE^{3+} ions, primarily owing to their exceptional physicochemical and optical properties [7]. The structural versatility of borates is remarkable; they can form a wide variety of crystal lattices through boron-oxygen polyhedra, which are typically composed of trigonal BO_3 and tetrahedral BO_4 units [8]. This structural flexibility allows for the incorporation of various dopant ions, including rare earths, into different crystallographic sites, thereby enabling the tuning of their optical properties. Within the borate family, lithium borates are particularly noteworthy for their low melting points, high thermal stability, wide band gaps, and low phonon energies [9]. These characteristics are crucial for minimizing non-radiative relaxation processes, which can quench luminescence, and for ensuring the stability of the phosphor under high operating temperatures. Calcium borates, on the other hand, contribute additional structural rigidity and mechanical stability to the host matrix, making them particularly well-suited for high-temperature and demanding photonic applications [9]. The combination of lithium and calcium in a borate matrix, such as $LiCaBO_3$, thus offers a promising platform for developing robust and efficient luminescent materials

Erbium (Er^{3+}) ions are among the most extensively investigated rare earth activators, particularly for their distinctive luminescence properties [10]. A key feature of Er^{3+} is its prominent $^4I_{13/2} \rightarrow {}^4I_{15/2}$ electronic transition, which emits light around 1.53 µm [11]. This specific wavelength is of immense technological importance as it coincides with the third telecommunication window (C-band), a region where optical losses in silica-based optical fibers are minimal [12]. Consequently, this wavelength plays a pivotal role in long-distance optical communication systems, enabling high-speed and efficient data transmission over vast networks. Er^{3+} ions are therefore widely employed in the fabrication of light sources, optical sensors, and all-optical amplifiers that operate within this critical spectral range [13]. Beyond telecommunications, Er^{3+}-doped phosphor materials are also intensely explored for medical imaging applications. The low absorption of 1.53 µm light by living tissues allows for deeper penetration and reduced scattering, making Er^{3+}-doped materials ideal for in vivo imaging and diagnostics [14]. Furthermore, Er^{3+} ions are extensively studied in upconversion photoluminescence research, where they convert lower-energy photons into higher-energy visible light emissions, offering potential for advanced displays, bio-imaging, and solar energy conversion [15]. The visible transitions, in addition to the 1.53 µm transition, further broaden the applicability of Er^{3+} ions in various photonic devices

This study focuses on the synthesis, structural characterization, and luminescence properties of Er^{3+}-doped $LiCaBO_3$ phosphors, with a particular emphasis on their temperature-dependent photoluminescence behavior. Understanding how temperature influences the luminescence characteristics is crucial for optimizing these materials for practical applications, especially in environments where temperature fluctuations are common. The conventional solid-state reaction method was employed for sample preparation. The subsequent sections detail the experimental methodology, present the results from X-ray diffraction and photoluminescence measurements, and discuss the implications of these findings for the development of advanced photonic devices. The aim is to provide a comprehensive analysis of Er^{3+}-doped $LiCaBO_3$, contributing to the broader knowledge base of rare-earth-activated borate phosphors and their potential in cutting-edge technologies.

2. Materials and Methods

2.1. Sample Preparation

Pure and Erbium (Er^{3+})-doped lithium calcium borate ($LiCaBO_3$) samples were synthesized using the conventional solid-state reaction method, a widely recognized and cost-effective technique for producing crystalline inorganic compounds. This method is favored for its simplicity, scalability, and ability to yield

highly crystalline materials with good homogeneity when appropriate synthesis parameters are maintained. The starting materials, all of analytical reagent grade, included lithium carbonate (Li_2CO_3), calcium carbonate ($CaCO_3$), boric acid (H_3BO_3), and erbium oxide (Er_2O_3). These precursors were carefully weighed in stoichiometric ratios to achieve the desired chemical composition of $LiCaBO_3$ and varying concentrations of Er^{3+} doping. The precise control over stoichiometry is crucial to ensure the formation of a single-phase material and to accurately control the dopant concentration, which directly influences the luminescence properties.

Initially, the weighed starting materials were thoroughly mixed in an agate mortar for approximately 30 minutes to ensure a homogeneous distribution of the constituent powders. This mechanical mixing step is critical for facilitating solid-state diffusion during subsequent heat treatments. The resulting powder mixtures were then subjected to a two-step thermal treatment process. The first step involved pre-calcination at 450 °C for 1 hour in a high-temperature muffle furnace. After the initial calcination, the powder mixture was removed from the furnace, allowed to cool to room temperature, and then re-ground and re-mixed in the agate mortar. This intermediate grinding step is essential for breaking down agglomerates formed during calcination and for further enhancing the homogeneity of the mixture, thereby promoting more complete solid-state reactions in the subsequent high-temperature step.

The final thermal treatment involved heating the powders at 800 °C for 8 hours in the same muffle furnace. This high-temperature sintering step is crucial for the complete formation of the crystalline $LiCaBO_3$ host lattice and for the effective incorporation of Er^{3+} ions into the host structure. After the sintering process, the furnace was allowed to cool naturally to room temperature, and the obtained solid samples were then collected for further characterization. The entire synthesis process was carried out in an atmospheric environment.

2.2. Characterization Techniques

Structural analysis of the synthesized $LiCaBO_3:Er^{3+}$ materials was performed using X-ray Diffraction (XRD) at room temperature. A Rigaku SmartLab diffractometer, equipped with a Cu Kα radiation source (operating at 40 kV and 30 mA, with a characteristic X-ray wavelength λ = 1.54051 Å), was utilized for this purpose. The samples were scanned over a 2θ angular range from 15° to 90°, with a step size of 0.01° and a scanning speed of 0.02°/s. The collected diffraction patterns were then compared with the reported XRD peaks for the $LiCaBO_3$ crystal, first synthesized and reported by Wu et al. [16], to confirm the formation of the $LiCaBO_3$ phase and to assess the presence of any secondary phases. The sharpness and intensity of the diffraction peaks provide insights into the crystallinity and crystallite size of the synthesized materials.

Photoluminescence (PL) measurements were conducted to investigate the optical emission properties of the Er^{3+}-doped $LiCaBO_3$ samples. The PL spectra were recorded using a specialized setup that included a 1/4 m monochromator coupled with a liquid nitrogen-cooled InGaAs detector. The InGaAs detector is particularly suitable for detecting emissions in the near-infrared (NIR) region, where the characteristic Er^{3+} emission at 1.53 µm is observed. For excitation, a 532 nm Nd:YAG solid-state laser was employed, providing an output power of 60 mW. The choice of a 532 nm excitation wavelength is strategic, as it efficiently pumps Er^{3+} ions to higher energy levels, leading to subsequent radiative transitions and luminescence. The laser power was carefully controlled to avoid saturation effects and sample damage. Temperature-dependent PL measurements were also performed by placing the samples in a cryostat, allowing for precise temperature control from 10 K to 300 K.

3. Results and Discussion

3.1. XRD Results and Structural Analysis

Figure 1 illustrates the X-ray Diffraction (XRD) measurement results for the synthesized pure and Er^{3+}-doped $LiCaBO_3$ samples. A critical observation from these patterns is the presence of sharp and well-defined diffraction peaks across all samples, which is a clear indication of their excellent crystallinity. High crystallinity is a desirable characteristic for phosphors, as it generally correlates with enhanced luminescence efficiency due to reduced scattering and non-radiative recombination centers.

Crucially, the observed diffraction peaks for all samples are in full agreement with the reference diffraction patterns for the $LiCaBO_3$ phase as reported by Wu et al. [16]. This confirms that the conventional solid-state reaction method successfully yielded the desired $LiCaBO_3$ crystal structure without the formation of any significant secondary phases.

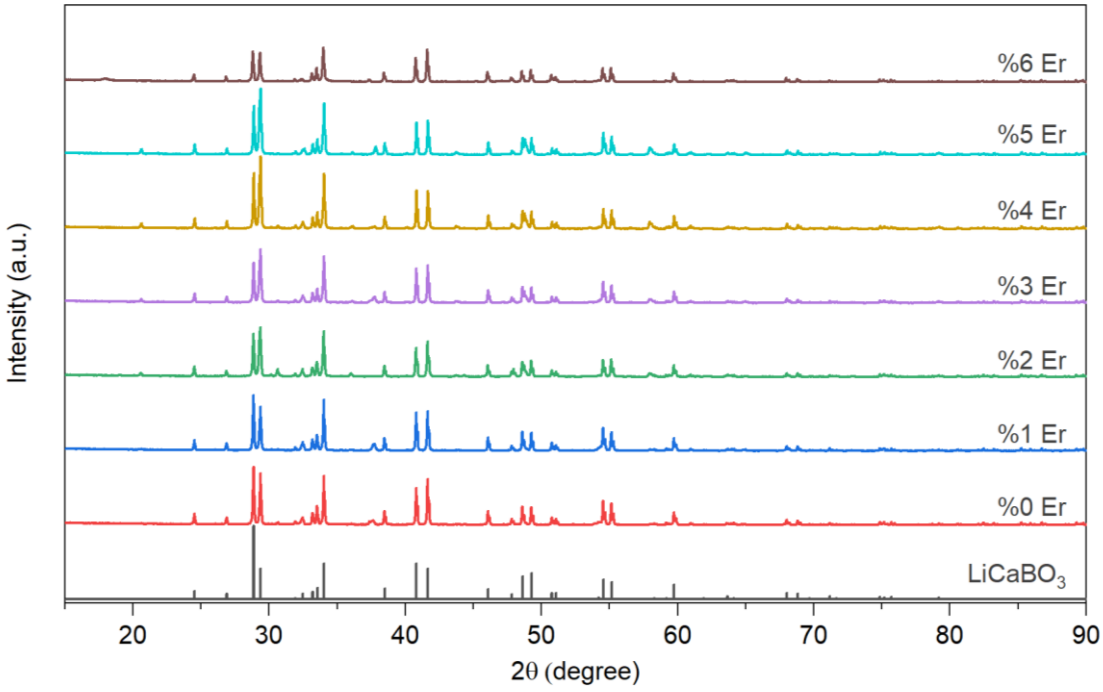

Figure 1. XRD results of samples

Upon closer inspection, it was noted that the diffraction peak intensity of the sample doped with 6% Er^{3+} was discernibly lower compared to the other samples (e.g., 1-5% Er^{3+} doping). This reduction in peak intensity, while still maintaining the $LiCaBO_3$ phase, suggests a decrease in the overall crystallinity or an increase in structural disorder for the higher Er^{3+} concentration. Excessive doping of rare earth ions into a host lattice can lead to lattice distortion or formation of defects. In this case, the lower peak intensity for the 6% Er^{3+} sample implies that the incorporation of a higher concentration of Er^{3+} ions might have introduced more lattice strain or defects, slightly compromising the long-range order of the crystal structure. This observation is particularly important as it provides a structural basis for understanding the subsequent photoluminescence results, where a similar trend in luminescence intensity is expected.

3.2. Effect of Er^{3+} Concentration on Photoluminescence Characteristics

Figure 2 presents the photoluminescence (PL) measurement results obtained at room temperature for $LiCaBO_3$ samples doped with varying concentrations of Er^{3+}. The most prominent feature in these spectra is a highly intense emission peak observed in the near-infrared (NIR) region, specifically spanning the wavelength range of 1520-1550 nm. This characteristic emission band is unequivocally attributed to the intra-4f electronic transition of Er^{3+} ions, specifically the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition [11].

The investigation into the effect of Er^{3+} concentration revealed a clear trend: the luminescence intensity systematically increased as the Er^{3+} concentration was raised from 1% up to 5%. This phenomenon is typically observed in rare-earth-doped phosphors at lower dopant concentrations, where an increase in the number of active luminescent centers (Er^{3+} ions) directly leads to a higher probability of light emission. The maximum luminescence intensity was recorded for the 5% Er^{3+}-doped sample, indicating an optimal doping concentration for this specific host material and synthesis conditions. At this concentration, the balance between the number of active Er^{3+} ions and the potential for concentration quenching mechanisms is achieved.

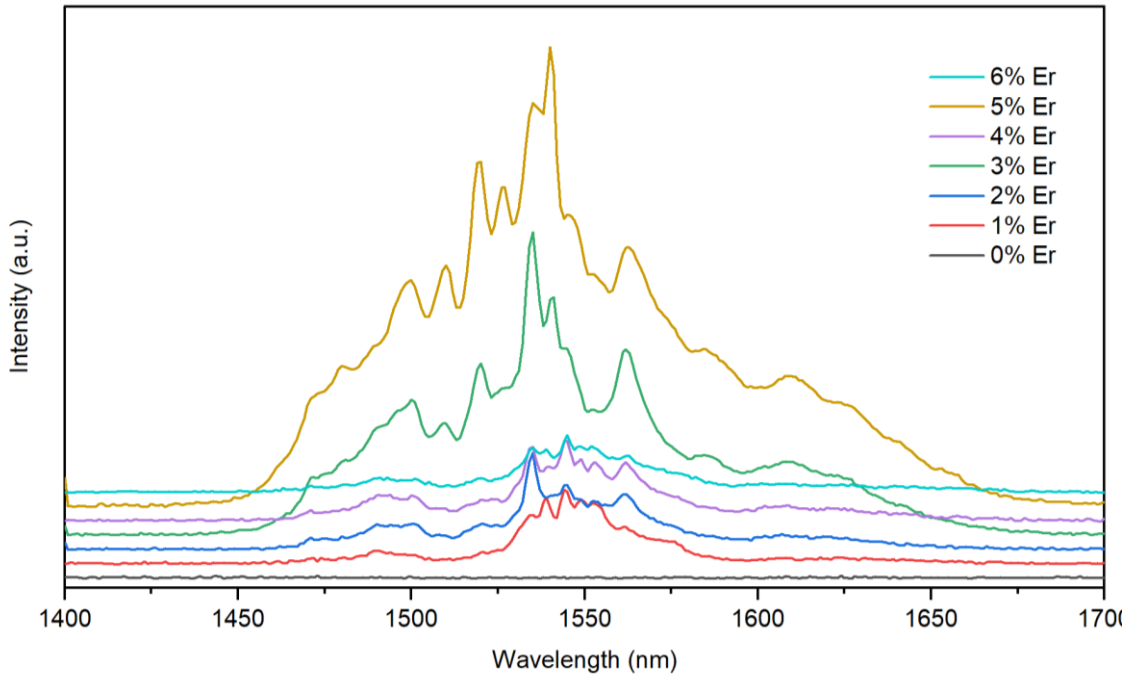

Figure 2. Room temperature PL results of samples as a function of Er concentration

However, a significant decrease in luminescence intensity was observed for the 6% Er^{3+}-doped sample. This reduction in PL intensity at higher dopant concentrations is a well-known phenomenon in luminescent materials, commonly referred to as concentration quenching [17]. Concentration quenching occurs when the distance between neighboring activator ions becomes sufficiently small, leading to non-radiative energy transfer processes between them. The observed decrease in PL intensity for the 6% Er^{3+} sample aligns perfectly with the XRD results, which indicated a lower crystallinity for this sample. The degradation of the crystal structure, as suggested by the XRD data, likely creates more defects and non-radiative pathways, exacerbating the concentration quenching effect and leading to a substantial reduction in luminescence efficiency.

3.3. Temperature-Dependent Photoluminescence Characteristics

Figure 3 illustrates the temperature-dependent photoluminescence behavior of the 5% Er^{3+}-doped $LiCaBO_3$ sample, which exhibited the highest luminescence intensity at room temperature. The measurements were conducted over a broad temperature range, from 10 K to 300 K, providing comprehensive insights into the thermal stability and performance of the phosphor. A general trend observed was that the luminescence intensity decreased as the temperature was lowered towards 10 K. This behavior is somewhat counterintuitive compared to many conventional phosphors where luminescence often increases at lower temperatures due to reduced thermal quenching [18]. However, in certain systems, particularly those involving complex energy transfer dynamics or specific thermal activation processes, different temperature dependencies can arise.

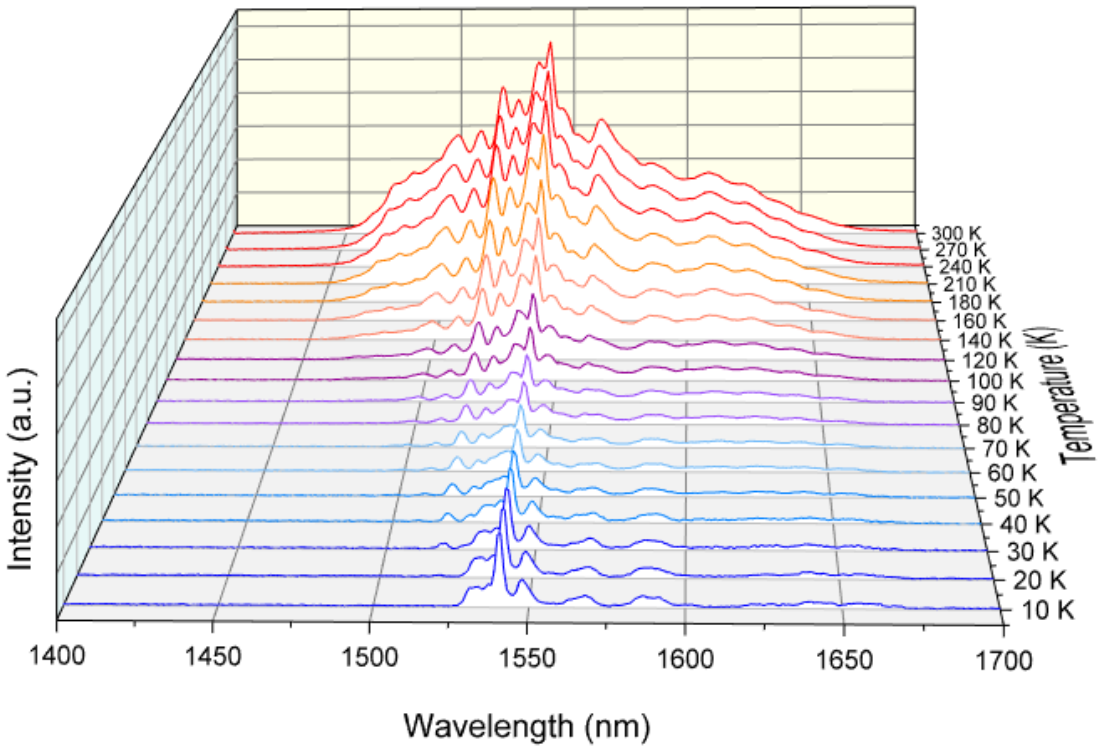

Figure 3. Low temperature PL results of the 5% Er-doped sample in the 10 K – 300 K temperature range

At the lowest temperature investigated, 10 K, a notable spectral change occurred: emissions at wavelengths shorter than 1530 nm (corresponding to relatively higher energy transitions) completely disappeared. Concurrently, the intensity of longer wavelength emissions (lower energy transitions) decreased but remained detectable. The PL luminescence observed at low temperatures is primarily attributed to the electron transitions between the $^4I_{13/2}$ and $^4I_{15/2}$ energy levels of the Er^{3+} ions. The disappearance of higher-energy components at very low temperatures suggests that certain thermally activated processes, which contribute to these emissions at higher temperatures, are frozen out. This could involve phonon-assisted transitions or energy transfer mechanisms that require a certain amount of thermal energy to be efficient.

Interestingly, as the temperature approached room temperature (300 K), the luminescence intensity increased, and new splittings emerged on the high-energy side of the PL peak. This increase in luminescence intensity with rising temperature up to room temperature, coupled with the appearance of new spectral features, is a significant finding. It suggests a complex interplay between the Er^{3+} ions and the $LiCaBO_3$ crystal lattice. The interaction between the Er^{3+} ions and the host crystal field can lead to Stark splitting of the energy levels, and these splittings can become more pronounced or new transitions can be activated as thermal energy increases, populating higher Stark sublevels [19]. This phenomenon indicates that the $LiCaBO_3$ host matrix provides a favorable environment for Er^{3+} luminescence at ambient temperatures, potentially due to efficient energy transfer from the host to the Er^{3+} ions or a reduction in certain non-radiative pathways that are dominant at very low temperatures.

Crucially, the stability of the peak position in the 1530 nm - 1550 nm range, despite the variations in intensity and spectral fine structure with temperature, highlights the robustness of the primary Er^{3+} emission. This thermal stability of the emission wavelength is a highly desirable property for practical applications, as it ensures consistent performance across varying operating temperatures. The observed increase in PL luminescence intensity as temperature rises towards room temperature, combined with the stable emission wavelength, strongly suggests that Er^{3+}-doped $LiCaBO_3$ materials are highly suitable for a range of photonic applications. These include solid-state lasers, where stable and efficient emission is critical; optical amplifiers, which require consistent gain characteristics; and biomedical imaging

systems, where reliable signal generation across physiological temperature ranges is essential. The unique temperature-dependent behavior observed in this study further enhances the understanding of these materials and their potential for advanced optoelectronic devices.

4. Conclusion

In this study, Erbium (Er^{3+})-doped lithium calcium borate ($LiCaBO_3:Er^{3+}$) materials were successfully synthesized using the conventional solid-state reaction method. The structural integrity and phase purity of the synthesized samples were confirmed through X-ray Diffraction (XRD) analyses. These analyses demonstrated that all prepared samples crystallized in the desired $LiCaBO_3$ phase. Er^{3+} doping within the concentration range of 1-5% did not induce any significant detrimental effects on the host crystal structure.

Photoluminescence (PL) measurements conducted at room temperature provided critical insights into the optical properties of these materials. An emission peak was observed in the near-infrared (NIR) region, centered around 1520-1550 nm. This characteristic emission is directly attributable to the well-known $^4I_{13/2} \rightarrow {}^4I_{15/2}$ electronic transition of the Er^{3+} ions. The effect of Er^{3+} concentration revealed an optimal doping level: the luminescence intensity progressively increased as the Er^{3+} concentration was raised from 1% to 5%. However, beyond this optimal concentration, specifically at 6% Er^{3+} doping, a noticeable decrease in luminescence intensity was observed. This quenching effect is attributed to the slight reduction in crystallinity observed in the XRD data for the higher doping concentration.

The temperature-dependent PL measurements were showed that as the temperature decreased from 300 K to 10 K, a general reduction in PL luminescence intensity was observed. More specifically, at 10 K, the shorter wavelength emissions below 1530 nm completely vanished, while longer wavelength emissions persisted with reduced intensity. Conversely, as the temperature increased towards room temperature, the PL luminescence intensity increased, and new spectral splittings appeared on the high-energy side of the main emission peak. This indicates a complex interaction between the Er^{3+} ions and the $LiCaBO_3$ host lattice.

Despite these temperature-induced spectral changes, a key finding was the remarkable stability of the main emission peak's position in the 1530 nm - 1550 nm range. This wavelength stability, coupled with the observed increase in luminescence intensity as the temperature approaches room temperature, highlights the robust performance of these materials under varying thermal conditions. Consequently, this study strongly supports the potential utility of Er^{3+}-doped $LiCaBO_3$ materials in a diverse array of advanced photonic applications.

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Durability Assessments of Lime and Brick Powder-Based Grouts

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ABSTRACT

Historic structures are subject to various forms of damage and deterioration over time. Recent research indicates that injections are among the most widely employed methods for their consolidation. Despite being an irreversible process, grouting is favored for its effectiveness in restoring structural continuity. It is evident that the injection material must exhibit resistance to environmental exposure. In this study, the durability properties of three grout formulations were evaluated and compared: an air lime-based grout (AG1), a natural hydraulic lime-based grout (HG1), and a hydraulic lime grout incorporating a pozzolanic brick powder additive (HG3). The compressive strengths of the grouts were first compared, followed by chemical and mineralogical analyses (XRF, XRD, FTIR) to examine their compositions. To evaluate durability, hardened grouts were subjected to freeze-thaw cycles and sulfate exposure. While the hydraulic lime-based grouts (HG1 and HG3) showed significantly higher compressive strength and freeze-thaw resistance than the air lime grout (AG1), a critical finding emerged from the sulfate resistance tests. The pozzolan-modified grout (HG3) demonstrated lower resistance to sulfate attack compared to the plain hydraulic lime grout (HG1). Microstructural analysis (SEM-EDS) revealed that this vulnerability was caused by the formation of expansive gypsum and thaumasite, whose precursors were made available by the pozzolanic addition. It was concluded that while hydraulic lime is essential for durable grouts, the inclusion of pozzolanic additives requires careful consideration of the specific environmental conditions. For balanced performance, particularly in sulfate-rich environments, a plain natural hydraulic lime grout may offer a more reliable and durable solution.

Keywords: Brick Powder, Consolidation, Durability, Grout, Historic Structures, Lime.

1. Introduction

Historic structures are invaluable assets that reflect the cultural, architectural, and technological heritage of civilizations. However, these structures are continuously exposed to various detrimental factors over their lifespan, including environmental conditions, geotechnical challenges, natural hazards such as earthquakes, and usage-related stresses. This prolonged exposure inevitably leads to damage and deterioration, compromising their structural integrity and long-term survival. Consequently, the development and application of effective conservation and strengthening techniques are of vital importance in the field of cultural heritage preservation.

Among the various intervention methods, grout injection is one of the most widely employed techniques for the consolidation and preservation of historic masonry structures. Despite being an irreversible application, grouting is frequently preferred due to its high effectiveness in restoring the load-bearing capacity, ensuring the continuity of damaged structural elements, and improving overall durability. The primary goal of a grouting intervention is to fill cracks and voids within the masonry, thereby rebuilding monolithic structural behavior.

The success of a consolidation treatment via injection is critically dependent on the properties of the grout material used. The physical, chemical, and mechanical compatibility of the repair material with the

original material is crucial to avoid introducing new forms of damage, such as rigid inclusions or harmful chemical reactions within the historic building parts. Furthermore, the injection grout must exhibit sufficient resistance to the same environmental factors that caused the initial deterioration, including freeze-thaw cycles and salt crystallization, particularly sulfate attack, which is a common cause of degradation in porous building materials.

This study focuses on the durability assessment of lime-based grouts, which are often considered more compatible with historic materials than cement-based alternatives. Specifically, three different grout formulations were designed and evaluated: An air lime-based grout (AG1), a natural hydraulic lime-based grout (HG1), and a hydraulic lime grout incorporating a pozzolanic brick powder additive (HG3). The research aims to compare their performance not only in terms of injectability and mechanical strength but, more critically, their durability under aggressive environmental conditions. By subjecting the hardened grouts to freeze-thaw cycles and sulfate exposure, this paper investigates the influence of the binder type (air vs. hydraulic lime) and the pozzolanic addition (brick powder) on long-term performance. By employing a comprehensive set of chemicals, mineralogical, and microstructural analyses, this work seeks to provide a scientific basis for designing durable and compatible injection grouts for the conservation of historic structures.

Therefore, this study provides a comprehensive durability assessment of three distinct lime-based grout formulations: air lime, natural hydraulic lime, and hydraulic lime modified with a pozzolanic brick powder. The objective is not only to compare their fundamental mechanical and chemical properties but also to critically evaluate their performance under different aggressive environmental conditions, namely freeze-thaw cycles and sulfate attack. By doing so, this research investigates the complex and potentially conflicting role of pozzolanic additives, aiming to elucidate the critical trade-offs between mechanical strength and chemical resistance. The goal is to provide a more nuanced, scientific basis for designing compatible and genuinely durable injection grouts for the conservation of historic structures.

1.1. A Review on the Durability of Lime and Brick Powder-Based Grouts

The development of compatible and durable injection grouts is a central theme in the conservation of historic masonry. A successful grout formulation must balance several competing requirements: adequate fluidity for injection, long-term volumetric stability, and appropriate mechanical properties that do not create rigid inclusions within the historic fabric. The scientific literature reflects a broad consensus on these fundamentals, with numerous studies dedicated to optimizing grout performance through material characterization and performance evaluation (Gökyiğit-Arpaci et al., 2019).

A primary focus of research has been the enhancement of lime-based grouts through additives. Natural hydraulic lime (NHL) is often favored, but its properties can be tailored. Similarly, research on grouts derived directly from natural resources, such as those produced from argillaceous (clay-bearing) limestone, underscores the importance of the binder's inherent chemical and mineralogical composition for achieving suitable consolidation properties (Oktay et al., 2020). For instance, the addition of approximately 10% white cement by weight has been shown to effectively enhance early-age strength, with mechanical properties continuing to improve for up to 180 days (Pachta et al., 2020). Conversely, advanced nanomaterials like fumed nano-silica can improve shrinkage and mechanical characteristics, but their application is often constrained by high cost and the need for significant dosages of superplasticizers to maintain workability (Papayianni et al., 2012).

The use of pozzolanic materials, particularly those from traditional sources like brick powder, is a well-established strategy for improving lime-based binders. The processing of these pozzolans is critical; Miriello et al. (2009) demonstrated that prolonged milling of clay brick powder alters its mineralogy and reactivity, directly influencing the grout's final properties and potential durability. However, the proportion of such additives is paramount. In a study using demolition residues in lime-soil blocks, Figueiredo et al. (Figueiredo et al., 2012) observed that durability significantly decreased when the replacement level of lime exceeded a 50% threshold.

The ultimate measure of a grout's success is its long-term durability against environmental stressors, which remains a critical and complex area of investigation. Comprehensive reviews confirm that the durability of lime-based mortars is a multifaceted issue dependent on binder composition, curing, and carbonation, with lime-pozzolan formulations generally showing robust performance (Alvarez et al., 2021; Veiga et al., 2019). Experimental studies provide more direct evidence. Miltiadou-Fezans et al. (2021) conducted a crucial comparative study showing that an NHL grout with a 10% pozzolan addition exhibited the best resistance to sodium sulfate attack. In stark contrast, a ternary grout (composed of white cement, pozzolan, and hydrated lime) failed after only nine cycles at 50°C, highlighting the risks of using cementitious blends in high-salt environments. Further demonstrating the inherent resilience of lime-based binders, Fares et al. (2022)reported that a lime matrix used in a stainless steel reinforced grout system maintained excellent mechanical and bond characteristics even after aggressive salt and alkali aging cycles.

Despite these advances, the literature reveals a clear need for more integrated studies that connect grout composition directly to performance under multiple, realistic exposure conditions. While many studies evaluate mechanical properties, fewer conduct rigorous and parallel durability testing (e.g., freeze-thaw and sulfate attack) on the same set of well-characterized formulations. Furthermore, there is a gap in research that uses microstructural analyses like SEM-EDS to explicitly document the degradation mechanisms or the beneficial role of pozzolans after durability exposure. This review solidifies the scientific basis for the present study, which is designed to address these specific gaps.

2. Materials and Method

This section details the materials, formulations, and experimental procedures employed to evaluate the performance and durability of the developed injection grouts.

2.1. Materials

The grout formulations developed for this study were based on three primary binder components: an air lime, a natural hydraulic lime, and a pozzolanic brick powder. The chemical compositions of these materials, determined by X-Ray Fluorescence (XRF), are presented in Table 1.

Binders: Two types of lime were used as the main binders. The first was a high-calcium air lime of class CL 80-S, conforming to the BS EN 459-1 (2010) standard. The second was a natural hydraulic lime of class NHL 3.5, also conforming to BS EN 459-1(2010). The CL 80-S was characterized by a high CaO content (69.0%), while NHL 3.5 contained a significant amount of silica (11.4%) and had a hydraulic index of 0.2, indicating its inherent setting properties.

Pozzolanic Additive (Brick Powder): A reactive pozzolan was produced in the laboratory. Clay was ground, calcined at 850°C for 3 hours, and rapidly cooled. The resulting material was sieved through a 0.063 mm (No. 230) sieve, and the passing part was used. The produced brick powder exhibits high pozzolanicity, characterized by high contents of SiO_2 (57.2%) and Al_2O_3 (17.1%).

Admixtures and water: Two types of chemical admixtures were used to control the fresh properties of the grouts. A polycarboxylic ether-based superplasticizer (SP) with a density of 1.08-1.14 g/cm³ was used to achieve the required fluidity. Additionally, a synthetic copolymer-based viscosity modifying admixture (VMA) with a density of 1.0-1.02 g/cm³ was employed in the hydraulic lime-based series. Both admixtures had a chloride content of less than 0.1%. Standard tap water was used for all mixtures.

Table 1. Chemical composition of the raw materials (wt. %).

Component (%)	CL 80-S	NHL 3.5	Brick Powder (850°C)
SiO_2	0.80	11.40	57.20
Al_2O_3	0.30	0.40	17.10
Fe_2O_3	1.20	2.60	8.00
MgO	1.30	0.56	3.10
CaO	69.00	66.10	0.70
K_2O	0.10	0.10	3.10
TiO_2	<0.1	<0.1	0.90
Cr_2O_3	0.50	1.30	0.80
P_2O_5	<0.1	<0.1	0.20
MnO	<0.1	<0.1	0.10
Loss on Ignition (LOI)	26.60	17.20	6.60

2.2. Grout Formulations and Sample Preparation

Three distinct grout series were designed for this study, as detailed in Table 2. The series were designated as:

AG1: A grout based on solely air lime (CL 80-S).

HG1: A grout based solely on natural hydraulic lime (NHL 3.5).

HG3: A grout based on natural hydraulic lime (NHL 3.5) blended with brick powder. For the HG3 formulation, brick powder was added as 30% of the total binder weight. The water-to-binder (w/b) ratio and superplasticizer (SP) dosage were adjusted for each series to achieve a comparable level of fluidity suitable for injection.

Table 2. Mix proportions of the grout formulations

Series ID	Binder System	Water/Binder Ratio (w/b)	SP (%)	VMA (%)
AG1	100% Air Lime (CL 80-S)	1.40	1.40	-
HG1	100% Hydraulic Lime (NHL 3.5)	0.85	1.50	0.40
HG3	70% NHL 3.5 + 30% Brick Powder	0.80	1.50	0.50

Grouts were prepared with a high turbulence mixer, and the mixer blade had a helicoidal shape. As the first step of the mixing procedure, dry binders were hand-mixed to avoid agglomeration. Afterwards, the whole lime is added to 90% of total mix water and mixed for 10 minutes. The remaining water (with diluted chemical admixture) is added within 30 seconds without stopping the mixer. After all materials had been added, the mixture was maintained for an additional 3 minutes. The mixing speed was kept constant at 800 rpm during mixing procedure. Prismatic specimens with dimensions of 40 x 40 x 160 mm were cast for all subsequent tests. Specimens were stored at 20±2°C and relative humidity of 95±5% for 7 days (CEN 1999a). After 7 days, the specimens were demolded and stored at 20±2°C and relative humidity of 65±5% until the testing day.

2.3. Test Methods

A comprehensive testing program was conducted to evaluate the mechanical, chemical, mineralogical, and durability properties of the hardened grouts.

2.3.1. Compressive Strength

The 28-day compressive strength of the hardened grouts was determined in accordance with the TS EN 1015-11 (2007) standard. The test was performed on the broken halves of 40 x 40 x 160 mm prismatic specimens previously subjected to flexural strength testing.

2.3.2. Chemical and Mineralogical Characterization

To investigate the composition of the hardened grouts, a suite of analytical techniques was employed on powdered samples (<90 μm) obtained from 28-day-old specimens.

X-Ray Fluorescence (XRF) was determined using a Bruker S8 Tiger model XRF spectrometer. X-Ray Diffraction (XRD of the samples were qualitatively identified using a Bruker D8 Advance model diffractometer. Fourier-Transform Infrared Spectroscopy (FTIR) were analyzed to complement the XRD results using a Perkin Elmer Spectrum 100 model spectrophotometer.

2.3.3. Durability Assessment

The resistance of the hardened grouts to environmental stressors was evaluated through freeze-thaw and sulfate attack tests on prismatic specimens.

Freeze-thaw resistance: The resistance to freeze-thaw was evaluated based on a procedure adapted from ASTM D560 (2012). Prismatic specimens (40x40x160 mm) were saturated in water for at least 24 hours before the test. A single cycle consisted of 24 hours of freezing at -23°C followed by 23 hours of thawing at 21°C in a 100% relative humidity environment. The test was concluded after 12 cycles or when the specimen disintegrated. Mass loss and visual appearance were recorded after each cycle.

Sulfate attack resistance: The resistance to salt crystallization was assessed using a method adapted from TS EN 12370 (2001). Cubic specimens (50x50x50 mm) were dried to a constant mass at 60°C and then subjected to repeated cycles. A single cycle consisted of 2 hours of immersion in a 14% (by weight) Na_2SO_4 solution at 20°C, followed by 20 hours of drying in an oven at 60°C, and finally 2 hours of cooling at ambient temperature. The test was terminated after 15 cycles or upon sample failure. Mass change and visual deterioration were documented after each cycle.

2.3.4. Microstructural Analysis

To investigate the deterioration mechanisms in samples subjected to sulfate attack, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) was performed. The analyses were conducted on fragments taken from the inner surface of the cycled HG1 and HG3 specimens to identify the morphology of the hydration products and the presence of degradation products like gypsum and thaumasite.

3. Results

This section presents the experimental results obtained from the characterization and durability tests performed on the three-grout series, which are air lime-based (AG1), hydraulic lime-based (HG1), and hydraulic lime with brick powder (HG3).

3.1. Compressive Strength Development

The compressive strength of the grout series was evaluated at 28 and 90 days to understand their mechanical performance over time. The results, including standard deviations, are presented in Figure 1.

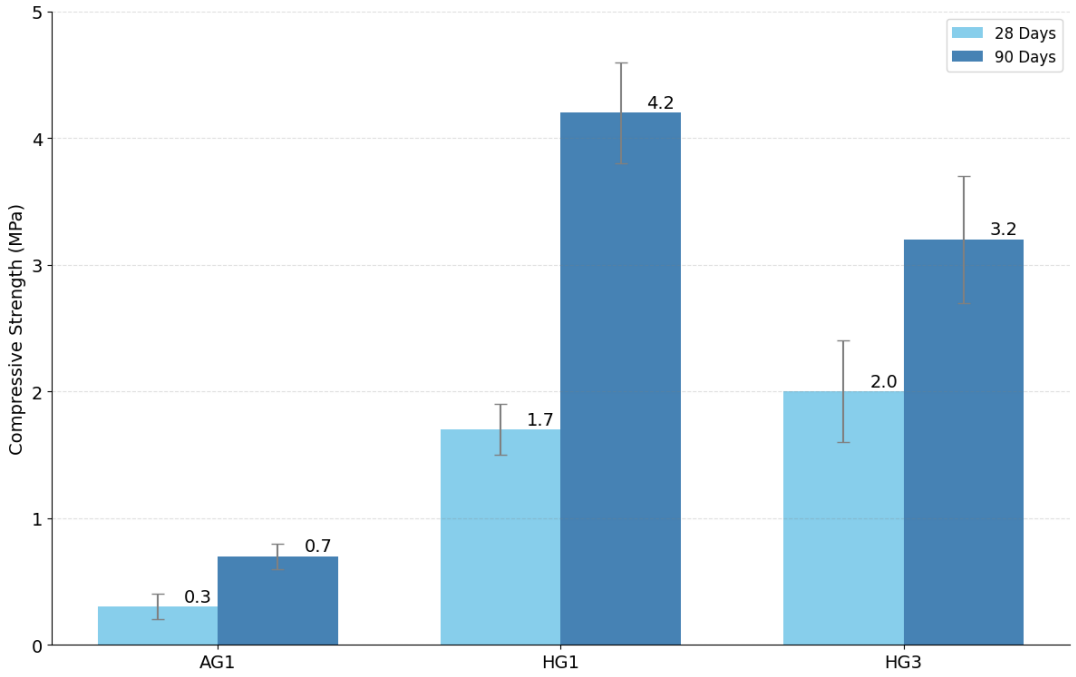

Figure 1. Comparison of 28- and 90-day compressive strength for the AG1, HG1, and HG3 grout series,

As shown in Figure 1, the binder type significantly influenced the mechanical performance. At 28 days, the highest compressive strength was achieved by the HG3 series (2.0 MPa), which contained both natural hydraulic lime and pozzolanic brick powder. The HG1 series, based solely on hydraulic lime, also developed considerable strength (1.7 MPa). In contrast, the air lime-based AG1 series exhibited a significantly lower compressive strength of only 0.3 MPa.

All series demonstrated an increase in strength between 28 and 90 days. The most substantial gain was observed in the HG1 series, which reached 4.2 MPa, more than doubling its 28-day strength. The HG3 series also showed a notable increase to 3.2 MPa. The AG1 series, while showing a slight increase to 0.7 MPa, confirmed the slow and limited strength development characteristic of non-hydraulic binders.

3.2. Chemical and Mineralogical Composition of Hardened Grouts

The chemical and mineralogical nature of the hardened grouts at 28 days was investigated to understand the relationship between the initial materials and the final products.

3.2.1. XRF Analysis

The bulk chemical compositions of the 28-day hardened grouts, determined by XRF, are presented in Table 3. The results show that the chemical composition of the hardened grouts is directly influenced by their initial binder systems. For the single-binder series (AG1 and HG1), the primary components are CaO and SiO_2, and their oxide percentages closely mirror those of the raw lime binders used in their production (as shown previously in Table 1). For instance, the CaO content in the hardened AG1 and HG1 grouts was 67.7% and 64.3%, respectively, which is very close to the 69.0% and 66.1% found in the raw CL 80-S and NHL 3.5 limes.

Table 3. Chemical composition of hardened grout series at 28 days (wt. %)

Component (%)	AG1	HG1	HG3
SiO_2	0.80	11.20	19.20
Al_2O_3	0.40	0.50	3.90
Fe_2O_3	0.20	0.20	2.10
MgO	1.20	0.50	1.00
CaO	67.70	64.30	53.80
K_2O	0.10	<0.1	0.70
SO_3	0.60	0.70	0.70
Loss on Ignition (LOI)	28.90	22.50	17.90

In contrast, the composition of the HG3 series reflects the significant contribution of the pozzolanic brick powder. Compared to the plain hydraulic grout (HG1), the HG3 grout exhibits substantially higher percentages of SiO_2 (19.2% vs. 11.2%), Al_2O_3 (3.9% vs. 0.5%), and Fe_2O_3 (2.1% vs. 0.2%). This confirms the effective incorporation of the silica- and alumina-rich pozzolan into the final matrix. The low levels of SO_3 detected across all series are likely attributable to the mixing water and the superplasticizer used.

3.2.2. Mineralogical Composition (XRD and FTIR Analysis)

The mineralogical composition of the 28-day hardened grouts was investigated using XRD and FTIR to identify the phases formed. A summary of the key findings, combining semi-quantitative XRD data with characteristic absorption bands from FTIR, is presented in Table 4.

Table 4. Chemical composition of hardened grout series at 28 days (wt. %)

Phase / Chemical Group	Identification Method	AG1	HG1	HG3
Portlandite ($Ca(OH)_2$)	XRD (%)	84.00	46.00	40.00
Calcite ($CaCO_3$)	XRD (%)	10.00	14.00	13.00
Quartz (SiO_2)	XRD (%)	-	-	13.00
Hydraulic Phases (Larnite. etc.)	XRD (%)	-	36.00	29.00
Hydroxyl Group (-OH)	FTIR (cm^{-1})	3643.00	3642.00	3643.00
Carbonate Group (CO_3^{2-})	FTIR (cm^{-1})	1429.00, 887.10	1417. 87, 4712.00	1406. 87, 3712.00
Silicate Group (Si-O)	FTIR (cm^{-1})	-	995.00	798.00

The XRD results reveal significant mineralogical differences driven by the binder system. The air lime grout (AG1) is predominantly composed of portlandite (84%), with limited carbonation (10% calcite). In contrast, the hydraulic lime grout (HG1) contains a lower amount of portlandite (46%) but a significant proportion of hydraulic phases (36%), confirming the formation of cementitious products inherent to the NHL 3.5 binder. The addition of brick powder in the HG3 series resulted in a further decrease in portlandite (40%), suggesting its consumption during pozzolanic reactions, which is supported by the presence of quartz (13%) and a high percentage of hydraulic phases (29%).

The FTIR analysis strongly corroborated these findings. All spectra showed a sharp absorption peak for the O-H group in portlandite (around 3643 cm^{-1}) and characteristic peaks for the C-O group in calcite (around 1420 cm^{-1} and 875 cm^{-1}). Crucially, the spectra for HG1 and HG3 also showed distinct bands for Si-O bonds. The HG1 series exhibited a peak at 995 cm^{-1}, associated with amorphous silica in the hydraulic phases. The HG3 series showed a peak at 798 cm^{-1}, which is characteristic of crystalline quartz from the brick powder, thus confirming the successful incorporation of the pozzolan and the formation of new silicate structures.exhibited a peak at 798 cm^{-1}, characteristic of crystalline quartz in the brick powder, thereby

3.3. Durability Performance

The resistance of the grout series to environmental stressors was evaluated through freeze-thaw and sulfate attack tests.

3.3.1. Freeze-Thaw Resistance

The performance of the grout series under freeze-thaw cycling varied significantly depending on the binder type, as visually documented in Figure 2. The air lime-based grout, AG1, failed catastrophically, completely disintegrating during the very first freeze-thaw cycle. This indicates a very low resistance to frost action.

In severe contrast, both hydraulic lime-based series, HG1 and HG3, demonstrated significantly higher durability. These specimens successfully completed all 12 freeze-thaw cycles without disintegration. By the end of the 12th cycle, minor surface cracking was observed on both series, but the specimens maintained their structural integrity and overall dimensions. The final state of all three series after testing is compared in Figure 2.

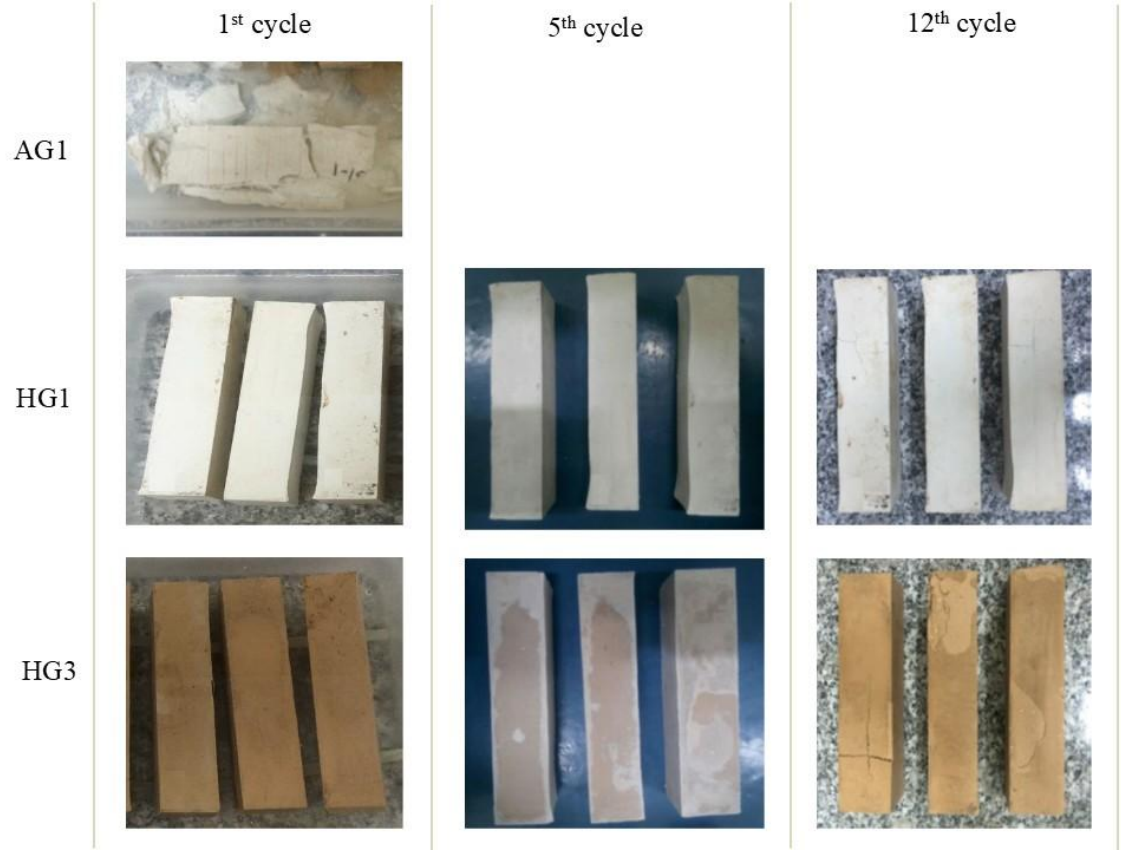

Figure 2. Visual state of the grout specimens after the freeze-thaw durability test.

3.3.2. Sulfate Resistance

The resistance of the grout series to sodium sulfate attack showed notable differences in performance and failure mechanisms, as summarized in Figure 3.

The air lime-based grout, AG1, exhibited the lowest resistance, completely disintegrating after only 5 cycles of exposure.

The hydraulic lime-based grouts demonstrated superior, albeit different, performance. The HG1 series (plain hydraulic lime) completed all 15 cycles, but showed significant deterioration, including erosion and rounding of the specimen's edges, although its core remained intact. In contrast, the HG3

series (hydraulic lime with brick powder) began to show signs of deterioration, such as spalling, after the 7th cycle and ultimately failed by disintegrating during the 14th cycle.

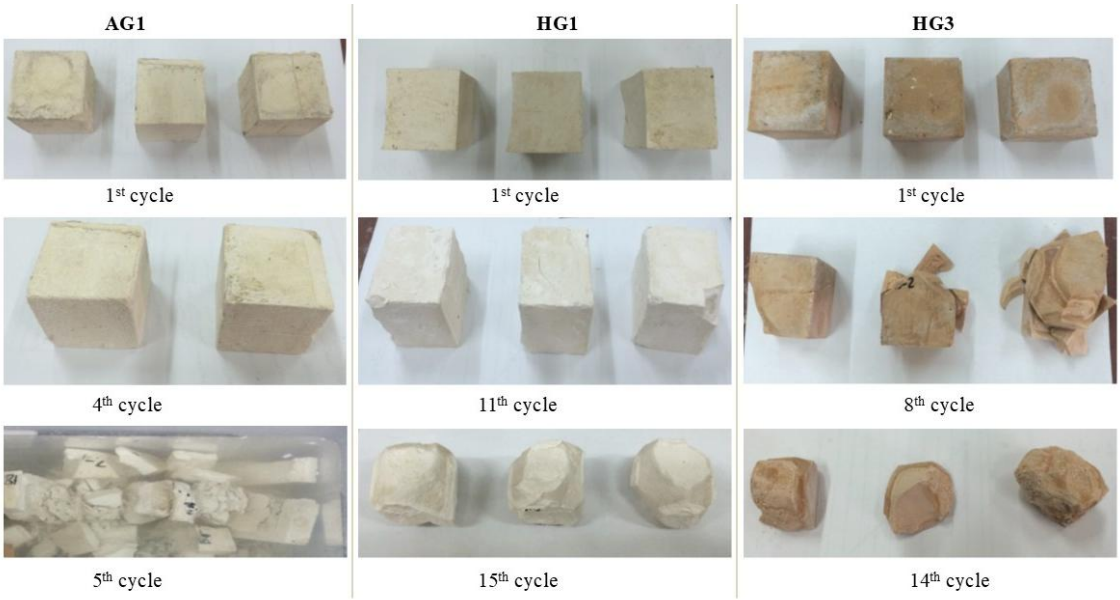

Figure 3. Comparative deterioration of grout specimens after exposure to sodium sulfate attack.

3.4 Microstructural Analysis After Sulfate Attack

To investigate the underlying causes of the observed differences in sulfate resistance, SEM-EDS analyses were conducted on the internal surfaces of the cycled HG1 and HG3 specimens. The key microstructural findings are presented in Figure 4.

In the HG1 specimen, which survived 15 cycles, the microstructure appeared dense. The EDS analysis confirmed that sodium sulfate had not penetrated deep into the matrix, and as a result, deleterious expansive products such as gypsum or thaumasite were not formed. While the typical morphology of calcium-silicate-hydrate (C-S-H) gel was not clearly visible in the SEM images, its presence was confirmed indirectly via EDS. The measured Ca/Si atomic ratio of approximately 1.8 falls within the widely accepted range (0.8–2.1) for C-S-H phases, thus confirming their formation within the HG1 matrix.

In stark contrast, the microstructural analysis of the HG3 specimen revealed the widespread formation of expansive crystalline products. The SEM micrograph in Figure 4 clearly shows the presence of these new phases disrupting the matrix. The accompanying EDS analysis confirmed their identity as gypsum ($CaSO_4 \cdot 2H_2O$) and thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$). The formation of thaumasite was facilitated by the presence of all necessary precursors in the HG3 system: a source of sulfates from the test solution, calcium carbonate ($CaCO_3$) from the carbonation of free lime, and a source of silica from both the hydraulic lime and the pozzolanic brick powder. The formation of these highly expansive products is the direct cause of the internal stress that led to the cracking and eventual disintegration of the HG3 samples.

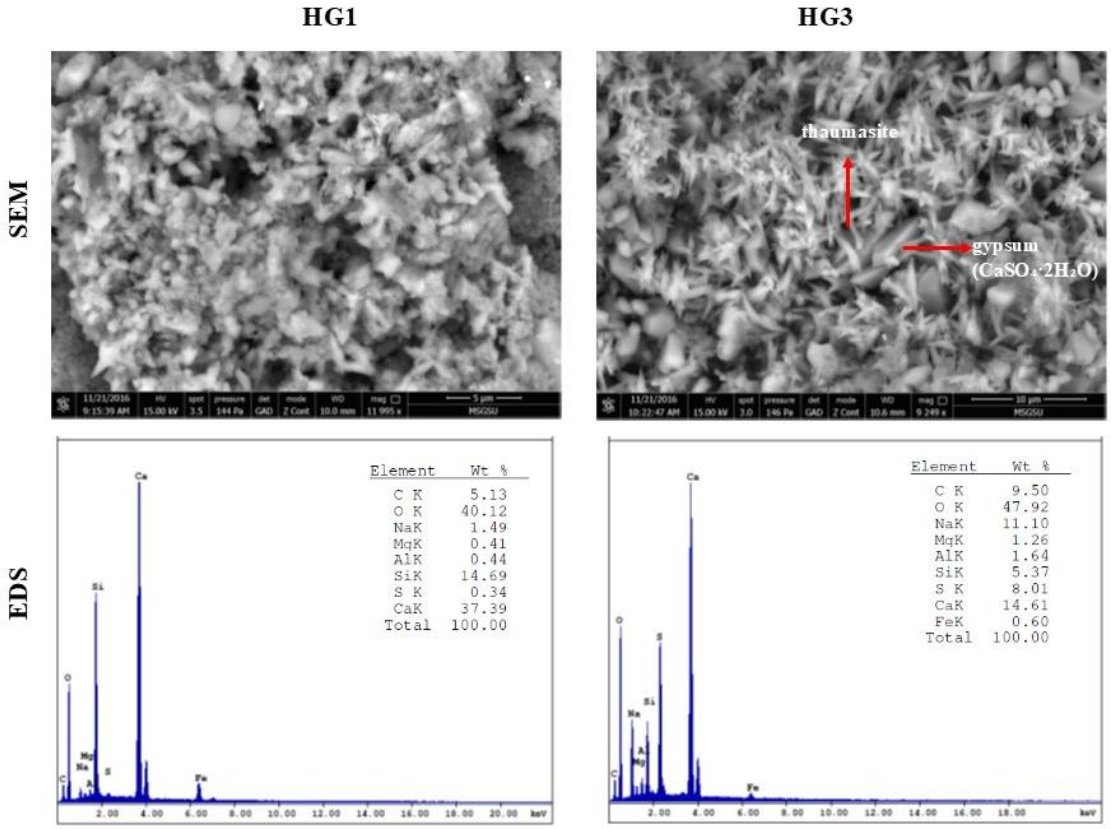

Figure 4. Microstructural analysis of grout specimens after sulfate attack.

4. Discussion

The experimental results of this study offer significant insights into the complex behavior of lime-based injection grouts, particularly concerning the interplay between binder composition, mechanical performance, and long-term durability. The discussion will focus on interpreting the key findings that are the fundamental role of hydraulicity in grout performance, the conflicting effects of pozzolanic additives under different exposure conditions, and the resulting implications for conservation practice.

A primary finding is the obvious superiority of hydraulic lime-based grouts (HG1 and HG3) over the air lime-based formulation (AG1). The rapid failure of AG1 in the freeze-thaw test and its minimal strength gain are attributable to its reliance on slow atmospheric carbonation, which results in a porous microstructure inherently vulnerable to frost-induced environmental effects. In contrast, the hydraulic binders in HG1 and HG3 facilitated the formation of a dense, cementitious matrix rich in calcium-silicate-hydrate (C-S-H) phases, as confirmed by XRD and FTIR. This denser microstructure provided the necessary mechanical strength and lower permeability to resist internal stresses, ensuring robust performance in both compressive strength and freeze-thaw tests.

Perhaps the most critical finding of this study is the dual, and ultimately conflicting, role of the pozzolanic brick powder. The addition of this pozzolan in the HG3 series enhanced 28-day compressive strength and contributed to a durable matrix under freeze-thaw conditions. However, this same modification rendered the grout more susceptible to sulfate attack than the plain hydraulic lime grout (HG1). The microstructural analysis explains this phenomenon: The pozzolanic reaction, while beneficial for strength, introduced a highly reactive source of alumina and silica. This created an ideal chemical environment for the formation of destructive, expansive phases—namely gypsum and thaumasite—when exposed to an external sulfate source. The HG1 grout, lacking this abundance of reactive alumina and silica, did not facilitate thaumasite formation and thus exhibited greater resilience, failing only by gradual surface erosion rather than catastrophic internal expansion. This highlights a critical principle, which is

enhancing one performance characteristic, such as strength, can inadvertently compromise durability under specific chemical attacks.

These findings have profound implications for the formulation of injection grouts for heritage conservation. It is evident that a grout's suitability cannot be determined by a single performance metric. The results demonstrate that a formulation optimized for mechanical strength may be dangerously inappropriate for an environment with aggressive chemical agents, such as sulfate-rich soils or groundwater. Therefore, the design process must be holistic, prioritizing chemical compatibility and long-term durability tailored to the specific threats of a given site. While pozzolanic additives are valuable, their use demands careful consideration and risk assessment, especially in environments with a known potential for sulfate exposure.

5. Conclusions

This study evaluated the durability of three lime-based grouts with different binder systems. Based on the experimental results, the following conclusions can be drawn:

Binder type is the primary determinant of performance. Hydraulic lime-based grouts (HG1 and HG3) significantly outperform air lime-based grout (AG1) in terms of both mechanical strength and freeze-thaw resistance, owing to the formation of a dense, cementitious matrix.

Pozzolanic additives introduce a critical performance conflict. The addition of pozzolanic brick powder (HG3) increased early-age strength but severely compromised the grout's resistance to sulfate attack. This was due to the creation of a chemical environment that facilitated the formation of destructive expansive products like gypsum and thaumasite.

The plain hydraulic lime grout offered the most balanced performance. The HG1 formulation, without pozzolanic additives, demonstrated the most reliable overall durability, showing adequate strength and superior resistance to both freeze-thaw cycling and sulfate exposure.

A holistic, site-specific approach to grout design is essential. The findings underscore that optimizing for a single property (like strength) can be detrimental to long-term durability. Grout selection for historic structures must prioritize chemical compatibility with the specific environmental conditions of the site, especially when a risk of sulfate attack is present.

5. Acknowledgement

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Influence of Strand Tensioning on The Strength and Elongation Characteristics of Wire Ropes

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ABSTRACT

Wire ropes are versatile products widely used across many sectors and applications, such as load lifting, handling, motion arresting, and other static functions. Structurally, wire ropes consist of outer strands closed around a core component, with the outer strands helically laid during the closing process. Due to the nature of this process, correct tensioning of each strand is critical for several reasons, including uniform load distribution among the strands, structural integrity, and dimensional consistency. Improper tensioning may result in premature failure caused by uneven load distribution, rope ovality, and reduced fatigue performance. Ensuring correct tensioning directly affects the strength performance of six-strand rope constructions, because the cumulative metallic area of the outer strands accounts for approximately 86% of the total metallic area of the rope. In this study, a six-strand rope will be produced at three different strand tension values, with all other variables held constant, to analyze the effects of varying tensioning on rope breaking strength and elongation. Production will be carried out on a closing machine equipped with servo-drive braking, which applies a constant and uniform braking force on all loaded strands, allowing for tension accuracy control within ±10%.

Keywords: breaking strength, elongation, strand tensioning, wire rope

1. Introduction

Wire ropes are versatile, high-strength, flexible materials used for a variety of applications including general lifting applications, static applications and specialised applications such as arresting/absorbing elements across industries such as the elevator, mining, and aeronautics [1]- [3]. Wire ropes are built from wires that are helically laid around a central component in specific patterns that are referred to as strand constructions, which are in turn, helically laid around a core component (i.e. closing) such as Fibre Core (FC) or Independent Wire Rope Core (IWRC) whereby the rope is formed [4]. The components that constitute a typical wire rope construction can be seen in Fig.1.

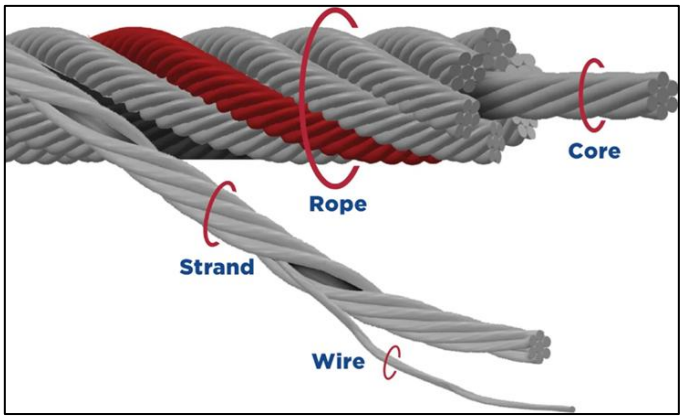

Figure 1. Components of a typical steel wire rope

The mechanical behavior of wire strands under tension has been subject to research due to its critical role in the performance of ropes and cable structures. Earlier analytical studies demonstrated that gaps between the core and helical wires significantly influence the load distribution and deformation characteristics of strands [5]. More recent modelling efforts highlight that purely geometrical representations of strands are insufficient, since they neglect the stresses induced during the stranding process; instead, finite element models that incorporate the stranding operation itself provide improved correlation with experimental results [6]. From a production standpoint, fluctuations in strand tension during cable twisting can arise from centrifugal forces, friction, and varying deflection paths, requiring advanced control methods to equilibrate strand forces [7]. Despite this, the number of studies focusing directly on strand tensioning and its impact on rope performance remains limited.

Balanced strand tensioning is essential to achieving uniform load distribution, structural integrity and dimensional stability. Improper tensioning during production or installation can lead to uneven load distribution, rope ovality, and premature fatigue failure, regardless of rope construction. These effects are particularly pronounced in six-strand ropes, where the cumulative metallic area of the outer strands accounts for about 86% of the total metallic area. In such cases, any deviation in strand tension may disproportionately influence the overall strength and durability of the rope. This study involves producing wire rope under different strand tension conditions, while keeping all other parameters constant, to evaluate how tension variations influence rope breaking strength and elongation.

2. Materials and Method

The test rope used in this study is a 6×K19S WS IWRC. A schematic view and picture of the test rope's cross section can be seen in Fig. 2. The construction includes six strands of "19S" construction laid over a steel core. The "19S" strand construction is comprised of 9 outer wires laid over 9 wires in the inner layer laid over a single centre wire. The strands of the test rope were subject to compacting which is an additional production process that reduces the diameter of the strand to achieve a more circular cross-section whereby it allows to reduce gaps, increases the fill factor, and improves breaking load [8].

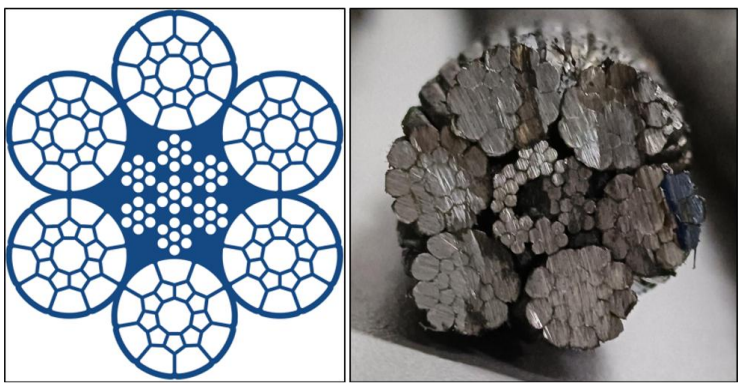

Figure 2. Schematic view (left) and picture (right) of the test rope's cross section

The nominal rope diameter of the test rope is 20 mm, manufactured with an independent wire rope core (IWRC). The rope was produced using high-carbon steel wires, with a tensile strength grade of 1570–1770 N/mm² (dual tensile). The rope had a minimum breaking load (MBL) of 265 kN, and a nominal rope mass of 1.79 kg/m. It was manufactured in accordance with EN 12385-4 standard requirements. The summary table of the design parameters is presented in Table 1.

Table 1. Design parameters of the test rope

1	Nominal rope diameter	[mm]	**20**
2	Diameter tolerance	[-%/+%]	**5**
3	Rope designation according to ISO 17893/ EN12385-2		**6xK19 S IWRC**
4	Core construction		**Steel Core**
5	Outer stand wire arrangement		**6[1+9+9]**
6	Nominal strength of wire	[N/mm2]	**1570-1770 (Dual-Tensile)**
7	Minimum breaking load (MBL)	[kN]	**265**
8	Lay type (LHOL=lef hand ordinary lay, RHOL=right hand ordinary lay, LHLL=left hand lang lay, RHLL = right hand lang lay)		**RHOL**
9	Wire material		**High Carbon Steel**
10	Rope weight per meter	[kg/m]	**1.79**
11	Surface of the wires: bright (U), galvanized EN 10264-2 Class AB/B (AB/B)	(U/AB/B)	**AB**
12	Standard		**EN 12385-4**
13	Discard criteria according to ISO 4309	(rope class number)	**RCN 02**

Rope production was carried out on a SKET Planetary Stranding Machine, designed for the manufacture of 6-strand and 8-strand wire ropes. This equipment allows precise control of strand tensioning during the closing process. The machine is equipped with a servo-drive braking system, which applies constant braking on all bobbins, enabling strand tension control with an accuracy of ±10%. This system allows adjustment of the strand tension within the range of 200 N to 3000 N, making it possible to apply and maintain the desired force levels during production.

All tensile tests were performed in accordance with TS EN ISO 6892-1 and TS EN 12385-1+A1 standards using a RAAGEN 100-ton hydraulic tensile testing machine. Rope samples were prepared according to ISO 3108 requirements to ensure consistency and reliability of test results. For each strand tension level, a single elongation test was conducted. Following completion of the elongation tests, the same samples were subjected to tensile breaking tests. The elongation procedure involved cyclically loading each rope 10 times between 5% and 80% of its minimum breaking load (MBL). This cycling process allowed the constructional stretch to stabilize prior to final testing. During all tests, a constant grip pressure of 280 bar was maintained to prevent slippage and ensure accurate force application.

3. Results and Discussion

Three rope samples were produced under different tension levels: 0.8 kN, 1.6 kN, and 2.4 kN. These values were selected to represent low, intermediate, and high strand tension conditions within the production machine's operating range. After production, each group was subjected to a series of examinations and tests to assess both dimensional stability and mechanical behavior.

3.1. Dimensional Properties

Firstly, dimensional checks were conducted on all rope samples, including measurements of rope diameter, lay length, helix height, and preformation rate. All dimensional measurements were performed

with calibrated equipment to ensure accuracy. The results for the three different strand tension levels (0.8 kN, 1.6 kN, and 2.4 kN) are summarized in Table 2.

Table 2. Dimensional measurements of the rope samples

Physical Properties	Rope Sample		
	0.8kN	1.6kN	2.4kN
Av. Diameter (mm)	**20.61**	**20.64**	**20.63**
Lay Length (mm)	**134.11**	**135.03**	**135.39**
Lay Factor (Lay Length/Av. Diameter)	**6.51**	**6.54**	**6.56**
Helix Height	**19.97**	**18.70**	**19.36**
Preformation Rate (Helix Height/Av. Diameter)	**97%**	**91%**	**94%**

The measured average diameters remained consistent across all tension levels, varying slightly between 20.61 mm and 20.64 mm, indicating that the nominal rope diameter was maintained independent of strand tensioning. The lay length showed a gradual increase with higher strand tension, from 134.11 mm at 0.8 kN to 135.39 mm at 2.4 kN, corresponding to an incremental rise in the lay factor from 6.51 to 6.56. This shows that higher strand tensioning during closing resulted in a slightly more extended rope lay. Notably, the preformation rate did not increase linearly with strand tensioning and instead, the intermediate tension value produced the most ideal structure. This suggests that factors beyond applied strand tension may influence the final preformation characteristic of the rope. Representative figures are provided to illustrate how the dimensional measurements (diameter, lay length and helix height) were carried out in Fig. 3.

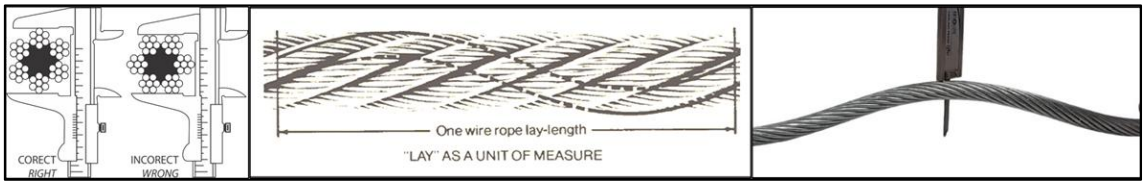

Figure 3. From left to right, the representations of diameter, lay length, and helix height measurements are shown.

3.2. Elongation Tests

Following dimensional evaluation, the ropes underwent elongation tests, where each sample was cyclically loaded 10 times between 5% and 80% of its minimum breaking load (MBL). This procedure allowed the constructional stretch to be applied and measured. Subsequently, the same specimens were tested to failure in tensile breaking tests to determine their tensile strengths. Table 3 summarizes the results for the three different strand tension groups (0.8 kN, 1.6 kN, and 2.4 kN)

The results show that all samples exhibited constructional stretch during the 10 loading cycles, with elongation gradually stabilizing as the cycles progressed. The rope produced at the lowest strand tension (0.8 kN) displayed the highest elongation (1.19%), while the rope produced at the highest tension (2.4 kN) showed the lowest elongation (1.03%). This indicates that increasing strand tensioning during closing results in reduced constructional elongation, as the strands are laid more tightly around the core and experience less adjustment under cyclic loading.

Table 3. Elongation results of rope samples under cyclic loading

	Elongation Test Samples					
	0.8kN		1.6kN		2.4kN	
L_0 (Initial Gauge Length) (mm)	807		811		812	
Loading Cycles	5% Load	%80 Load	5% Load	%80 Load	5% Load	%80 Load

	(13.25kN)	(212kN)	(13.25kN)	(212kN)	(13.25kN)	(212kN)
1.Cycle	**808.80**	**825.00**	**812.75**	**828.40**	**813.44**	**828.39**
2.Cycle	**816.90**	**825.40**	**820.27**	**828.90**	**820.26**	**828.79**
3.Cycle	**817.50**	**825.60**	**820.92**	**829.11**	**820.77**	**828.96**
4.Cycle	**817.70**	**825.75**	**821.23**	**829.24**	**821.08**	**829.11**
5.Cycle	**817.82**	**825.90**	**821.41**	**829.38**	**821.29**	**829.21**
6.Cycle	**818.05**	**826.00**	**821.58**	**829.45**	**821.35**	**829.32**
7.Cycle	**818.20**	**826.05**	**821.69**	**829.52**	**821.58**	**829.39**
8.Cycle	**818.30**	**826.10**	**821.79**	**829.61**	**821.65**	**829.45**
9.Cycle	**818.38**	**826.15**	**821.87**	**829.66**	**821.80**	**829.52**
10.Cycle	**818.44**	**826.18**	**821.95**	**829.72**	**821.85**	**829.57**
ΔL (mm)	**9.64**	**1.18**	**9.20**	**1.32**	**8.41**	**1.18**
Total Elongation (%)	**1.19%**	**0.14%**	**1.13%**	**0.16%**	**1.03%**	**0.14%**

Breaking tests were conducted on the same elongation samples after completion of the cyclic loading procedure. The measured breaking forces were 301.4 kN for the 0.8 kN sample, 301.7 kN for the 1.6 kN sample, and 301.3 kN for the 2.4 kN sample. Despite the different strand tension levels during closing, once constructional stretch was applied through the elongation cycles, the resulting breaking strength values were found to be nearly identical, with differences of less than 0.5 kN across the samples. The period in which the rope undergoes constructional stretch is referred to as bedding-in [9]. The results suggest that the process of bedding-in largely equalized any initial differences introduced by strand tensioning. Accordingly, strand tensioning can be considered to primarily influence the rope's ability to undergo and stabilize constructional stretch.

3.3. Breaking Test Results

In addition to the breaking force tests carried out on the elongation samples, three further breaking tests were conducted for each strand tension group. The outcomes, expressed as Actual Breaking Load (ABL), are summarized in Table 4.

Table 4. Additional breaking test results of rope samples

	0.8kN (B1)	0.8kN (B2)	0.8kN (B3)	1.6kN (B1)	1.6kN (B2)	1.6kN (B3)	2.4kN (B1)	2.4kN (B2)	2.4kN (B3)
A_{gt} (%)	**4.75**	**4.70**	**4.76**	**4.58**	**4.86**	**5.08**	**4.60**	**4.80**	**4.62**
A_{gt} - Standard Deviation	**0.03**			**0.25**			**0.11**		
E (Gpa)	**51.35**	**51.38**	**50.94**	**51.87**	**55.84**	**56.05**	**57.26**	**56.38**	**54.18**
E (Gpa) - Standard Deviation	**0.25**			**2.36**			**1.59**		
F_m (kN)	**296.55**	**295.25**	**294.53**	**299.37**	**298.68**	**296.97**	**298.96**	**297.62**	**295.12**
F_m (kN) - Standard Deviation	**1.02**			**1.24**			**1.95**		

The results show that the average breaking load exceeded the minimum breaking load (MBL) of 265 kN specified for the rope by a considerable margin in all test groups. Among the samples, the 1.6 kN tension group achieved the highest average ABL at 298.34 kN, corresponding to approximately 12% above the required MBL. These findings confirm that although all three groups comfortably satisfied the MBL requirement, slight variations in strand tension produced measurable differences in average breaking load. Unlike the earlier results obtained after constructional stretch had been applied, these additional tests were performed on as-produced samples. As a result, the breaking load values showed greater variation between the tension groups, indicating that the absence of prior constructional stretch allows the influence of strand tensioning to be more directly reflected in the measured strength.

The failure mode of these tests was also observed, providing further insight into how load distribution and gripping conditions influenced the breaking behaviour of the rope specimens. Fig. 4 presents two specimens from the 0.8 kN tension group. The specimen on the left (Sample B1) demonstrates the ideal failure mode, with all outer strands and the core breaking in a balanced manner. In contrast, the specimen on the right (Sample B3) shows a localized failure, where only a single outer strand fractured while the remaining strands stayed intact. This difference in failure mode was also reflected in the corresponding Actual Breaking Load (ABL) results, with the ideal specimen exhibiting a higher breaking load compared to the non-ideal specimen.

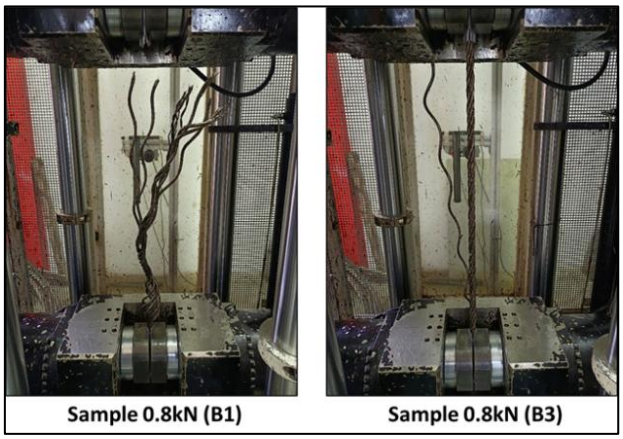

Figure 4. Failure modes of 0.8 kN samples: ideal (left) vs. localized strand failure (right).

4. Conclusions

All strand tension samples met the required tolerances for diameter and lay length, but only the 1.6 kN group achieved the target preformation ratio, making intermediate tensioning the most effective for dimensional accuracy

Elongation tests showed that proper strand tensioning reduces constructional stretch, improving dimensional stability and limiting bedding-in elongation. Breaking tests confirmed that once constructional stretch is applied, differences caused by strand tension largely disappear, resulting in more uniform strength values

Without cyclic loading, the 1.6 kN tension group had the highest breaking strength. Nevertheless, the larger standard deviations observed in these results emphasize the need for additional testing to better quantify the influence of strand tensioning across different groups

Overall, the findings highlight that while breaking strength is not significantly affected once constructional stretch is applied, strand tensioning plays a critical role in controlling dimensional parameters and managing constructional stretch, thereby contributing to the consistency and reliability of rope performance. Future research should broaden the range of rope constructions, increase sample sizes, and include fatigue testing to evaluate long-term performance.

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State-of-the-Art Review of Analytical Formulations to Determine Specific Lengths of Different Flow Regimes for Manifold Fluid Flow

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ABSTRACT

In the present study, the specific mathematical formulations are derived with considering a manifold fluid flow consists of the specific pipe lengths of the segments in which the different flow regimes (i.e., fully turbulent, turbulent, transition and laminar) occur along its length. Hence, variation of flow regime in the specific pipe segments is characterized with decreasing of the Reynolds number along direction of flow. Distribution of outlet pressure head and non-uniform outflow profile, friction drop, and flow velocity and the Reynolds number variation in accordance with the distance ratio are depicted as dimensionless curves in the design figures, for the sake of comparison.

Keywords: Water pipelines; Steady-state analysis; Hydraulic networks; Velocity head; Flow regime; Turbulent flow.

1. Theoretical Background

1.1. Velocity Head Gradient

Assuming that outlets along the pipeline have uniform outflow $\bar{q}$, then the total flow rate that passes through the pipe section located at any distance *l* from the pipeline inlet Q(*l*) is commonly given as (Wu and Gitlin 1975, Scaloppi and Allen 1993)

$$Q(l) = \left(N - \frac{l}{s} \right) \bar{q} = Q_I (1 - i) \tag{1}$$

where Q(*l*) = the discharge at a section of length *l* measured from the pipeline inlet; $Q_I = N\bar{q}$ = total inflow rate for the entire length of the pipeline; N = total number of equally spaced operating outlets for the entire pipeline; s = outlet spacing; and *i* = dimensionless variable of distance *i* = *l*/L, which is the percentage of the length to the total length.

According to Eq. (1) the average flow velocity also varies linearly along the pipeline and, the velocity head gradient can be written as follows

$$S_V(l) = \frac{2H_{VI}}{L}(i - 1) \tag{2}$$

where $S_V(l)$ = velocity head gradient at any distance *l*; and $H_{VI} = 8(N\bar{q})^2 / \pi^2 g D^4$ = velocity head at the inlet of the pipe; and D and L = internal diameter and length of the pipe.

Integrating the gradient of the velocity head given by Eq. (2) between the limits 0 and *l* and then, the velocity head at any distance *l* is obtained as

$$H_V(l) = H_{VI}(1 - i)^2 \tag{3}$$

where $H_V(l)$ = velocity head for the pipe section located at any distance *l*.

1.2. Flow Rate Distribution for Non-uniform Outflow Approach

To this point the preliminary analytical derivations presented above are similar to the referred paper (Anyoji and Wu 1987). In the following analytical derivation, the energy-grade line will be improved for the nonuniform outflow profile. Instead of the traditional Eq. (1), to describe variation of flow rate along the pipeline Q(*l*), a simple but sufficiently accurate exponential function (Scaloppi and Allen 1993; Valiantzas 1998, 2002; Yıldırım and Ağıralioğlu 2004a) is given by

$$Q(l) = Q_l (1 - i)^{\beta} \tag{4}$$

where β = nonuniform outflow exponent; then the outflow from each multiple outlets will not be uniform along the pipeline. It should be noted that, a similar form of Eq. (4) was presented in the recent papers (Valiantzas 1998, 2002) on the basis of the average outlet flow approximation (Eq. 23 of Valiantzas 2002) $\left\{ \overline{q} = (k/Ns)\left[\int_{l_0}^{l_{Ql}} H^x(l)dl \right] \cong (k/Ns)\left[\int_{l_0}^{l_{Ql}} H(l)dl \right]^x \right\}$ which directly referred to the paper of Anyoji and Wu (1987).

However, according to the opinion of Wu (personal communication 2002) this approximation used is not possible in the mathematical consideration (the power of function x must be inside of the integration), except for a special case of the value of the emitter discharge exponent, x = 1.0. Further analysis and discussion for this approximation was presented in the recent papers (Yıldırım and Ağıralioğlu 2003; 2004a, b; 2005a, b).

If Eq. (4) is evaluated for the upper half segment of the pipeline (*i* = 0.5), then arranged with the expression for the flow rate entering over the upper half segment of the pipeline, $Q_{0.5} = (kN/2)\overline{H}^{x}{}_{0.5}$ finally the β can be evaluated from

$$\beta = 1 - 3.322x \log\left(\frac{\bar{H}_{0.5}}{\bar{H}} \right) \tag{5}$$

where $\overline{H}_{0.5}$ = average pressure head along the upper half segment of the pipeline.

1.3. Determination of Pipe Segments in Different Flow Regimes

Consider a pipeline with multiple outlets consists of the specific lengths of the segments in which the different flow regimes (i.e., fully turbulent, turbulent, transition and laminar) occur along its length. The variation of flow regime in the specific pipe segments is characterized with decreasing of the Reynolds number in direction of flow.

The variation of the Reynolds number for nonuniform outflow profile exponentially varies along the pipeline in accordance with the flow rate distribution Q(*l*) as given by Eq. (4)

$$R(l) = R_l (1\text{-}i)^{\beta} \tag{6}$$

in which R(*l*) = Reynolds number for any distance *l* from the pipeline inlet.

Multiple outlets pipelines are generally made of smooth materials. Flow in a pipeline with multiple outlets is usually turbulent, sometimes fully turbulent flow exists at the upstream end of the pipeline and, low becomes laminar at the downstream reach where the flow velocity decreases to zero. The transition flow occurs for the interval, 2000 < R $\leq$ 3000, and the flow characteristics are indeterminate for the transition zone (Miller 1990).

In the following, the expressions for the specific pipe segments in different flow regimes are deduced from the definitions of the flow regimes characterized by the specific intervals of the Reynolds number.

For fully turbulent flow, the pipe segment in which fully turbulent flow regime prevails along its length can be represented by

$$l_{fully-turbulent} = L \times \left[1 - \left(\frac{10^5}{R_I} \right)^{1/\beta} \right]$$

(7)

The turbulent flow length for the cases of either fully turbulent flow or no fully turbulent flow exists at the inlet of the pipeline, can be deduced by the following Eqs. (8) and (9), respectively

$$l_{turbulent} = L \times \left[\frac{10^{5/\beta} - 3000^{1/\beta}}{R_I^{1/\beta}} \right]$$

(8)

$$l_{turbulent} = L \times \left[1 - \left(\frac{3000}{R_I} \right)^{1/\beta} \right]$$

(9)

For the length of the transition zone, the following expression is given by

$$l_{transition} = L \times \left[\frac{3000^{1/\beta} - 2000^{1/\beta}}{R_I^{1/\beta}} \right]$$

(10)

Although the length of the transition zone can be determined by Eq. (10), the current design procedure assumes the most usual case in which the turbulent flow length is practically extended to the start of aminar flow section omitting the transition zone.

Finally, the laminar flow length can be determined as follows

$$l_{la\,\min ar} = L \times \left[\frac{2000^{1/\beta} - 1}{R_I^{1/\beta}} \right]$$

(11)

2. Design Example

Determine the energy grade-line along the pipeline for the nonuniform outflow concept and, the corresponding flow characteristics for a horizontal (S_0 = 0) manifold (x = 0.5), using given the following data: total number of outlets, N = 33 which are equally spaced at s = 12. 0 m; the inlet spacing ratio from the main pipe, $\mu = s_l/s$ = 1.0. Lateral pipe is of aluminum (equivalent roughness, ε = 0.1 mm); irrigation water is at 20 ^{0}C (kinematic viscosity, $\nu = 1.01 \times 10^{-6}$ m^{2}s^{-1}); and acceleration due to gravity, g = 9.807 ms^{-2}. The required average sprinkler discharge and corresponding nozzle pressure head are, $\bar{q}$ = 0.315 ls^{-1} and $\overline{H}$ = 31.61 m, respectively. The internal diameter of the lateral is considered, D = 101.6 mm ($\cong$ 4 in). Consider neglecting minor head losses in sprinkler risers except for the energy losses due to couplers. The friction loss multiplier is taken 1.08 for energy losses in couplers for the value of the common outlet spacing s = 12 m (Jensen 1981).

3. Analytical Solution

Inlet flow rate Q_l = $N\bar{q} = 1.04 \times 10^{-2} m^3 s^{-1}$; the kinetic head $H_{V1} = 8(N\bar{q})^2 / \pi^2 g D^4$ = 0.084 m; the inlet Reynolds number R_l = $(4N\bar{q} / \pi D\nu)$ = 128,979; the distance between first and last outlets L_0 = 384 m; and total lateral length L = = 396 m ($\theta = L_0/L$ = 0.9697), are found. The fully-turbulent flow ($10^5 < R_l$ = 128,979 < 10^7) occurs at the sprinkler lateral inlet (c_1 = 0.130 and m = 1.828). In order to do a detailed comparative analysis, the solution of the design problem is extended to cover various combinations of design parameters, varying outlet discharge exponents (x = 0.2, 0.5, 0.54 and 1.0) and different uniform line slope conditions (S_0 = 0.00, -0.02, -0.05, 0.02 and, 0.05).

For the Design Example (S_o = 0.0 and x = 0.54), for the pressure heads at the inlet, H_I, at the first and last outlets, H_1, and H_N; the analytical solution yields 8.70 m, 8.66 m and 6.66 m respectively, whereas the SBS numerical method yields the same value for both H_I and H_1 as 8.86 m and, 6.91 m for H_N. Note that, the H_I is equivalent to H_1 disregarding inlet spacing from the main pipe to the first outlet, for the SBS trickle lateral design procedure (Hathoot et al., 1993). For all design cases the results obtained from the analytical solution and those of the SBS numerical method are in a good justification. As shown in Fig. (1), different flow regime zones (turbulent, transition and, laminar) from the inlet section and, their lengths across the length of trickle lateral, were also presented. From this figure, the following findings can be observed: Between *l* = 113 m and 114 m ($i_{turbulent}$ = 75%) flow becomes laminar (including the transition zone) and, for the downstream length, *l* = 38 m, flow is actually laminar ($i_{laminar}$ = 25%).

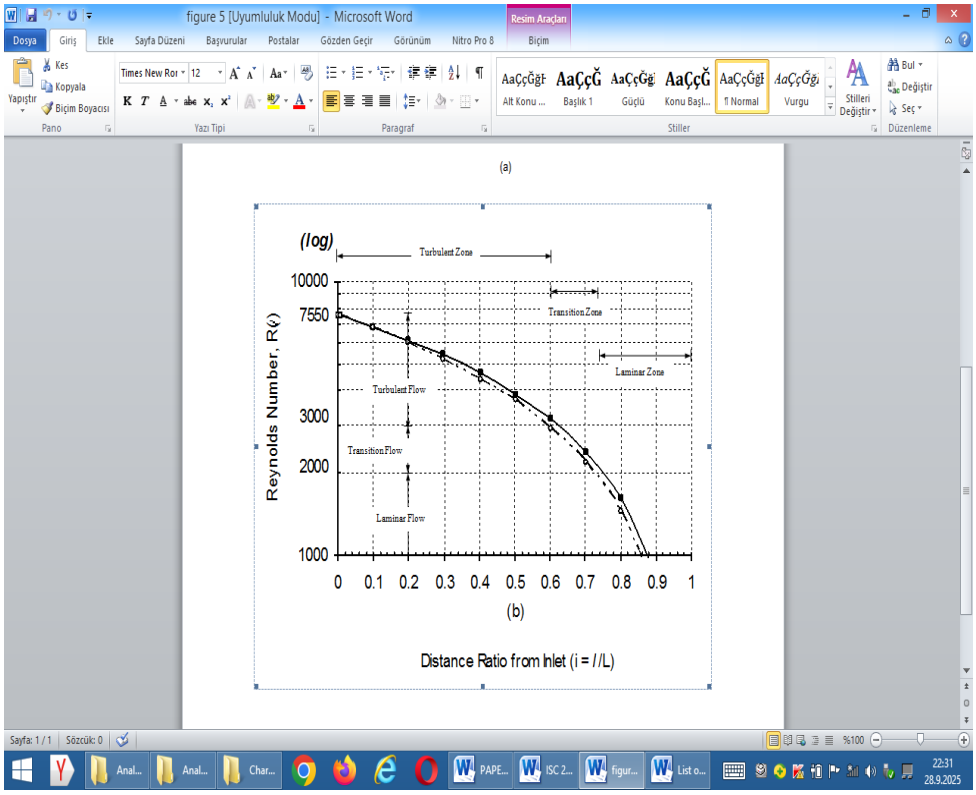

Figure 1. Variation of Reynolds number and Pipe Zones with Different Flow Regimes

4. Summary and Conclusion

The determination of the proper operating inlet pressure head is important for hydraulic design of the multi-outlet plastic pipelines in irrigation subunits. This paper offers simple, direct but sufficiently accurate relationships to determine the specific pipe segment in which different flow regimes occurred along the manifold line (i.e., fully turbulent, turbulent, transition and laminar) occur along its length. Hence, variation of flow regime in the specific pipe segments is characterized with decreasing of the Reynolds number along direction of flow. Distribution of outlet pressure head and non-uniform outflow profile, friction drop, and flow velocity and the Reynolds number variation in accordance with the distance ratio are depicted as dimensionless curves in the design figures, for the sake of comparison. Practical results for an extensive comparison test covering different pipe slopes and outlet discharge exponents indicate that, the performance of the proposed technique is sufficient in comparison with those of the previous accurate analytical and numerical design procedures.

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Comparative Analysis of Analytical Continuous-Nonuniform and Discrete-Variable Outflow Approaches

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ABSTRACT

This paper is mainly focused on presenting the essentials of manifold fluid flow hydraulics and fundamental principles consist of basic governing formulations, and analyzing some hydraulic properties; such as determination of hydraulic and energy-gradient lines, working inlet pressure head, distribution of inlet discharge, variation of average flow velocity and the Reynolds number, head loss due to friction, water application uniformity, based on the analytical continuous non-uniform outflow and the stepwise discrete-variable discharge approaches. In the analytical solution, the specific mathematical formulations are derived with considering a manifold consists of the specific pipe lengths of the segments in which the different flow regimes (i.e., fully turbulent, turbulent, transition and laminar) occur along its length. Hence, variation of flow regime in the specific pipe segments is characterized with decreasing of the Reynolds number along direction of flow. Distribution of outlet pressure head and non-uniform outflow profile, friction drop, and flow velocity and the Reynolds number variation in accordance with the distance ratio are depicted as dimensionless curves in the design figures, for the sake of comparison. Comparison test shows that the presented the continuous-nonuniform and discrete-variable discharge approaches are in a good justification, for all performed simulation.

Keywords: Steady-state analysis; Hydraulic networks; Continuous Non-uniform Outflow; Discrete variable outflow; Energy-Gradient-Line.

1. Governing Formulations for Determining Hydraulic and Energy-Gradient Line

1.1. For Discrete-Variable Outflow Approach

Hydraulically, flow in a submain unit pipeline is considered to be a steady, spatially varied flow with decreasing outlet outflow in the downstream direction. With decreasing discharge along the line, the energy gradient line decreases. Generally, outlets are usually identical, and installed at an equal spacing on the line. The flow characteristics of the outlets are typically described by a function of the form (Howell and Hiler, 1974; Keller and Karmeli, 1974).

Table 1 shows basic fundamental principles or governing formulations for discrete-variable outflow approach such as, pressure head-outflow discharge relationship, conservation of mass law or principle (continuity equation), conservation of momentum law or principle (impuls-momentum equation), continuous head (energy) losses due to friction (Darcy-Weisbach equation), local or minor head losses dua to individual outlet barb connection (Borda-Carnot & Belanger's equation), conservation of energy law or principle /Bernoulli's equation).

Table 1. Fundemental Principles & Governing Formulations for Discrete-Variable Outflow Approach

Description of Basic Equation	***Formulation***

Pressure head - outflow (discharge) relationship	$q_n = cH_n^{\,y}$ $q = \left(\frac{c}{s}\right)H_n^{\,y}$
Conservation of mass law & principle: Continuity equation	$\frac{dQ}{dx} + \frac{dA}{dt} = -q$ $Q_{n+1} = Q_n - q_n$
Conservation of momentum law & principle: Impuls-momentum equation	$\Delta F = \rho(Q_{n+1}V_{n+1} - Q_nV_n)$ $\Delta H_{n+1} = \frac{\Delta p}{\gamma} = \frac{\Delta F}{A\gamma} = \frac{\rho(Q_{n+1}V_{n+1} - Q_nV_n)}{A\gamma}$ $\Delta H_{n+1} = \frac{\rho}{A\rho g}\left(\frac{Q^2{}_{n+1} - Q^2{}_n}{A}\right) = \frac{(Q^2{}_{n+1} - Q^2{}_n)}{gA^2}$
Continuous head (energy) losses due to friction: Darcy-Weisbach equation	$H_{fn+1} = f_{n+1}\frac{s}{D}\frac{Q_{n+1}^{\,2}}{2gA^2}$ $f = 8\left[(8/R)^{12} + 1/(A+B)^{3/2}\right]^{1/12}$ $A = \left\{2.457\ln\left[1/\left((7/R)^{0.9} + 0.27(\varepsilon/D)\right)\right]\right\}^{16}$; $B = (37{,}530/R)^{16}$
Local or minor head losses due to individual outlet barb connection: Borda-Carnot & Belanger equation	h_k' = $h_c + h_e = \frac{(V_c - V_r)^2}{2g} + \frac{(V_r - V_{n+1})^2}{2g} = \left(\frac{1}{C_c r} - 1\right)^2\frac{V_{n+1}^{\,2}}{2g} = K\frac{V_{n+1}^{\,2}}{2g}$
Conservation of energy law & principle: Bernoulli's equation	$H_n + \frac{V_n^{\,2}}{2g} + z_n + h_{kn}' = H_{n+1} + \frac{V_{n+1}^{\,2}}{2g} + z_{n+1} + H_{fn+1} + \Delta H_{n+1} + h_{kn+1}'$

1.2. For Continuous-Nonuniform Outflow Approach

Table 2 shows analytical relationships for continuous-nonuniform outflow approach such as, flow rate or discharge distribution, energy gradient for velocity head, friction drop and pressure head distributions for both the uniform and non-uniform outflow approaches.

Table 2. Fundemental Principles & Governing Formulations for Continuous-Nonuniform Outflow Approach

Description of Basic Equation	***Formulation***
Pressure head - outflow (discharge) relationship	$q = kH^x \qquad q = \left(\frac{c}{s}\right)H_n^{\,y}$

Analytical Relationships fort he Inlet Flow Rate or Discharge, Velocity head gradient - Velocity head and friction slope or the slope of Energy-Gradient-Line r	$Q(l)=\left(N-\frac{l}{s}\right)\overline{q}=Q_I(1-i)$ $S_V(l)=\frac{2H_{VI}}{L}(i-1) \qquad H_V(l)=H_{VI}(1-i)^2$ $S_f(l)=\frac{dH_f(l)}{dl}=\frac{f}{D}H_V(l)=\frac{C}{D^n}Q^m(l)$ $f=c_1\left[R_I\right]^{m-2} \quad C=\frac{8c_1(\nu/4)^{2-m}}{g\pi^m}$
Energy Gradient for Total head losses due to friction - Total head losses due to friction - Friction Drop Ratio (R_i)	$H_f(l)=H_{f(L)}\left[1-(1-i)^{m+1}\right]$ $H_{f(L)}=FH_{f0}=\frac{1}{(m+1)}H_{f0}$ $H_{f0}=f\frac{L}{D}H_{VI}=C\frac{Q_I{}^m}{D^n}L \qquad R_i=H_f(l)/H_{f(L)}$ $H_{f(L)}=F_CH_{f0}$
Energy Gradient for Pressure Head Distribution for Uniform Outflow Approach	$H(l)=H_I+H_{VI}\left[1-(1-i)^2\right]-H_{f(L)}\left[1-(1-i)^{m+1}\right]-pi\Delta S$ $\Delta S=S_0L \;\; \overline{H}=H_I-(\overline{H}_f+p\overline{\Delta S})$ $\overline{\Delta S}=\frac{\Delta S}{2} \;\; \overline{H}_f=\frac{1}{L}\int_{l=0}^{l=L}dS=\frac{1}{L}\int_{l=0}^{l=L}H_f(l)dl=\left(\frac{m+1}{m+2}\right)H_{f(L)}$ $H(l)=\overline{H}+H_{VI}\left[1-(1-i)^2\right]+H_{f(L)}\left[(1-i)^{m+1}-\frac{1}{(m+2)}\right]-p\Delta S\left(i-\frac{1}{2}\right)$
Energy Gradient for Pressure Head Distribution for Non-uniform Outflow Approach	$H(l)=\overline{H}+H_{VI}\left[1-(1-i)^2\right]+H_{f(L)}\left[(1-i)^{m_\beta+1}-\frac{1}{(m_\beta+2)}\right]-p\Delta S\left(i-\frac{1}{2}\right)$ $\beta=1-3.322x\log\left[1+\frac{H_{VI}}{\overline{H}}+\lambda\frac{H_{f(L)}}{\overline{H}}+\frac{1}{4\overline{H}}(p\Delta S)\right]$ $\lambda=\left(\frac{1-0.5^{m+1}}{m+2}\right)$

2. Summary and Concluding Remarks

In this paper a comprehensive comparison test for the sake of comparison between the discrete-variable outflow and the analytical continuous-nonuniform outflow approaches for manifold fluid flow hydraulic computation. The basic governing formulations are examined for various design combinations and different line slope cases indicates that, the results of the proposed analytical approach had been found to be sufficiently accurate in comparison with the accurate numerical stepwise (SBS) method. The performance of this procedure for all design cases examined is satisfactory especially for a large range of variation in the uniformity coefficient U_C. The analytical development presented is preferred to the numerical techniques which need large amounts of execution time and complex computer operations.

Based on the presented study, the following conclusions are underlined:

1. The Christiansen's friction correction factor (F_C) accurately predicts the friction head loss since F_C is an accurate approximation of the stepwise correction factor (F_{sw}). The traditional correction factor (F) tends to underpredict systematically with respect to the F_C and F_{SW} for finite number of outlets;

particularly, as the number of outlets have the extreme small values, the deviation from these factors (F_C and F_{SW}) being more significant.

2. The friction drop ratio [$R_i = H_f(l) / H_{f(L)}$] is an important indicator to show the friction drop profile along a multiple outlets pipeline. Investigation of the friction head loss distribution along the laterals for both trickle and sprinkler irrigation system shows that, for zero slope case, at the middle outlet (emitter or sprinkler) about 85% of the total friction drop occurs, whereas half of the total friction drop occurs at about 22% of the full length of the lateral and, 75% of the total friction drop occurs at about 39% of the full length of the lateral, respectively. As a consequence, the friction drop ratio in the upstream section is more than that of downstream section of a multiple outlets pipeline.

3. The average head loss due to friction for the entire length of the lateral $(\overline{H}_f)$ and, for the upper half length of the lateral $(\overline{H}_{f0.5})$ are about 73% and 51% of the total friction drop at the downstream closed end of the lateral $(H_{f(L)})$, respectively, when the Darcy-Weisbach formula is used.

4. For zero slope case, in the middle of the lateral, total reduction (with respect to the initial values at the lateral inlet) in emitter pressure head and outflow are about 80% and 89% (which are approximately equal to the average values; $\overline{H}, \overline{q}$) and, in lateral flow rate is about 52% are occurred, respectively.

5. The pressure head profile for the nonuniform outflow concept indicates, the value of the pressure head (or outflow) at the middle outlet is independent from the various uphill and downhill uniform line slope conditions and, its value at this point is approximately equal to the average pressure head (or outflow).

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An Assessment for Pressure Profile along Manifold Considering Design Effect of Minor Head Losses

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ABSTRACT

Evaluation of energy losses is usually carried out by assuming the hypothesis that minor or local head losses can be neglected, even if the previous experimental studies indicated that minor losses due to outlet barb connection, can become a significant percentage of total energy losses as a consequence of the high number of emitters installed along manifold line. In this study, a simple analytical procedure is presented to evaluate the effect of minor losses which characterized by a coefficient α_i, expressing the amount of minor head losses as a fraction of the kinetic head, on manifold line design. According to both the design cases of without and including minor losses, the dimensionless design curves were developed for both the various manifold diameters and lengths. The results of two practical examples for designing either the diameter or the length indicated that, in some design cases, neglecting minor losses may lead to designs of the manifold diameter and length, in significant error.

Keywords: Water pipelines; Manifolds; Hydraulic design; Analysis; Outlets; Local losses.

1. Theoretical Background

The insertion of outlets along a manifold line modifies the flow streamlines, inducing local turbulence that results in additional local pressure losses, sometimes called minor losses, rather than the pipe friction losses. To accurately evaluate total energy losses in the pipeline, these minor losses due to the protrusion of outlet barb connections in the pipe wall that must be added to the friction losses occurring in the pipe (Jeppson 1982). In the past, numerous researches have been done on the hydraulic analysis manifold pipeline networks. As a matter of fact, a significant amount of these researches (Wu and Gitlin 1975; Wu 1992; Scaloppi and Allen 1993; Hathoot et al. 1993; Valiantzas 1998, 2002; Vallesquino and Luque-Escamilla 2001, Yıldırım 2006a) do not taken into account the effect of local losses in the design procedure, although the importance of minor losses has been recently presented in the experimental analysis (Howell and Barinas 1980; Al-Amoud 1995; Bagarello et al. 1997; Juana et al. 2002b; Provenzano and Pumo 2004; Provenzano et al. 2005), and the alternative analytical and numerical approaches (Jeppson 1982; Kang and Nishiyama 1996; Hathoot et al. 2000; Vallesquino and Luque-Escamilla 2002; Juana et al. 2002a, 2004; Yıldırım and Ağıralioğlu 2006; Yıldırım 2006b, c). This paper intends to present a simple analytical procedure for hydraulic design of manifold pipelines which takes into consideration the effect of minor head losses as well as the effect of the individual outlet outflow nonuniformity, the kinetic head change, the number of outlets, and different uniform line slopes, on the manifold line hydraulic computations.

2. Methodology

2.1. Energy Relationships

The presence of an individual outlet along manifold line, determines a local pressure loss λ_i, which is frequently expressed as a fraction α_i of the kinetic head (De Marchi 1954):

$$\lambda_i = \alpha_i \frac{V_I^2}{2g} \tag{1}$$

Although each individual outlet usually determines a small local head loss given by Eq. (1), the sum of all these minor losses in a lateral line can become significant, since outlet spacing can be very small and many outlets are inserted along pipeline (Howell and Barinas 1980; Al-Amoud 1995; Bagarello et al. 1997). The total minor head losses along the pipeline $H_{s(L)}$, through local singularities produced at outlet insertions of on-line, in-line and integrated outlets, can be evaluated from

$$H_{s(L)} = F_C N \lambda_i \tag{2}$$

Total energy losses along the lateral $H_{T(L)}$, includes friction and minor losses can be formulated by the following expression

$$H_{T(L)} = H_{f(L)} + H_{s(L)} = F_C \left[C \frac{Q_I^{\,m}}{D^n} L + \left(\frac{8}{\pi^2 g} \right) N \alpha_i \frac{Q_I^{\,2}}{D^4} \right] \tag{3}$$

The pressure head change from lateral inlet to a given length *l,* is a linear combination of the pressure head changes due to friction and uniform slope along the pipeline. Applying conservation of energy equation between the pipe segments *l* = 0 and *l* = *l,* then the pressure head profile, H*(l)*, can be expressed by:

$$H(l) = \overline{H} + H_{VI} \left\{ \left[1 - (1-i)^2 \right] + (\psi - 1) \left[1 - (1-i)^{m_\beta + 1} \right] \right\} + H_{f(L)} \left[(1-i)^{m_\beta + 1} - \frac{1}{(m_\beta + 2)} \right] - p \Delta S \left(i - \frac{1}{2} \right) \tag{4}$$

$$\psi = 1 - F_C N \alpha_i \tag{5}$$

in which H(*l*) = pressure head at a given section of length, *l* from the pipeline inlet (m); $\overline{H}$ = average pressure head for the entire of the pipeline; $H_{VI} = 8(N\overline{q})^2 / \pi^2 g D^4$ = velocity head at the pipeline inlet; $m_\beta = \beta \times m$ = improved value of the velocity exponent m; ψ = kinetic head reduction factor that accounts minor losses due to outlet barb insertions; $\Delta S = S_0 L$ = total head loss or gain due to change of elevation at the closed end of the pipeline; and S_0 = line slope assuming to be uniform along the pipeline. Noting that in this procedure, the slope of a downhill lateral is negative (*p* = -1), and the slope of an uphill lateral is positive (*p* = 1).

According to the analysis presented here, the energy grade line based on the nonuniform outflow concept is determined by Eq. (5) in which the velocity exponent m should be replaced by its improved value m_β ; then, the nonuniform outflow exponent β, can be approximated by the following relationship:

$$\beta = 1 - 3.322x \log \left[1 + \psi \frac{H_{VI}}{\overline{H}} + \lambda \frac{H_{f(L)}}{\overline{H}} + \frac{1}{4\overline{H}} (p \Delta S) \right]; \qquad \lambda = \left(\frac{1 - 0.5^{m+1}}{m+2} \right) \tag{6}$$

in which *β* = nonuniform outflow exponent then, the outflow from each multiple outlets will not be uniform along the pipeline.

2.2. Extreme Pressure Heads

Hydraulic design procedure for a manifold line with multiple outlets usually establishes the maximum difference in the outlet operating pressure heads along the pipeline is equal to the maximum allowed difference, ΔH. Wu (1992) proposed the following uniformity parameters (δ_H and δ_q) which can be specifically used as the design criteria in a submain unit.

$$\delta_H = \frac{\Delta H}{H_{\max}} = 1 - \frac{H_{\min}}{H_{\max}}; \qquad \delta_q = \frac{\Delta q}{q_{\max}} = 1 - \frac{q_{\min}}{q_{\max}}; \qquad \delta_q = 1 - (1 - \delta_H)^x \quad (7)$$

where δ_H = pressure head variation along a manifold line or in a submain unit; $\Delta H = H_{max} - H_{min}$ = maximum allowable difference in the outlet operating pressure head along the manifold; H_{max} and H_{min} = maximum and minimum values of outlet operating pressure head, respectively; δq = the outlet flow variation along manifold line or in a submain unit in submain irrigation system; $\Delta q = q_{max} - q_{min}$ = maximum allowable difference in the outflow along a submain line; q_{max} and q_{min} = maximum and minimum values of the outlet outflow, respectively.

In downhill lines, the location of the maximum and the minimum operating pressure heads is variable and depends on the relationship between the total energy gain or loss due to uniform slope and the total head losses due to pipe friction. The location of the maximum operating pressure head is found either to the first emitter near the lateral inlet ($i_{max} = \mu\ s/L$) or at the first emitter from the downstream closed end point ($i_{max} = 1.0$). In downhill lines, the current design procedure assumes the most usual case in which the maximum operating outlet pressure head occurs at the first outlet near the downstream closed end of the pipeline

$$i_{\max} = \frac{l_{\max}}{L} = 1 \quad (8a)$$

The location of the minimum operating pressure head is determined where the first derivative of the pressure head distribution given by Eq. (8a) is equal to zero. For simplification of this derivative procedure, the velocity head term can be omitted in this equation, then the location i_{min} where the minimum pressure head occurs, can be approximated by

$$i_{\min} = \frac{l_{\min}}{L} = 1 - \left[\frac{(-p\Delta S)}{F_S H_{f(L)} (m_\beta + 1)} \right]^{1/m_\beta} \quad (8b)$$

Using Eqs. (8a) and (8b) for i_{max} and i_{min} into Eq. (4) and, the result into Eq. (7), then for downhill slope case, the δ_H is expressed by

$$\delta_H = \frac{\left[H_{VI} \left[(1 - i_{\min})^2 + (\psi - 1)(1 - i_{\min})^{m_\beta + 1} \right] - H_{f(L)} (1 - i_{\min})^{m_\beta + 1} - p\Delta S (1 - i_{\min}) \right]}{H_{\max}} \quad (9a)$$

In uphill and zero slope conditions, the maximum operating pressure head is always located at the first outletfrom the lateral inlet ($i_{max} = \mu\ s/L$), whereas the minimum operating pressure head is always found at the first outlet from the downstream closed end of the pipeline ($i_{min} = 1.0$). Using the expressions for i_{max} and i_{min} in Eq. (4) and the result into Eq. (7), finally for uphill slope case, the δ_H can be similarly obtained as follows

$$\delta_H = \frac{\left[H_{f(L)} \theta^{m_\beta + 1} + H_{VI} \left[(1 - \psi) \theta^{m_\beta + 1} - \theta^2 \right] + p\Delta S \theta \right]}{H_{\max}} \quad (9b)$$

where $\vartheta = L_0/L$ = length ratio which is the percentage of the distance between the first and last outlets to the full length of the lateral; $L_0 = (N-1)s$ = length of the distance between the first and last outlets except for the inlet spacing, s_I; and $L = (N + \mu - 1)s$ = full length of the pipeline as defined in the previous section.

3. Design Application

Determine the percentages of total energy losses for two on-line outlet models (labyrinth and orifice-vortex) considering horizontal manifold having the internal diameter D = 13.37 mm and, by setting the outlet spacing, s, equal to the commercially available values of 0.3, 0.6, 0.9 and, 1.2 m, respectively. The following experimental relationships with minor loss coefficients for both the outlet models are considered as follows:

Labyrinth on-line outlet model: $q_{(lph)} = 1.32 \times \overline{H}_{(m)}^{0.5}$; $\overline{q} = 4.1$ (lph) ($\alpha_i = 0.34$)

Orifice-vortex on-line outlet model: $q_{(lph)} = 1.65 \times \overline{H}_{(m)}^{0.4}$; $\overline{q} = 4.2$ (lph) ($\alpha_i = 0.67$)

For both the outlet models examined, the length of the pipeline is increasing with increasing outlet spacing, whereas the number of outlets is decreasing. As a consequence of reducing the number of outletsand increasing the length of the manifold pipeline, the amount of minor losses is decreasing with increasing outlet spacing, whereas the pipe friction losses are increasing. For a certain manifold line design, therefore, the amount of minor losses, Φ_s, expressed as a percentage of the total energy losses, is decreasing with increasing outlet spacing, with values that can reach 33.5% and 50.0%, respectively, for the labyrinth and orifice-vortex outlet models, with the highest Φ_s value obtained for the outlet model characterized by the highest α_i.

4. Summary and Concluding Remarks

The proposed equations, taking into consideration the influence of local energy loss (i.e., minor loss), can be applied for various types of individual outlets, different flow regimes and different uniform line slope ranges. For any desired uniformity level, the procedure provides an opportunity to evaluate the influence of local energy loss, on the pipe geometric characteristics (pipe size and length), and on the corresponding hydraulic variables (operating inlet pressure head, downstream end pressure head and total energy loss). It may be concluded that, the performance of the presented technique is found to be sufficiently accurate in all cases examined even for uphill slope condition in comparison with a revised step-by-step (R-SBS) method. The procedure can be applied easily for practical purposes without an excessive calculation effort, and preferred instead for the numerical techniques which need a very long execution time and complex computer operation

Based on the presented research, the following conclusions are underlined:

1. The minor losses due to the outlet barb insertions increases with decreasing the manifold pipe inner diameter and increasing the manifold length in relation to the high number of outlets, located along the pipeline.

2. Reducing the number of outlets and increasing the length of the pipeline, the amount of minor losses decreases with increasing outlet spacing, whereas the pipe friction losses increase. For a certain manifold design, therefore, the amount of minor losses, Φ_s, expressed as a percentage of the total energy losses decreases with increasing outlet spacing, with values that can reach 33.5% and 50.0%, for the labyrinth and orifice-vortex outlet models, respectively, with the highest Φ_s value obtained for the outlet model characterized by the highest value of the minor loss coefficient, α_i.

3. Examination of the results of two practical design examples shows that neglecting the effect of minor losses may lead to design diameters in error by 25% and lengths in error by 7%, approximately.

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Impact of Deposition Parameters on the Properties of SnO_2 Thin Films for Perovskite Solar Cells

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ABSTRACT

Perovskite solar cells (PSCs) are set to transform the energy industry. Their remarkable power conversion efficiencies and cost-effective fabrication processes make them the obvious choice for the future. The electron transport layer (ETL) is a crucial component that significantly influences device performance. Here, tin oxide (SnO_2) has emerged as a highly promising candidate due to its excellent electrical conductivity, wide optical bandgap, and chemical stability. This study systematically investigates the effects of varying deposition pressures (5, 10, and 15 mTorr) and substrate temperatures (150 and 300°C) on the structural, optical, morphological, and electrical properties of SnO_2 thin films deposited with Physical Vapor Deposition (PVD). The SnO_2 films deposited at 300 °C and 15 mTorr performed best in all areas of investigation. They boasted the best combination of morphological uniformity and high optical transmittance. These findings are crucial for optimising SnO_2-based ETLs for high-efficiency PSCs and other optoelectronic devices.

Keywords: SnO_2, Electron Transport Layer, Perovskite Solar Cells.

1. Introduction

The development of perovskite solar cells (PSCs) has been a subject of considerable research interest in recent years due to their high-power conversion efficiencies (PCEs), low production costs, and ease of fabrication. One of the key components in PSCs is the electron transport layer (ETL), which facilitates the efficient extraction of electrons from the perovskite absorber layer and directs them toward the electrode (Damgacı &Seyhan, 2023). Among the various materials explored for use as ETLs, tin oxide (SnO_2) has attracted significant attention due to its favorable electrical conductivity, optical transparency, and excellent chemical stability. SnO_2 exhibits a wide optical band gap (≈3.6–4.0 eV), excellent electrical conductivity, and high chemical and thermal stability (Liu et al., 2003).

The deposition method of SnO_2 strongly influences its structural, optical, and electronic properties. While solution processing methods have been widely adopted, physical vapor deposition (PVD) has recently gained significant interest due to its better control over film thickness, uniformity, and reproducibility (Gupta et al., 2004). The performance of SnO_2 as an ETL is influenced by its structural, optical, and electrical properties, which can be tailored by adjusting the deposition parameters during thin film fabrication (Kashyap et al., 2009). In this context, the deposition of SnO_2 films using PVD under varying conditions, such as pressure and temperature, offers a route to optimize these properties for enhanced PSC performance. Tao and the research group investigated the impact of sputtering power on the performance of SnO_2 ETLs deposited via radio frequency magnetron sputtering at room temperature for PSCs. They found that reducing the sputtering power from 120 W to 60 W lowered the surface roughness of the SnO_2 films, improved the ETL/perovskite interface, and enhanced charge extraction. As

a result, the power conversion efficiency increased from 8.19% to 12.58%. This study emphasizes the significance of controlling PVD parameters to maximize ETL quality and device performance (Tao et al., 2019). Another research group investigated the impact of working gas flow rate and oxygen content on the growth of intrinsic SnO_2 (i-SnO_2) layers during RF sputtering. Their findings revealed that the films had an amorphous-like nanocrystalline structure with surface roughness values ranging from 1.715 to 3.936 nm. XPS analysis also indicated the presence of point defects such as tin interstitials and oxygen vacancies, which significantly influence the film's electronic properties and interface quality (Al-Mansoori et al., 2017). Gong et al. (2019) performed a comprehensive investigation into the temperature-dependent optical characteristics of SnO_2 thin films utilizing spectroscopic ellipsometry. The study revealed that modifications in substrate temperature induced substantial variations in the optical transmittance spectra and refractive index dispersion, attributable to temperature-mediated alterations in film densification, lattice ordering, and defect state distribution.

In this study, SnO_2 thin films were deposited using the PVD method at two different substrate temperatures (150 °C and 300 °C) and under three distinct chamber pressures (5, 10, and 15 mTorr) to systematically investigate the influence of deposition conditions on the morphological and optical properties of the films for potential use as ETLs in perovskite solar cells.

2. Materials and Method

SnO_2 thin films were deposited onto soda-lime glass substrates sized 2.5 × 2.5 cm^2 and with a thickness of 1.1 mm using a radio frequency (RF) magnetron sputtering system. The sputtering target used was high-purity SnO_2 (99.999%, 5N). The sputtering process was conducted at a target rotation speed of 8 rpm, producing films with an average thickness of approximately 100 nm. The PVD coating method was chosen because it provides precise control over deposition rate and film thickness.

2.1. Thin Film Deposition

To evaluate the influence of ambient pressure on film properties, depositions were performed under three different working pressures: 5, 10, and 15 mTorr. Additionally, the substrate temperature was systematically 150 °C and 300 °C to examine the impact of temperature on the optical and surface morphology properties of the SnO_2 films.

Figure 1. Fabrication of SnO_2 Thin Films Using Physical Vapor Deposition

2.2. Characterization

To evaluate the morphological and optical properties of the SnO_2 thin films, Atomic Force Microscopy (AFM) and UV-Vis spectroscopy analyses were conducted. AFM (Innova, Bruker) was utilized to investigate the surface topography and quantify the root mean square (RMS) roughness of the films with high spatial resolution. Surface roughness plays a crucial role in determining the interface quality of thin films, particularly in optoelectronic device applications. Optical characterization was performed using a UV-Vis spectrometer (Shimadzu 3600i Plus) to determine the optical transmittance and estimate the optical

bandgap of the films. These analyses were instrumental in correlating the surface and optical properties of the SnO_2 layers with varying deposition conditions.

3. Results and Discussion

The optical properties of the SnO_2 thin films, as characterized by their UV-Vis transmission spectra, are highly dependent on the deposition parameters, specifically substrate temperature and deposition pressure. Similarly, AFM characterization reveals that deposition parameters, including substrate temperature and pressure, significantly influence the surface morphology and roughness of SnO_2 thin films. Lower roughness values, which are achieved under optimized conditions, encourage the formation of uniform SnO_2 ETLs and reduce interfacial recombination losses.

3.1. Impact of Deposition Parameters on Optical Properties

A definitive correlation exists between the substrate temperature and the optical properties of the deposited SnO_2 thin films, with deposition pressure also playing a significant role (Bin et al., 2021; Nwanna et al., 2022). Films fabricated at an elevated substrate temperature of 300°C exhibit substantially higher average transmittance values across the visible wavelength range compared to those deposited at 150°C, and this improvement is further influenced by the deposition pressure, where coatings performed at 5, 10, and 15 mTorr show notable variations in optical transmission and film quality.

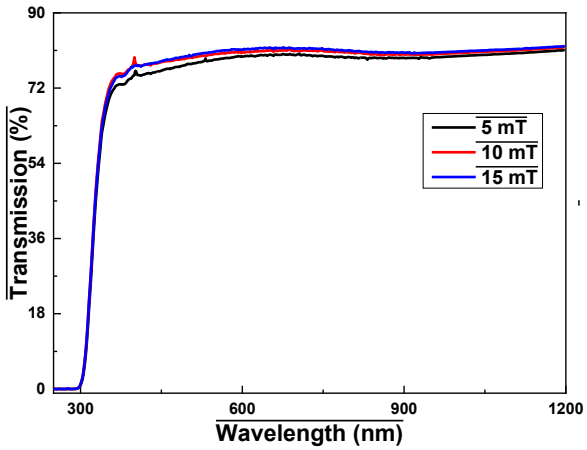

Figure 2. Transmission spectra of SnO_2 thin films at 150 °C under 5, 10, and 15 mTorr

The SnO_2 thin films deposited at 150°C exhibit average transmittance values ranging from 78.28% to 80.18% within the 400-700 nm wavelength region. A gradual increase in optical transmittance is observed with rising deposition pressure, reaching its maximum at 15 mTorr. This finding suggests that, even under relatively low-temperature conditions, the deposition pressure exerts a substantial influence on enhancing the quality of the film by affecting its density and crystallinity. It can thus be concluded that an increase in pressure at 150°C results in enhanced optical transparency and a decrease in defect concentration within the films.

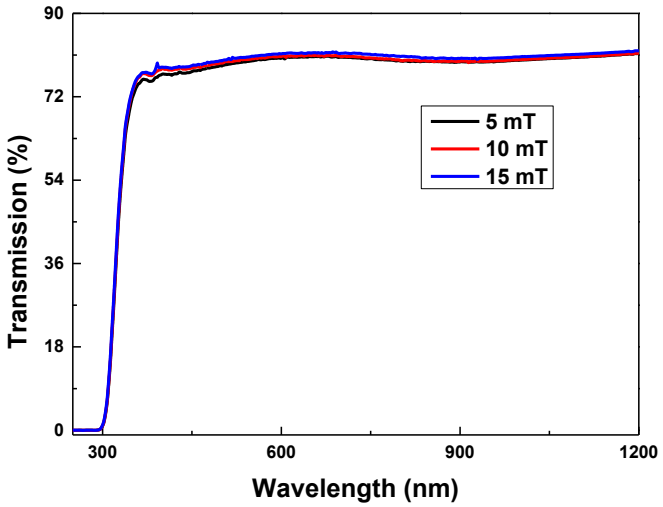

Figure 3. Transmission spectra of SnO_2 thin films at 300 °C under 5, 10, and 15 mTorr

At 300 °C, the SnO_2 films exhibit slightly higher transmittance values, ranging from 79.28% to 80.31%. In a manner analogous to the lower-temperature condition, an incremental increase in transmittance is observed with increasing pressure, reaching a maximum at 15 mTorr. However, the magnitude of this improvement is less pronounced compared to that at 150 °C. This indicates that elevated substrate temperatures already promote enhanced crystallinity and surface ordering, rendering the effect of deposition pressure on optical properties relatively minor.

3.2. Effect of Deposition Parameters on Surface Topography of Thin Films

A comparison of AFM results at 150 °C and 300 °C indicates that higher substrate temperature generally promotes smoother and more uniform films at low (5 mTorr) and high (15 mTorr) pressures in Figure 4. However, at 10 mTorr, both temperatures lead to pronounced roughness, with the effect being more severe at 300 °C. These findings suggest that substrate temperature and deposition pressure must be carefully optimized together to achieve homogeneous SnO_2 thin films suitable for device integration. Overall, the AFM analysis emphasizes that deposition parameters, especially substrate temperature and pressure, critically determine nanoscale roughness, which in turn plays a decisive role in the optoelectronic performance of SnO_2-based electron transport layers.

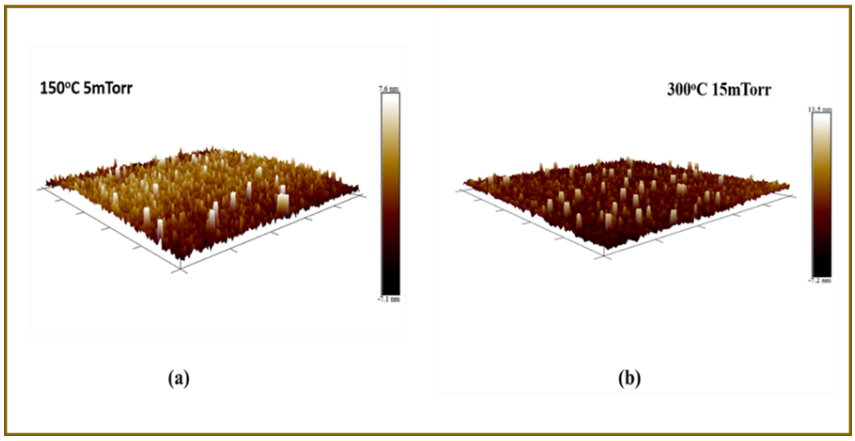

Figure 4. AFM three-dimensional surface morphology images of SnO_2 thin films deposited under different conditions: (a) at 150 °C and 5 mTorr; (b) at 300 °C and 15 mTorr

4. Conclusions

These findings suggest that controlling the deposition temperature and pressure can optimize SnO_2 films for specific optoelectronic and sensing applications. The SnO_2 thin film deposited at 15 mTorr and annealed at 300 °C exhibited the most favorable surface characteristics for photovoltaic applications, offering an optimal combination of morphological uniformity, structural continuity, and interfacial compatibility with the perovskite absorber layer.

Future studies will investigate the role of additional factors, such as doping and film thickness, on the band gap properties of SnO_2.

5. Acknowledge

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Artificial Intelligence Applications in Nutrition and Dietetics: Recent Advances and Ethical Considerations

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ABSTRACT

The integration of artificial intelligence (AI) technologies into health sciences has led to remarkable advancements, particularly in the field of nutrition and dietetics. This review examines the definition, historical development, and current role of AI in healthcare, with a focus on personalized nutrition recommendations, mobile applications, glucose monitoring systems, and AI-powered chatbots. The potential of tools in nutritional planning is discussed alongside the increasing prevalence of clinical decision support systems and user-friendly digital platforms. Additionally, this study addresses ethical concerns such as patient privacy, data security, and the implications of AI applications in healthcare ethics. Findings from the literature suggest that AI contributes significantly to the practice of nutrition and dietetics; however, its adoption must be approached cautiously within ethical, legal, and cultural frameworks. The study emphasizes the need for greater support and awareness in the local development and implementation of such technologies.

Keywords : Artificial intelligence, ethics, mobile health applications, nutrition and dietetic, personalized nutrition

Beslenme ve Diyetetikte Yapay Zekâ Uygulamaları: Güncel Gelişmeler ve Etik Yaklaşımlar

ÖZET

Yapay zekâ (YZ) teknolojilerinin sağlık bilimlerine entegrasyonu, son yıllarda özellikle beslenme ve diyetetik alanında dikkat çekici gelişmelere yol açmıştır. Bu derleme çalışmasında, yapay zekânın tanımı, tarihsel gelişimi ve sağlık sektöründeki yeri incelenmiş; özellikle bireyselleştirilmiş beslenme önerileri, mobil uygulamalar, glukoz takip sistemleri ve sohbet robotları gibi teknolojilerin diyetetik uygulamalardaki yansımaları ele alınmıştır. Yapay zekâ destekli araçların beslenme planlamasında sunduğu potansiyel, klinik karar destek sistemlerinin geliştirilmesi ve kullanıcı-dostu dijital platformların yaygınlaşmasıyla birlikte değerlendirilmektedir. Ayrıca, hasta mahremiyeti, veri güvenliği ve etik ilkeler bağlamında yapay zekâ uygulamalarının yol açabileceği riskler de tartışılmıştır. Literatürden elde edilen bulgular, yapay zekânın beslenme ve diyetetik pratiğine birçok yönden katkı sunduğunu; ancak etik, hukuki ve kültürel çerçevede dikkatli bir şekilde ele alınması gerektiğini ortaya koymaktadır. Çalışma, bu teknolojilerin yerel ölçekte geliştirilmesi ve uygulanması için daha fazla destek ve farkındalık oluşturulması gerektiğini vurgulamaktadır.

Anahtar Kelimeler : Beslenme ve diyetetik, etik, kişiselleştirilmiş beslenme, mobil sağlık uygulamaları, yapay zekâ

1. Introduction

Rapid technological advancements have brought about fundamental transformations in many areas of life, including the healthcare sector. At the heart of this transformation lies artificial intelligence (AI), which has started to play a significant role in recent years, particularly in the field of nutrition and dietetics. From wearable technologies to personalized dietary recommendations, and from digital health

applications to big data analysis, AI systems are reshaping the decision-making processes of both healthcare professionals and individuals [1, 2].

The concept of intelligence has been defined from various perspectives by different disciplines throughout history. According to Gardner, intelligence is a multidimensional construct that can be developed through environment, education, and experience [3]. Wang (2006), on the other hand, defines intelligence as the ability to find sufficiently good solutions rather than always the most accurate one [4]. In this context, artificial intelligence is a general term for systems that can mimic the cognitive functions of human intelligence, learn, adapt, and solve problems [5, 6].

The core objective of AI is for computers to exhibit human-like intelligent behavior. In this regard, Alan Turing laid the groundwork for the field of artificial intelligence in his 1950 paper, "Computing Machinery and Intelligence," where he proposed the "Turing Test" to measure the capacity of machines to think [7]. The term "artificial intelligence" was first formally defined at the 1956 Dartmouth Conference, which systematized scientific research in this field [8]. Over the years, with applications like IBM's Deep Blue program (1997), Watson (2011), and Google DeepMind's AlphaGo Zero, AI has enhanced its proficiency across various domains [9, 10].

AI applications in healthcare have transformed numerous processes, such as the analysis of patient data, the development of diagnostic and treatment recommendations, and the creation of clinical decision support systems [11]. In the field of nutrition and dietetics, AI-powered tools analyze individuals' dietary histories to offer personalized recommendations, create diet plans, and play a supportive role in patient counseling [12, 13]. However, the ethical, legal, and social dimensions of these technologies have not yet been fully resolved [14].

This article evaluates AI applications in the field of nutrition and dietetics, along with their historical background and technological infrastructure. Additionally, it discusses the ethical aspects and potential risks of these applications in light of the current literature.

2. Current AI Applications in Nutrition and Dietetics

In the field of nutrition and dietetics, artificial intelligence (AI) technologies are used across a wide range of applications, from creating individualized nutrition programs to the early diagnosis of diseases and health monitoring. In recent years, thanks to advances in big data analysis and machine learning techniques, optimized nutritional recommendations are being developed by considering multiple factors such as individuals' genetic makeup, metabolic characteristics, lifestyle, and health history [15].

Mobile apps and wearable devices track users' daily eating habits and analyze crucial data like calorie intake, and macronutrient and micronutrient balance in real time. These technologies help identify vitamin and mineral deficiencies and provide early warnings that can prevent the development of chronic diseases like obesity and diabetes [16]. For example, AI algorithms can track parameters such as a person’s blood glucose levels, activity level, and food intake to offer personalized recommendations for diabetes management [17].

In the research domain, AI techniques allow for drawing meaningful conclusions from large-scale nutritional data. Machine learning methods are used to decipher the complex relationships between nutrition and health, which in turn enables more effective planning of public health policies [18]. Additionally, AI-powered analyses can help detect changes in nutritional trends and risk factors more quickly.

Applications like Health Master Global are AI-supported tools that aim to reduce error rates in diagnosis, treatment, and monitoring processes by leveraging thousands of algorithms, serving a broad spectrum of purposes [19].

Applications like Cronometer, MyFitnessPal, and Noom allow users to receive personalized support for calorie tracking, macronutrient analysis, and behavioral changes. In a randomized controlled trial by Turner-McGrievy et al. (2015), the effect of the MyFitnessPal application on weight loss among young adults was evaluated. The research showed that participants who used the app lost more weight compared to those who only received information. This result demonstrates that the application directly

contributes to weight management and nutritional awareness through personalized support and data tracking [20]. Similarly, a study by Kull et al. (2020) examined the psychological and behavioral change approaches adopted by apps like Noom to improve dietary habits in a sustainable way. They noted that these applications do not focus solely on calorie tracking but also help users understand the psychological reasons behind their eating behaviors, thus encouraging long-term behavioral change [21].

Applications such as the Glooko Device System and the WellDoc Diabetes Manager System simplify management processes for both patients and healthcare professionals by monitoring blood glucose data [22].

However, the ethical dimensions of AI applications are also of significant importance. Ongoing discussions revolve around data privacy, algorithmic biases, and situations where the human factor should not be entirely eliminated. The responsible and ethical use of AI in healthcare is critically important for the sustainability of its benefits [23].

Large language models like ChatGPT have the potential to offer personalized solutions for nutrition-related conditions such as obesity, diabetes, and cardiovascular diseases. These platforms can analyze patients' physical characteristics and medical history to provide tailored nutrition plans, exercise recommendations, and even psychological support options [12].

For instance, ChatGPT can take into account a description of the foods in a user's pantry or refrigerator and instruct them on how to eat healthily, prescribe diets, plan recipes, or provide a shopping list. To test the capabilities of ChatGPT, Chatelan et al., (2023) requested it to define the ideal diet for a person with type 2 diabetes, as shown in Figure 1 [13].

Our prompt:

What are the key components of an optimal dietary regimen for an individual with Type 2 diabetes?

ChatGPT answer:

The primary objective of a dietary regimen for individuals with Type 2 diabetes is to achieve optimal glycemic control and enhance overall metabolic health.

1. Carbohydrate intake: Carbohydrate consumption is a primary determinant of postprandial blood glucose levels, necessitating careful monitoring and regulation of their intake. The preference should be given to complex carbohydrates, such as whole grains, vegetables, and fruits, over simple carbohydrates like refined grains and sugary foods. This approach is supported by the role of dietary fiber in complex carbohydrates, which helps to modulate glycemic response and stabilize blood sugar levels.

2. Protein intake: Proteins are fundamental to the synthesis and repair of tissues and the preservation of lean muscle mass. Recommended sources include lean meats, fish, legumes, nuts, and low-fat dairy products.

3. Fat intake: While fat consumption requires moderation, the inclusion of healthy fats such as those present in nuts, seeds, and fish can beneficially influence both glycemic control and serum cholesterol levels.

Figure 1: ChatGPT's response regarding the ideal diet for patients/clients with Type 2 diabetes [13].

According to an AI chatbot, the recommendations provided for an individual with Type 2 diabetes seem generally successful and accurate. While a dietitian might specifically differentiate between rice and bulgur, ChatGPT appears to have overlooked this or was inadequate in its screening. It's also noted that ChatGPT did not create a separate heading for vegetables and fruits. Considering that dietitians often

include fruits as a snack and recommend that diabetics not consume them alone, it is thought that this information should have been addressed. Even though it lacks a lot of detail, the general portfolio it created seems successful.

However, the accuracy and reliability of information provided by AI chatbots are critically important. As seen in the study by Chatelan et al. (2023), while ChatGPT's general recommendations for individuals with Type 2 diabetes are successful, it cannot fully replicate the detailed and individualized approach of a dietitian [13].

3. Data Analytics and Machine Learning in Nutrition and Dietetics

Data analytics enables the integration and analysis of data collected from various sources, such as food consumption habits, metabolic parameters, and genetic information. This makes it possible to optimize dietary plans and more accurately predict disease risks [24]. For example, in the prevention and management of metabolic diseases like Type 2 diabetes and obesity, machine learning-based models can learn from patient data to recommend individualized interventions [25].

Another significant application of machine learning is the automatic classification of food content and consumption patterns. By using image processing and natural language processing techniques, automation can be achieved in dietary tracking and food analysis, thereby reducing the need for manual data entry [26].

Clinical nutrition management is a critical field for determining patients' nutritional needs based on their individual health conditions and supporting treatment processes. AI technologies provide clinicians with decision support systems in this process, allowing treatment plans to become more effective and personalized [27].

AI-based systems analyze a wide range of data, including patients' medical records, laboratory results, nutritional habits, and metabolic parameters, to automatically create clinical nutrition plans. This contributes to a reduction in mortality and morbidity rates, especially for patients receiving nutritional support in intensive care and chronic disease management [28].

Machine learning and deep learning algorithms, in particular, offer significant advantages in modeling complex variables such as patients' energy needs and macro- and micronutrient requirements. These technologies can perform continuously updated analyses to monitor the effectiveness of nutritional therapies and optimize interventions when necessary [29].

Data analytics and machine learning present significant opportunities in the field of nutrition and dietetics for creating personalized nutrition plans, early diagnosis of disease risks, and overall health improvement. The future development of these technologies will lead to revolutionary advancements in nutritional science [24].

4. Ethical and Social Dimensions

With the increasing use of AI applications in nutrition and dietetics, ethical responsibilities are becoming more and more crucial. Data privacy is one of the most critical issues in AI applications. Nutritional data includes sensitive information such as individuals' health history, genetic information, and lifestyle habits, so this data must be protected from unauthorized access. Additionally, AI systems must process this data in accordance with ethical standards to ensure the protection of individuals' right to privacy [30].

Algorithmic bias and the problem of justice are also significant ethical issues. Due to imbalances in training data, AI models may make biased decisions against certain groups. In nutrition and dietetics, this can specifically prevent different socioeconomic and ethnic groups from receiving equitable services. Therefore, data sets must be diversified and continuously audited to ensure algorithms are fair and inclusive [31].

Furthermore, the societal impacts of AI applications must be considered. As automation increases, the transformation or reduction of certain professions may change the roles of nutrition professionals. In

this transformation process, updating professional education and acquiring skills compatible with AI are socially important [32].

Moreover, it is essential that human oversight continues in the decision-making processes of AI applications. The recommendations from AI should be blended with the expertise of dietitians and healthcare professionals to prevent misinformation and potential harm [33]. AI should be used as a supportive tool, and the process of empathy and communication between a patient or user and a human should not be overlooked.

The decision-making processes of AI systems must be transparent and accountable. In clinical decision support systems, the ability for patients and healthcare workers to understand AI recommendations contributes to increasing trust in these systems [34].

5. The Future of AI and Nutritional Science

The application of artificial intelligence (AI) technologies in nutritional science has gained significant momentum in recent years, and these developments are poised to play a decisive role in the future transformation of the field. The development of personalized nutrition approaches is being made possible through the high-volume analysis of genomic, metabolomic, and phenotypic data, with the goal of minimizing disease risks and ensuring optimal health [35].

Thanks to advanced biosensors, mobile health apps, and wearable technologies, it is becoming possible to monitor food intake, metabolic status, and physiological parameters in real time. This data, processed by AI algorithms, allows for the provision of instant feedback on individuals' eating habits and the dynamic adaptation of nutritional strategies [36].

Machine learning and deep learning techniques are crucial for interpreting complex biological data and modeling the interactions between nutrition and health [37]. These technologies integrate individuals' genetic profiles, microbiome composition, and lifestyle factors to develop highly specific dietary recommendations. In this way, traditional generalized approaches are being replaced by more precise and effective interventions.

In tele-dietetics, AI-based systems are emerging as effective tools for monitoring patient compliance, diet quality, and nutritional behaviors [38]. These systems empower dietitians' decision-support mechanisms, contributing to the optimization of personalized nutrition plans.

Furthermore, with the help of AI-powered devices and applications, the instant tracking of food intake, energy expenditure, and health parameters will become feasible, making them an important tool for the prevention and management of chronic diseases [39].

6. Conclusion

The integration of artificial intelligence (AI) technologies into the field of nutrition and dietetics is leading to revolutionary changes in healthcare services. Today, AI is being used in numerous applications, from personalized nutritional recommendations to clinical nutrition management, through methods such as big data analysis, machine learning, and natural language processing [40, 41]. These technologies provide a more precise and objective assessment of nutritional status, making significant contributions to the prevention and management of diseases [42].

However, the proliferation of AI applications necessitates a comprehensive consideration of their ethical and social dimensions. Patient privacy and data security are among the most fundamental concerns. The potential for AI algorithms to exhibit data bias and the requirement for a high-tech infrastructure can undermine the principle of equal access to healthcare services. Furthermore, planning for the education and adaptation of nutritionists and healthcare professionals is crucial so they can work effectively with AI-supported systems [43].

In the future, the collaboration between AI and nutritional science will deepen through multidisciplinary approaches, enabling the early diagnosis of diseases, treatment planning, and the development of personalized health strategies [44]. These advancements will also be influential in shaping public health policies and creating sustainable healthcare models. Nevertheless, the long-term success of

the technology depends on its development and implementation within an ethical and socially responsible framework.

In conclusion, the potential benefits of AI applications in the field of nutrition and dietetics are vast, but realizing these benefits depends on technological innovations advancing in a way that aligns with ethical standards. Therefore, the joint efforts of researchers, healthcare professionals, and policymakers will make it possible to use the opportunities provided by AI effectively and equitably.

In Turkey, increasing and supporting applications in this field will not only elevate the quality of healthcare services but also enhance the country's competitiveness in health technologies. To this end, the development of AI applications should be encouraged, adequate financial support should be provided for these projects, and the confidentiality of patient data should be guaranteed within an ethical framework.

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Süperpiksel Özellikleri Kullanılarak Asfalt Karışımı Görüntülerinin Makine Öğrenmesine Dayalı Sınıflandırılması

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ÖZET

Bu çalışma, asfalt karışımı görüntülerinde piksellerin agrega veya arka plan sınıfına ait olup olmadığını belirlemeye yönelik makine öğrenmesi temelli bir yaklaşım sunmaktadır. Süperpiksel segmentasyonu ile elde edilen geometrik, yoğunluk ve renk tabanlı öznitelikler sınıflandırma sürecinde kullanılmıştır. Lojistik Regresyon (LR), Rastgele Orman (RF), k-En Yakın Komşu (KNN) ve Destek Vektör Makineleri (SVM) algoritmaları uygulanmış ve performansları doğruluk, kesinlik, duyarlılık, F1 skoru, ROC-AUC ve PR-AUC ölçütleriyle değerlendirilmiştir. Ayrıca karışıklık matrisleri ve ROC eğrileri karşılaştırılmıştır. Sonuçlara göre, KNN modeli en yüksek doğruluğu (%92,25) sağlarken, RF modeli en yüksek duyarlılık (%92,77) ve ROC-AUC (0,975) değerlerine ulaşmıştır. Bulgular, topluluk (ensemble) ve komşuluk tabanlı algoritmaların agrega–arka plan ayrımında güçlü bir performans sergilediğini ve asfalt karışımı görüntü analizinde güvenilir bir hesaplamalı yöntem sunduğunu göstermektedir.

Anahtar Kelimeler : Piksel sınıflandırma, Asfalt karışımı görüntüleri, Agrega tespiti, Makine öğrenmesi, Süperpiksel öznitelikleri.

Machine Learning-Based Classification of Asphalt Mixture Images Using Superpixel Features

ABSTRACT

This study presents a machine learning-based framework for pixel-level classification of aggregate and background regions in asphalt mixture images. Using a superpixel segmentation approach, geometric, intensity, and color-related descriptors were extracted as features. Four supervised classifiers—Logistic Regression (LR), Random Forest (RF), k-Nearest Neighbors (KNN), and Support Vector Machines (SVM)—were trained and evaluated. Model performance was assessed through accuracy, precision, sensitivity, F1-score, ROC-AUC, and PR-AUC, along with confusion matrices and ROC curve comparisons. The results revealed that KNN achieved the highest accuracy (92.25%), while RF provided the best sensitivity (92.77%) and ROC-AUC (0.975). These findings demonstrate that ensemble- and neighborhood-based classifiers deliver strong discrimination between aggregate and background pixels, offering a reliable computational framework for asphalt mixture image analysis.

Keywords: Pixel classification, Asphalt mixture images, Aggregate detection, Machine learning, Superpixel features.

1.Introduction

Asphalt represents one of the most fundamental components of modern transportation infrastructure, directly influencing the performance of road pavements [1]. The durability, safety, and cost-effectiveness of asphalt pavements largely depend on the quality of adhesion between bitumen and aggregates. While bitumen serves as a binding agent, aggregates constitute the primary structural material providing mechanical strength [2]. Inadequate bonding between these two components leads to a phenomenon known as stripping, which occurs predominantly when water penetrates the bitumen–aggregate interface and severely compromises pavement durability [3]. The stripping percentage is therefore a critical indicator for evaluating pavement service life and traffic safety. High stripping levels

result in surface distress, cracking, and pothole formation, ultimately increasing maintenance costs and jeopardizing road safety [4]. Consequently, preventing stripping is not merely a technical necessity but also an economic and environmental imperative. Strategies such as the use of anti-stripping additives, proper aggregate selection, and bitumen modification can enhance adhesion and minimize the risk of stripping. The prevention of stripping extends pavement lifespan, reduces maintenance and repair costs, and contributes to enhanced driving comfort, reduced fuel consumption, and environmental sustainability [5]. Hence, strengthening bitumen–aggregate adhesion is of strategic significance not only from an engineering standpoint but also in terms of economic and societal benefits. Stripping percentage serves as a fundamental parameter for quantitatively evaluating adhesion between bitumen and aggregates. Typically, asphalt specimens prepared under laboratory conditions are subjected to water exposure, during which they are immersed for a specified period and temperature. The extent of bitumen film detachment from the aggregate surface is subsequently determined through visual inspection or image analysis techniques. Stripping percentage is then calculated as the ratio of the bitumen-covered surface to the total aggregate surface area, expressed as a percentage [6].

Traditional full-reference image quality assessment (IQA) algorithms are primarily based on patch-level feature comparisons, which often fail to capture semantic coherence. In contrast, the superpixel approach groups pixels with similar visual properties into perceptually meaningful regions, enabling more reliable assessments [7]. Motivated by this concept, Sun et al. [8] introduced a novel superpixel-based similarity index and evaluated image quality through superpixel luminance similarity, chrominance similarity, and pixel gradient similarity. By incorporating superpixel-based regional gradient consistency into the assessment, the method demonstrated improved detection of structural distortions. The findings indicated that the proposed approach achieved competitive performance compared to state-of-the-art IQA metrics. Advances in Earth observation satellites have increased data volume and dimensionality, creating challenges for environmental monitoring. To overcome these, Estefania et al. [9] applied a superpixel-based dimensionality reduction on NDVI time series (2002–2022), achieving over 9% accuracy improvement while reducing errors from coarse-resolution data by up to 25%. This demonstrates the efficiency of superpixel preprocessing in minimizing subpixel heterogeneity for large-scale applications.

Recent studies have shown the potential of recycled plastics in improving the rheological performance of asphalt binders. Salehi et al. [10] employed ensemble machine learning models to predict the behavior of recycled plastic modified bitumen (RPMB), reporting high accuracy (R^2 = 0.98 for complex shear modulus, R^2 = 0.93 for phase angle). The analysis highlighted temperature, loading frequency, polymer content, and base bitumen penetration as the most influential factors, offering practical guidance for mixture design. Image-based methods are increasingly used for asphalt mixture evaluation, yet accuracy depends on acquisition and analysis standards. Shi et al. [11] emphasized that camera tilt (<15°), sieve passing rate errors (<5%), and at least ten cross-sectional images are essential for reliable contact parameter analysis, providing practical guidance for improving precision. Additives are widely used to improve bitumen performance and predicting viscoelastic parameters such as G* and δ is crucial. Hosseini et al [12] demonstrated that Ensemble Regression provides superior predictive accuracy based on DSR data, underscoring the value of machine learning for evaluating modified bitumen.

Recent developments have also proposed a multi-phase image segmentation methodology grounded in fuzzy superpixel decomposition, aggregation, and merging. Within this approach, dense fuzzy superpixels are generated using a variational fuzzy decomposition algorithm, and refined regions are extracted through hierarchical normalized cuts. These refined superpixels are projected into low-dimensional feature spaces via multidimensional scaling, followed by mean-shift-based merging with adaptive spatial bandwidth adjustment. Leveraging both the structural constraints of fuzzy superpixels and their spatial affinities, this method enhances the accuracy of segmentation. Comparative evaluations have demonstrated that the approach outperforms existing techniques, yielding superior segmentation quality [13].

In the present study, images of nine different samples were segmented into perceptually meaningful regions using the superpixel method. A comprehensive set of geometric and color-based features—including distance to center, area, compactness, mean intensity, neighbor color difference, foreground color difference, median hue (H), median saturation (S), median value (V), and black ratio—was extracted from each region. Each region was subsequently labeled as either background or non-background. Finally,

multiple machine learning algorithms were applied for classification, and their predictive performances were systematically compared. This methodological framework provides a robust basis for assessing the effectiveness of superpixel-based feature extraction in conjunction with machine learning models for reliable image classification.

2. Material and Method

The overall workflow of the proposed methodology is illustrated in Figure 1. The process begins with the acquisition of sample images, which are subsequently partitioned into homogeneous regions using a superpixel-based segmentation technique. From these segmented regions, a set of geometric and color-based features is extracted to represent both spatial and intensity-related characteristics. These features serve as the input for a machine learning framework designed to classify regions into background and aggregate classes. Finally, the performance of different classifiers is systematically evaluated, and the best-performing model is identified. The methodological framework is structured into three main components: Superpixel-Based Segmentation, Machine Learning Framework, and Performance Evaluation, which are described in detail in the following subsections.

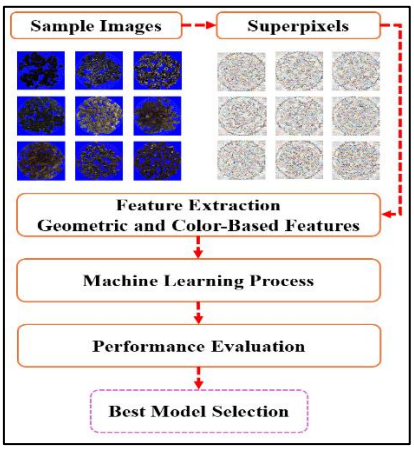

Figure 5. Flowchart of the methodology

2.1. Superpixel-Based Segmentation

In this study, images obtained from nine different samples were segmented into perceptually coherent regions using a superpixel-based approach (Fig. 2). This method groups pixels with similar visual characteristics, thereby preserving local variations in both geometry and color while maintaining semantic consistency.

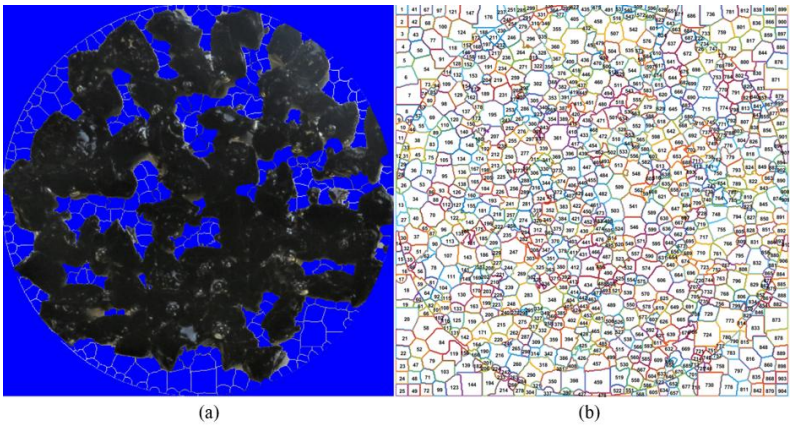

Figure 6. Superpixel segmentation of sample images: (a) original sample with superpixel boundaries (b) indexed superpixel

As shown in Figure 2, the original aggregate image (a) was partitioned into superpixels (b), where each region represents a homogeneous cluster of pixels. From these superpixels, a comprehensive set of

geometric and color-based features was extracted, including distance to center, area, compactness, mean intensity, neighbor color difference, foreground color difference, median hue (H), median saturation (S), median value (V), and black ratio. These descriptors provided the fundamental input variables for the subsequent machine learning framework.

2.2. Machine Learning Framework

The classification of superpixel regions into background and aggregate classes was performed using multiple supervised machine learning algorithms, each representing different methodological families to allow for a comprehensive comparison. Logistic Regression (LR) was selected as a baseline linear model, while Support Vector Machine (SVM) was employed to capture non-linear decision boundaries. Random Forest (RF), as a representative ensemble method, was included due to its robustness in handling feature interactions and noise. In addition, the k-Nearest Neighbors (KNN) algorithm was tested as a distance-based non-parametric classifier. To ensure rigorous and unbiased model evaluation, a nested cross-validation strategy was employed. In the outer loop, the Leave-One-Image-Out (LOIO) procedure was adopted, where the samples belonging to one image were completely withheld for testing, and the remaining images were used for training. This approach prevents data leakage between training and testing subsets and guarantees that performance metrics reflect the model's generalization capability across independent images. Within the training folds, an inner Group K-Fold cross-validation was performed to optimize hyperparameters. This hierarchical evaluation ensured that hyperparameter selection was conducted independently from the outer validation set, thereby avoiding overfitting and overly optimistic results. Hyperparameter optimization was carried out using a randomized search strategy, which enables efficient exploration of a predefined parameter space while reducing computational cost compared to exhaustive grid search. For LR, the regularization strength and solver type were optimized; for SVM, penalty parameter (C) and kernel width (γ) were tuned; for RF, the number of trees, maximum depth, minimum samples per split, and feature selection strategy were adjusted; and for KNN, the number of neighbors, weighting scheme, and distance metric were optimized. This systematic optimization framework ensured that each model was evaluated under its best-performing configuration.

2.3. Performance Evaluation

The trained models were evaluated using a wide range of performance metrics to provide a multidimensional understanding of classification quality. Standard measures included accuracy, precision, recall (sensitivity), and F1-score, reflecting the balance between correctly detected classes and misclassifications. In addition, the area under the receiver operating characteristic curve (ROC-AUC) and the area under the precision-recall curve (PR-AUC) were calculated to capture model performance in imbalanced scenarios and to assess the trade-off between true positives and false positives. To further analyze model behavior, confusion matrices were generated for each classifier, providing detailed insights into error distributions. Receiver operating characteristic (ROC) curves were also plotted to visually compare the discriminatory power of the algorithms. Finally, to enhance interpretability, a permutation importance analysis was conducted on the Random Forest model. This post-hoc analysis quantified the relative influence of each input feature on classification outcomes, thereby identifying the most informative descriptors in distinguishing background regions from aggregates.

3. Findings and Discussion

The performance evaluation of the proposed framework was conducted using four different classifiers: LR, RF, KNN, and SVM. The confusion matrices provide a clear visualization of the classification outcomes, illustrating the distribution of true positives, true negatives, false positives, and false negatives for each model (Fig. 3). Among these, KNN achieved the lowest number of misclassifications, with 314 false positives and 334 false negatives, while LR exhibited slightly higher misclassification rates (Fig. 3).

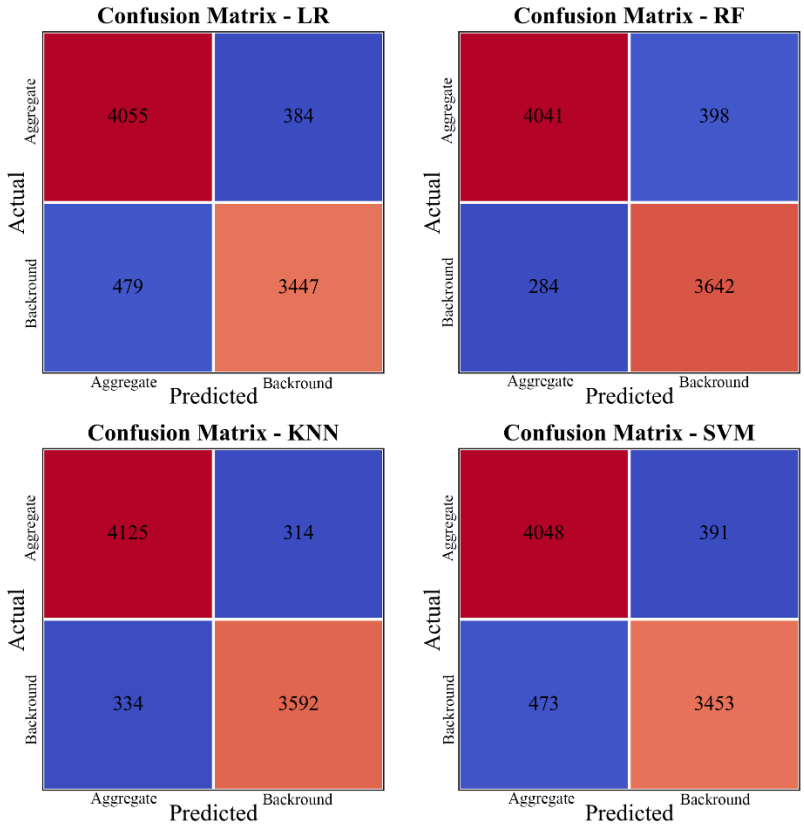

Figure 7. Confusion Matrices of LR, RF, KNN, and SVM

The receiver operating characteristic (ROC) analysis was further employed to evaluate the discriminative ability of the classifiers. As shown in Figure 4, RF achieved the highest area under the curve (AUC = 0.975), followed closely by KNN (AUC = 0.973). LR and SVM yielded slightly lower AUC values of 0.951 and 0.945, respectively. These curves demonstrate that RF and KNN models are more effective in distinguishing between classes across varying thresholds, highlighting their robustness in handling imbalanced cases (Fig. 4).

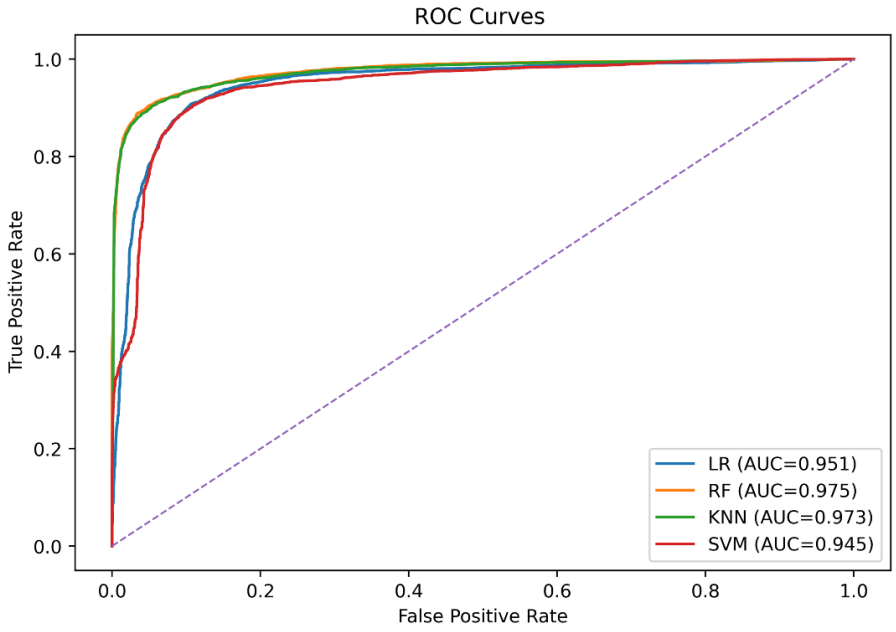

Figure 8. ROC Curves of the Classifiers

The numerical performance metrics summarized in Table 1 further support these findings.

Table 1. Performance Summary of Classifiers (LOIO Validation)

Model	Accuracy	Precision	Sensitivity	F1-Score	ROC-AUC	PR-AUC
RF	0.9185	0.9015	0.9277	0.9144	0.9751	0.9769
KNN	0.9225	0.9196	0.9149	0.9173	0.9734	0.9730
LR	0.8968	0.8998	0.8780	0.8887	0.9506	0.9395
SVM	0.8967	0.8983	0.8795	0.8888	0.9446	0.9368

KNN yielded the highest accuracy (92.25%) and precision (91.96%), while RF achieved the highest sensitivity (92.77%) and F1-score (91.44%). In contrast, LR and SVM demonstrated relatively lower performance, both with an accuracy of approximately 89.7%. Furthermore, precision-recall AUC (PR-AUC) analysis revealed the superiority of RF (0.9769) and KNN (0.9730) compared to LR (0.9395) and SVM (0.9368). Collectively, these results indicate that tree-based and instance-based learning methods outperform linear models in this context.

4. Results

The results demonstrate that the superpixel-based feature extraction method provides highly effective representations for the classification of aggregate samples. Among the tested models, RF and KNN consistently outperformed LR and SVM, achieving superior accuracy, sensitivity, and AUC values. KNN achieved the highest accuracy (92.25%), while RF provided the strongest sensitivity (92.77%) and the highest ROC-AUC (0.975). Although LR and SVM performed slightly lower, both models still achieved reliable classification performance, with accuracies near 90% and ROC-AUC values exceeding 0.94. Overall, these findings confirm that both RF and KNN are well-suited for the classification of visual aggregate data, offering reliable performance across multiple evaluation metrics. More importantly, the results highlight that the proposed framework demonstrates strong capability in distinguishing aggregate from background pixels and provides a robust computational methodology for asphalt mixture image analysis. The consistently high-performance metrics across all models further indicate the robustness and applicability of the proposed framework in real-world aggregate evaluation tasks.

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Use of nano silica in the construction industry

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ABSTRACT

Nanomodification of construction materials has led to improved mechanical properties while meeting environmental requirements, resulting in innovative, sustainable, environmentally friendly, and smart materials. Nanomaterials (NM) are characterized by nanometer-scale dimensions and exhibit distinct activity and behavior compared to their bulk counterparts due to their high specific surface area and the presence of large numbers of atoms at surfaces or interfaces. Silica is the most abundant material on Earth, consisting of small particles smaller than 100 nanometers dispersed in liquids and known as nanosilica. It also exists as a powder, where particles smaller than 2 nm aggregate into clusters a few micrometers across. Numerous studies in the literature have demonstrated that nanosilica improves concrete properties due to its highly reactive pozzolanic material and filling capacity. Nanosilica consists of ultrafine particles smaller than 100 nm. The properties of the particles depend significantly on their particle size, agglomeration level, and dispersion within the paste/matrix. Various methods have been used in the production of nanosilica, including sol-gel, chemical vapor deposition, precipitation, flame synthesis, and others. This study examined the use of nanosilica in the construction industry.

Keywords: Nano silica, concrete, mechanical properties, physical Properties .

1. The Use of Nanosilica in the Construction Industry and Its Contribution to Concrete

Nano-modification of construction materials has led to improved mechanical properties while satisfying environmental requirements, resulting in innovative, sustainable, eco-friendly, and smart materials. Nanomaterials (NM) are characterized by nanometer-scale dimensions in one, two, or three directions and exhibit different activity and behavior compared to their bulk counterparts due to the high specific surface area and the presence of large numbers of atoms at surfaces or interfaces. Silica is the most abundant substance on Earth, consisting of small particles smaller than 100 nanometers dispersed in liquids, known as nanosilica, and is also found as a powder, where particles smaller than 2 nm aggregate into clusters of a few micrometers [1]. Numerous studies have shown that nanosilica improves concrete properties thanks to its highly reactive pozzolanic material and filling capacity. Nanosilica consists of ultrafine particles smaller than 100 nm. The particle properties are highly dependent on particle size, agglomeration level, and dispersion within the paste/matrix. Various methods, including sol-gel, chemical vapor deposition, precipitation, flame synthesis, and others, are used in nanosilica production [2]. Due to its physicochemical properties, nanosilica is the most widely used particle in concrete. Nanosilica is a white crystalline solid with a chemical structure similar to diamond, consisting of numerous five-, six-, and seven-membered rings and a SiO_2 stoichiometry. Construction materials have a significant impact on overall carbon dioxide emissions. The use of nanogranite waste particles as a partial replacement for cement and fine aggregate in mortar has the potential to reduce carbon dioxide emissions during production and transportation. Despite the widespread use of nanogranite waste in construction applications, limited information is available on its impact on mortar. Nanosilica in cement can improve concrete through its ability to reduce permeability and increase overall strength. The high production energy associated with Portland cement is also a limitation; by its nature, nanoparticle-based materials can reduce cement content. Nanosilica in cement is generally characterized by excellent strength performance, especially when exposed to high temperatures. Nano silica improves concrete properties

through pore refinement, enhanced particle packing, accelerated cement hydration, and formation of additional calcium silicate hydrates, leading to increased strength, reduced porosity, and enhanced durability; its large surface area also facilitates repair of nanometer-scale pores existing before hydration [2-6]. The presence of nano-scale particles activates heterogeneous nucleation and crystal growth of various cement hydration phases, further enhancing concrete properties. Many studies emphasize the pivotal role of nano silica in cement hydration and property enhancement of cementitious materials, including concrete. Combining nanotechnology with cement as a fine additive, nanosilica densifies the microscopic particles of concrete and improves its microscopic structure, increasing strength. Samples containing nanosilica exhibit a denser microstructure with higher compressive strength and fewer pores compared to control samples. Nanosilica, reacting with calcium hydroxide, further increases strength by reducing the crystal size and quantity. Evenly distributed throughout the sample, nanoparticles fill the pores and act as hydration nuclei, accelerating cement hydration and significantly improving tensile and compressive strengths. The addition of nanosilica significantly enhances concrete's strength and performance. The resistance of concrete to aggressive substances and environmental effects is commonly referred to as concrete durability. Durability is closely related to density, permeability, and porosity of concrete. Suitable materials, water/cement ratio, compaction, curing, etc., are the main factors that influence concrete durability.

Some research contains insufficient data and suffers from a lack of clarity in instrumentation and analysis procedures, making the derivation of any general insights difficult during the considerable processing of relevant information. The compressive strength of concrete containing nano silica reaches its maximum value at 28 days, with a significant gain in strength occurring at early ages. Concrete strength could be enhanced by using nano silica to replace cement at lower curing ages [7-11]. Notably, the compressive strength of concrete increases with time when nano silica is present, and it is generally higher than that of concrete with ordinary cement. For concrete containing nano silica, replacing the fine aggregate with recycled fine aggregates reduced compressive strength; however, its effect was not as significant as that of compactness for concrete with recycled fine aggregates. In contrast, the inclusion of nano silica greatly mitigated the reduction in strength caused by replacing normal coarse aggregate with recycled coarse aggregate. Adding nano silica to cement paste generally improves durability performance, with pore structure and microstructure playing an important role in such performance [7,12-20].

2. Conclusions

Nanosilica's role in increasing strength and durability in construction projects is often a primary function. Its importance in a sustainable construction environment is a top priority for every project and designer. By increasing strength, it helps protect the environment by reducing material consumption. This increases durability, extends the lifespan of the built environment, and reduces the amount of material required for maintenance and repair throughout its lifecycle. Nanosilica's unique properties in construction help produce asphalt mixtures with longer fatigue life and less permanent deformation. Its incorporation into bricks and blocks increases strength and weatherability, potentially reducing recommended mortar thickness. Paints and other coatings using nanosilica benefit from enhanced adhesion and weatherability, while also protecting the materials.

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Investigation into the Use of Plastic Waste as a Substitute Material in Concrete

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ABSTRACT

Large amounts of plastic waste pose a major environmental problem, particularly in developing countries. The inability to manage the large volumes of waste generated and the long-term degradation of plastic have led to serious accumulation problems in residential areas, damaging ecosystems. The use of materials made from or containing recycled plastic offers an attractive solution. If these materials could be used in concrete, the world's most widely used building material, the sustainability of its production would be significantly increased. Construction and demolition offer additional opportunities to reduce the environmental impact of industry and the waste sector. Investigating the potential for substituting plastic waste in concrete, particularly as a potential partial replacement for sand, aggregate, or fibers, is a priority for an environmentally and economically sustainable construction industry. This research explores the use of plastic waste as a construction material.

Keywords: Plastics, concrete, recycling, environmental contribution.

1. Use of Plastic Waste as a Substitute Material in Concrete

Environmental sustainability is an increasingly significant subject in construction concerning material reuse and waste recycling. Concrete and cement production account for approximately 7% of global carbon emissions annually, whereas the world produces around 280 million tons of plastic every year that are discarded as waste and pose substantial threats to the environment [1]. Plastic waste is widely generated in various sectors, including packaging, construction, building, and medicine. Its long-term environmental persistence further exacerbates its harmful impact on aquatic and terrestrial ecosystems [1,2]. Since plastics are not biodegradable, they do not readily decompose and require a long time to be degraded. Although unavoidable, excessive plastic waste production has become an increasingly concerning issue, especially with rapid global population growth. Plastic waste is not biodegradable, it causes environmental problems due to its disposal, toxic leakage, exhaust gases resulting from combustion and storage problems, causes landfills to fill up and has negative effects on marine and aquatic life. The abundance of plastic waste has exacerbated ecological and aesthetic problems globally, and various uses of recycled waste are being explored to minimize and recycle plastic waste. Concrete is a mixture of cement, water, coarse aggregate, and fine aggregate. The workability of concrete refers to how easily it can be mixed, placed, and finished. Workability depends on the water-cement ratio, the type and size of the aggregate, and the amount and type of additives used. Plastic waste can be used as an aggregate in concrete, replacing coarse or fine aggregate. The use of plastic waste as an aggregate affects the workability of concrete. Using plastic waste instead of coarse aggregate results in an increase in the workability of concrete, as indicated by a higher slump value. Workability increases with an increase in the percentage of plastic aggregate. Plastic waste is less dense than natural aggregate, which reduces the density of the concrete. Plastic waste also has a smooth surface texture, which affects both workability and its bonding properties with the cement paste. Concrete is generally defined as the mixing of cement, sand, and water. Since its inception, concrete has been widely used due to its affordability and availability. In conventional production, concrete produces approximately 10 percent of global carbon dioxide emissions, or approximately 2,000 million tons of carbon dioxide emissions annually. Consequently, substitutes for less energy-intensive materials are often sought to reduce production costs and overall carbon footprint. In this context, researchers have investigated the incorporation of various economical

waste materials into concrete and proposed ways to improve waste management and ensure sustainability. [2-6]. Consequently, incorporating plastic waste into concrete as a supplementary material emerges as a viable strategy. Plastic materials such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), and polyethylene terephthalate (PET) are added to concrete to enhance its properties. These plastics are characterized by precise chemical structures, high strength, lightweight attributes, low toxicity, cost-effectiveness, resistance to corrosion, and minimal moisture absorption. Using such materials not only provides an effective waste management solution but also contributes to the development of concrete with reduced thermal conductivity, facilitating the creation of more sustainable building environments [7-9]. Concrete, known for its strength, durability, and low cost, serves as a primary construction material. However, its tensile strength is low and is therefore enhanced by fiber reinforcement, with synthetic fibers being the most common. Several studies have investigated the use of recycled waste including plastic to strengthen concrete [1]. Two approaches for incorporating the processed plastic into the concrete matrix are prevalent. In the first method, the plastic particles replace a specified volume of fine aggregate within the conventional concrete mixture. In the alternative technique, detailed in, the plastic wastes are introduced into a cementitious base composed of Portland cement, sand, and water in proportions. Although plastics possess low strength, their poor bonding with concrete microstructures causes a considerable reduction in the strength of composite materials. Enhancing the adhesion between plastic fibers and concrete through increased wettability via surfactants may improve performance. Larger plastic particles and higher replacement percentages significantly diminished tensile strength by increasing void spaces. Studies in the literature indicate that the most influential factor on mechanical performance is the percentage of replacement, rather than the curing conditions. Strength reductions are paralleled by the amount of plastic added due to poor bonding with the cement matrix. While most research has focused on workability and strength, durability assessments remain limited. The use of recycled plastics as a fine aggregate replacement is anticipated to offer environmental and economic benefits by reducing excessive sand extraction [9-13].

2. Conclusions

With the increasing demand for plastics, the ever-increasing amount of plastic waste can be readily incorporated into concrete in low-quality construction where high-strength concrete is not required. The use of recycled high- and low-density polyethylene, polypropylene, and PET, combined with appropriate texturing to improve interaction with the cement matrix, demonstrates the potential for direct use in structural concrete. The use of plastic waste is optimal with only 5% substitution, as demonstrated by strength and durability tests; beyond this limit, the strength deficiency becomes even more pronounced due to decreased bonding and increased porosity. Consequently, glass bead blasting is recommended as an additional texturing technique because it can contribute to the strength of the plastic by removing the weak surfaces on the plastic particles and enhancing the bearing capacity of the plastic. In summary, the use of plastic waste in concrete offers a viable option for removing large amounts of non-degradable waste from the environment and can be particularly beneficial when substitution rates are limited to 5% to 10% and workability can be maintained at the required levels. Future research will focus on the best texturing method and which properties can be improved with additives, and the use of plastics will be increased when a reasonable method for producing new mortar suitable for extrusion is developed.

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Research on the use of glass powder in briquettes

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ABSTRACT

Glass powder is obtained by sifting glass waste through recycling and grinding it into flour in mills. Glass powder is used in many different sectors, including composites, ceramics, plastics, concrete, insulation, epoxy, adhesives, and abrasives, to improve quality and reduce costs. Glass powder, used in concrete, can also be used in briquette production, increasing both its environmental and economic benefits. Studies on the use of glass powder in briquettes are quite limited. This study investigates both the uses of glass powder and its usability in building materials such as bricks and briquettes.

Keywords: Glass powder, briquette, mechanical properties.

1. Use of glass powder in briquettes

Glass dust is a fine-particle material generated during the production and shaping operations of the glass industry. These dusts are generally produced as by-products of the melting, shaping, or processing of glass. Glass dust, which plays a significant role in recycling processes, is notable for its various properties. Its chemically inert structure ensures long-term durability and reduces environmental impact. Furthermore, its high heat resistance and durability make it suitable for use in various construction materials. The glass dust production process is optimized to take into account high costs and energy consumption. Grinding and refining the glass cullet are key stages in this process. The high operating temperatures and specialized techniques used to pulverize glass significantly affect its properties [1-4]. Glass dust exhibits unique chemical properties thanks to the silicon oxide and other oxide compounds it contains. These properties increase the material's mechanical and thermal resistance. The use of glass dust in briquette production is particularly advantageous in areas such as structural durability and thermal insulation. The use of glass dust in briquettes results in lighter and more durable products compared to traditional materials. At the same time, due to its environmental sustainability, it is an important alternative for the recycling of waste glass. Briquettes can also be produced by adding agricultural wastes such as charcoal dust, shredded paper, palm fiber, and sawdust, or by adding processed coals such as anthracite coal and lignite dust instead of firewood or coal. Other materials commonly used in the briquette production process include bentonite, molasses, cement, and tapioca flour. The addition of glass powder contributes to the ability to improve briquette integrity and performance, characterized by its high silicon dioxide content and thermal and mechanical properties. Glass powder consists of finely ground waste from different types of glass, which can replace various binders. The main purpose is that the glass powder vitrifies during the molding stage and thus acts as a binder. The addition of glass powder during briquetting enhances structural cohesion without compromising the fuel's combustion properties by increasing its binding potential These properties demonstrate the promise of glass powder as a multifunctional additive capable of improving briquette durability and energy release during combustion [1,5-9] The use of glass powder in briquettes has significant applications in the construction and building materials sectors. This use offers significant advantages, particularly in terms of environmental sustainability and energy efficiency. Glass powder is preferred for increasing the durability of briquettes due to its high transparency and chemical resistance. Furthermore, the recycling and utilization of glass waste contributes to the conservation of natural resources. The integration of this material into briquettes improves mechanical strength and thermal insulation properties, and is particularly used in the design of structural elements that enhance the thermal insulation of buildings. Proper impregnation of glass powder and its combination with a binder enhances the chemical resistance of the briquettes, resulting

in a structure more resistant to external influences. In industrial production, the inclusion of glass powder reduces production costs and improves product performance. This application contributes to the development of sustainable building materials both environmentally and economically. Furthermore, as new-generation briquette materials in the construction sector, products containing glass powder are used particularly in lightweight building elements and insulation materials, expanding their application areas. This allows for the construction of energy-efficient, environmentally friendly, and long-lasting structures. Therefore, the application of glass powder in briquettes plays a significant role in the search for sustainable and economical solutions in modern construction technologies [7-12].

2. Conclusions

The use of glass powder in recycling contributes to both reducing environmental pollution and lowering costs. Consequently, the use of glass powder in briquettes is a significant development in terms of both improving material performance and supporting environmental sustainability. Therefore, its use is increasingly widespread in research and applications, and new areas of development are emerging. A portion of the cement from waste glass can be supplemented, and at certain rates (especially 10–20%), it can maintain or even improve its mechanical properties. However, it is known that higher rates negatively impact durability and workability. There are not many publications on the use of glass powder in briquette-related studies.

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Investigation Of the Use of Composite Waste in The Construction Industry

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ABSTRACT

The construction sector, while a cornerstone of economic development, also carries with it a high volume of natural resource use and energy consumption, along with environmental impacts. Therefore, the sector's sustainability has gained significant importance. In recent years, the management of waste generated during the production and use of building materials has been reshaped by innovative solutions and circular economy approaches. Composite waste, in particular, has emerged as a new material alternative for structural and surface applications and is the subject of significant research regarding its usability in the construction sector. Composite waste, a mixture of different material types, does not occur naturally in nature and is generally generated through industrial production processes. Recycling and reusing this waste provides both economic and environmental advantages. The emphasis is on the cost advantages derived from using this waste as material during construction, reducing waste volumes, and reducing dependence on natural resources. Furthermore, the proper recycling and integration of composite waste into new products is considered a significant step in supporting sustainable construction practices. Therefore, the management and utilization of these wastes has become a fundamental element in improving quality and safety within the sector while also reducing environmental impacts. In this context, raising awareness among industry stakeholders, developing standards, and keeping up with technological innovations are critical to the effective use of composite waste in construction.

Keywords: Composite waste, recycling, building materials.

1. The use of composite waste in the construction industry

Composite materials consist of two or more constituents with different physical and chemical properties that remain separate at the macroscopic or microscopic scale within the finished structure. Their attractive physical properties, such as high temperature and corrosion resistance and excellent mechanical properties, have found extensive application in many industrial fields where they totally or partially replace other traditional materials. Time to market and return on investment are all reduced in industries that adopt and implement additive manufacturing (AM) methods. The majority of composite waste is treated by grinding into powder, mixing with commonly used matrix materials such as resin and concrete, or burning to recover fiber; however, many problems that cause secondary pollution appear through this procedure. In this context, the investigation into the potential of composite waste within the construction industry takes on increasing importance [1,2]. Composite materials have been commercially exploited for a long time, with technologies developed to adapt to market demands. Their use has considerably increased, mainly due to the development of the aerospace industry. A composite material is composed of at least two different components whose combination results in properties superior to those of the individual constituents [2,3]. Composite materials can be classified according to the matrix into polymer composites, metal composites, and ceramic composites. Polymer matrix composites possess low density, easy synthesis, corrosion resistance, and toughness, which have been exploited to constitute a wide number of polymers, ceramics, and metal system combinations to create materials with improved properties. The matrix can be thermoplastic (e.g., polyethylene, polystyrene, polyvinyl chloride) or thermoset (e.g., epoxy, unsaturated polyester, novolac resin). Other polymeric materials, such as those resulting from recycling, pose low interest due to the difficulty to shape and modify their mechanical

properties. [2-4]. The key objective is to combine the higher stiffness of fibres with the ductility of the polymer matrix. Fibre-reinforced composites are by far the most commercially exploited systems. Polymer composites reinforced with particulate fillers constitute a valid alternative to fibre reinforcement, since they are often easier to process and less expensive. A sufficiently high aspect ratio distinguishes powders from short fibres. Fillers used in particulate composites include talc, mica, quartz, alumina, silica, and carbon black, with sizes ranging from nanometres to millimetres. Composite materials can deliver excellent mechanical, thermomechanical, and tribological properties when prepared according to precise procedures. Due to their outstanding behaviour, composite materials are considered a strategic research area in many sectors. Their positive impact on the environment is of great interest, especially following the EU's strategy to reduce carbon dioxide emissions. Globally, construction and demolition (C&D) activities generate approximately four billion tonnes of waste annually, accounting for 30–40% of total waste worldwide. Composite waste use in construction arises from environmental efforts to reduce pollution and resource depletion, along with economic motivations to minimize large-scale costs, especially in end-of-life-phase reduction The aggregate industry is one of the most important raw material suppliers in construction. As a consequence of construction works, demolition of old infrastructure and maintenance of urban equipment, construction and demolition wastes (CDW) are generated. CDW must be reduced, recovered and recycled in order to minimize the environmental impact and process costs [3-11]. Various incentives drive greater adoption in the construction sector, corresponding with ongoing construction-bricoleur development. The growing popularity of composite waste in construction stems from increasing industrialization, urbanization, and population growth, which accelerate the waste cycle and drive the search for alternative materials. Economic considerations motivate the sector to incorporate significant quantities of new raw materials, including post-consumer industrial waste, into its manufacturing processes. Economic efficiency gains remain the most direct influence on the increased use of composite waste in construction; environmental gains, although recognized, are more indirect. The European Union on its own produces 800 Mt of construction waste each year, with the UK and Germany contributing between 100 and 150 Mt annually. The sheer volume of C&D waste is attributable to the extensive use of building materials such as metal, concrete, asphalt, glass, wood, and plastics, which are employed in construction, renovation, and demolition works [7-15] . In line with the growing importance of sustainable development, there is also an imperative to reduce C&D waste through reuse and recycling strategies. Efficient recycling contributes to the preservation of landscapes and natural resources, reduces environmental impacts, and supports energy. As self-compacting concrete (SCC) gains prominence throughout the construction industry, China, among other nations, faces a depleted supply of natural resources and escalating C&D waste. Recycling C&D waste as filler for SCC prevents the occupation of additional land and mitigates C&D disposal problems. For the year 2017, China imported US$ 144.3 billion in construction goods and equipment, signaling escalating construction demand and a corresponding surge in C&D waste. Given the limited extent of studies on utilizing C&D waste as filler in SCC, investigating this potential application for waste reuse and natural resource conservation remains paramount. Despite concerted efforts, a significant proportion of C&D waste continues to be stored in landfills. By the end of 2010, EU Member States generated over 900 Mt of construction waste, with landfilling and recovery rates varying [1,2,9].

2. Conclusions

The construction industry is ranked as the largest economic activity worldwide, driven by a growing awareness of the importance of reducing its environmental impact and improving sustainability. The correct use of composite waste in construction has the power to contribute significantly to this goal by reducing the environmental impact and landfill pressure resulting from the intensive use of natural resources. Furthermore, reusing composite waste reduces the economic impact of industrial activities by reducing production and raw material procurement costs.

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Boronizing Process Using Sol-Gel Method

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ABSTRACT

Boronized materials, with their high surface hardness, enhanced wear resistance, low friction and improved corrosion resistance, are widely used in harsh environments such as the aerospace, automotive, metal cutting, mining and textile industries. The sol-gel technique offers an economical and environmentally friendly approach compared to some boron deposition methods for producing high-purity, homogeneous boron coatings with excellent thermal stability and resistance to water and chemical attack. Unlike traditional liquid boronizing methods that involve high temperatures, toxic chemicals, and hazardous waste, the sol-gel process has not yet been sufficiently investigated in this application, although it may have the potential for widespread commercial use in various coating technologies.

Keywords: Sol-gel technique, boronizing, steel, coating.

1. Sol-Gel Method and Boronizing

The sol-gel method is a low-temperature chemical solution process used to deposit thin films on metal or ceramic surfaces. In boronizing applications, boron-containing precursor compounds (e.g., boric acid, B_4C, B_2O_3, borates) are prepared in solution (sol) and then coated onto the surface using dipping, spraying, or spin-coating techniques. After drying and heat treatment, the mixture transforms into a gel phase, forming a boron-rich layer on the surface. Sol-gel boronizing is a low-temperature method developed as an alternative to traditional solid (powder), liquid, or gas-phase boronizing methods. It offers homogeneous coating capabilities. The basic principle is to prepare boron-containing precursor compounds (e.g., boric acid, boron oxide, or organoborates) into solution using the sol-gel method, then apply them as thin films by coating them on the metal surface (dip-coating, spin-coating, spray-coating, etc.). The film is then baked during the heating (calcination/heat treatment) phase, allowing for boron diffusion on the surface. The advantages of this method include: It can be applied at low temperatures. It provides homogeneous and controlled film thickness. It is environmentally friendly and does not require toxic gases. Surface modifications can be made at the micro/nano scale. The disadvantage is that the layer thickness is limited (usually a few microns). The diffusion depth is lower than with conventional boronizing methods. Performance under high mechanical loads may be limited. The sol-gel boronizing method shows particular potential for cutting tools, thin-film coatings, biomedical implant surfaces, and steels with increased corrosion resistance. It is also being used in conjunction with nanotechnology to produce boron-doped functional coatings (e.g., boron-based TiO_2 and boron-based ZrO_2 films) [1-6].

Pehlivan et al. (2018) boronized Inconel alloy using the sol-gel method. As a result of the boronizing process, they achieved boride layer thicknesses of approximately 10 microns on all three materials. Unfortunately, no other studies on boronization using the sol-gel method exist in the literature [7].

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Comparison Of Different Methods of Boronization

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ABSTRACT

Boron coating is a surface coating process used to protect metal surfaces and improve their functional properties. This method is particularly preferred for increasing durability, wear resistance, and corrosion resistance. Due to its unique chemical and physical properties, boron is applied to metal surfaces using various coating techniques. Boron coatings are generally used to increase mechanical strength, and various application methods are chosen depending on the available resources. Boron compounds are integrated onto metal surfaces under high temperature and pressure to form protective layers. Boriding describes the diffusion of boron onto a metal surface, creating a protective, hardened microstructure that provides chemical and thermal stability. The method used depends on the medium and application; powder-solid, liquid, gas, paste, plasma, fluidized bed, laser and similar methods will be compared.

Keywords: Boriding, powder, liquid, gas, paste, plasma.

1. Boronization methods

Surface modification plays a crucial role in the manufacturing industry to improve properties such as wear resistance, corrosion resistance, adhesion, lubrication, friction, thermal stability, oxidation resistance, and fatigue strength. Among various techniques, boriding is an economical thermochemical treatment that involves the formation of hard borid phases on the substrate, increasing the surface hardness by approximately five times when compared with other materials. The treatment of steels and alloys to enhance properties such as corrosion resistance, wear resistance, and mechanical strength has increasingly leveraged surface engineering techniques. Boriding-in which boron atoms diffuse into the material surface to produce boride layers-provides significant benefits in these areas. Boriding can be combined with other treatments, such as nitriding, on the same surface because the outer surface also undergoes hardening and corrosion-fatigue enhancement. Boron diffusion within iron during solid-state reactions forms phases with significantly higher hardness than the substrate. The specific phases depend on the matrix composition and treatment process. In cast irons, Fe_2B and FeB phases are typical, whereas steels tend to form Fe_2B layers. Boron effectively lowers iron's melting temperature and promotes the formation of particular phase regions, producing surface layers with enhanced hardness, wear resistance, and corrosion protection. Since its discovery in the early 1920s, boriding has attracted significant attention for improving the performance of steels used in wearable and corrosion applications. Boriding can be performed using different media, including solid, liquid, gaseous, and pack processes[1-4].

In the solid boriding process, the boron atoms diffuse from the solid-state boron medium onto the surface of the substrate. This diffusion produces a good adhesion of the coating layers and an excellent hardness and wear resistance [2]. This is the most widely used technique. Parts are embedded in boron powder mixtures (5% B_4C + 5% NaF, 98% B_4C + 2% KBF, 95% amorphous boron + 5% KBF_4, etc.) and subjected to diffusion at 800–1000°C. While thick layers (20–200 µm) can be obtained, the process time is long and surface cleaning is difficult. Furthermore, high temperatures can cause distortion in steels [3-5].

Boronizing is a process in which boron compounds such as anhydrous borax ($Na_2B_4O_7$), anhydrous boric acid (B_2O_3), metaboric acid (HBO_2), borax, and boron carbide are used. Reducers such as silicon carbide,

ferrosilicon, graphite, NaCl, and Al are used. This involves immersing the workpiece in a molten salt containing boron compounds, activators, and reducing agents.

Boronizing is carried out at 900-1100°C for 2-9 hours. Boronizing in a molten salt bath allows for faster diffusion. However, the borax and borate baths used pose environmental risks Furthermore, if the temperature drops below 850°C, the fluidity of the molten borax decreases, making boronizing impossible [6,7]. Gas boriding involves a gaseous medium to enrich an iron-based material surface with boron. As nitrogen or hydrogen borides are unstable in a gaseous state, they typically do not form as by-products. Direct interaction between gaseous reagents and the substrate metal is therefore essential to facilitate the boronizing process. Common boron sources include boron halides such as boron trichloride (BCl_3) and diborane (B_2H_6), although these substances present toxicity and explosion hazards that constrain widespread application. A selected gaseous mixture emerges from the continuous flowing of these agents, enabling the determination of the boronizing depth without interrupting the treatment procedure conducted in an open retort [1,8].

Paste boronizing is used when box boronizing is difficult, more expensive, or time-consuming. A paste made from 45% B_4C and 55% cryolite, or a traditional boronizing powder mixture of B4C+SiC+KBF_4, mixed with a good binding agent, is applied to the entire surface or the desired area of the material using a brush or spray gun. It is easy to apply, allows for localized boronizing, and is cost-effective. However, layer uniformity is low, and thickness control is difficult. Plasma boronizing is a boronizing process in which BCl_3, B_2H_6, BF_3 or $B(OCH_3)_3$ (trimethylborate) as a boron source and Ar and H_2 gases are used together in a plasma environment created at a temperature of 800-1000°C and a low pressure of approximately 10^{-2} Pa. The difference from gas boronizing is that the boronizing process is carried out under vacuum and plasma [9-11].

Plasma paste boronizing is performed in a plasma environment between 700-1000°C using gases such as Ar and H_2 under a specific vacuum pressure. Because the process is carried out under vacuum, no protective atmosphere is required. By using boron-containing powders as the paste, plasma paste boronizing allows steel to be boronized at lower temperatures and for shorter periods of time, creating complex boride layers on the steel [12].

Induction boriding is a thermal processing method that heats metal parts by applying a high-frequency electromagnetic field to their surfaces. This process aims to change the properties of only the desired areas of the metal part by heating them. Induction boriding is an effective surface hardening method, particularly used in industrial applications [13].

Boriding is done by bringing boron powder into contact with the part in a fluidized bed. The powder is then liquefied by the use of an oxygen-free gas. The boronizing process takes place in a fluidized bed containing the boron powder and an oxygen-free gas as a base material [14].

Laser boriding is considered an alternative to the conventional diffusion boronizing technique, aiming to reduce the brittleness of the boride layer. This approach can be applied through two different procedures. In the first, the laser beam re-melts the substrate surface that has been pre-coated with a boron paste. In the second, boron-containing alloy powder is directly supplied into the molten zone created by the laser. Both methods contribute to improving the mechanical performance of the treated material and often eliminate the limitations associated with diffusion boronizing [15].

Ultra-fast boriding uses a simple electrochemical cell operating at high current density (50 to 700 mA/cm^2) and low voltage (1-15 V). The main ingredients of the molten electrolyte for the cell are mainly borax, $Na_2B_4O_7$ (70-90 wt.%), and sodium carbonate, Na_2CO_3 (10-30 wt%). These chemicals are very cheap and non-toxic (naturally occurring), and do not result in any type of hazardous emissions or wastes [16].

In thermochemical boriding carried out in molten salts, the treatment medium includes a boron source. (most commonly sodium tetraborate, $Na_2B_4O_7$). Also other compounds such as boron oxide (B_2O_3), potassium tetrafluoroborate (KBF_4), or potassium tetraborate ($K_2B_4O_7$) can also be used. Along with this, a reducing agent is required, typically boron carbide (B_4C), silicon carbide (SiC), or various metals and alloys. To improve the physicochemical characteristics of the boriding mixtures-particularly the crystallization onset temperature and viscosity-alkali metal chlorides or carbonates are sometimes incorporated. The process is generally performed within a temperature range of 850–1050 °C [17].

2. Conclusions

Different boronizing methods all have their advantages and disadvantages. Considering these advantages and disadvantages, choosing among these boronizing methods is crucial to ensuring the environmentally friendly, appropriate method for the material, and meeting specific production requirements.

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Femoral Stem Optimization Using Groove Design and Its Role in Hip Prosthesis Stability

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ABSTRACT

The design of the femoral stem plays the most important role in the stability of the hip prosthesis due to its direct connection to the bone canal. Osseointegration and acceptance of the prosthesis by the supporting tissue are also very important. In this regard, designing and optimizing the shape and surface of the prosthesis can have a positive effect on this. The stem surface must become a suitable place for bone tissue growth, which will be made possible by the grooved design. From another point of view, the fusion of the stem with bone tissue and the growth of osteogenic cells within the grooves can maximize the adaptation of the hip prosthesis to the human body. The integration of vertical and horizontal grooves within the structural framework of femoral stem systems marks a significant advancement in biomechanical engineering. These grooves are strategically designed to align with anatomical contours and natural movement axes while minimizing localized stresses on musculoskeletal components. grooved structures contribute to balanced weight distribution, reduced fatigue during repetitive motion, and improved long-term comfort and endurance. The versatility of groove-based designs allows adaptation across a range of anatomical regions and load-bearing conditions, making them suitable for diverse biomedical and biological applications. In addition to functional benefits, grooves can be mechanically optimized to respond to user specific motion dynamics, effectively transforming rigid exoskeletal elements into responsive interfaces. On the other hand, optimizing the stem geometry and eliminating angles that cause stress concentration are important, which is achieved by using a curved design at the stem edges. Ultimately, this design philosophy reflects a shift toward human-centric stem innovation-one that values dynamic interaction, mechanical adaptability, and the seamless integration of form and function in biomedical engineering. We found that only the combination of a structurally flexible stem with anatomical curvature and grooves improves strain-shielding compared to other designs. The clinical implications in vivo of this initial strain-shielding difference are currently under evaluation in an ongoing clinical analysis

Keywords: Femoral stem, shape optimization, stability, osseointegration, grooves.

1. Introduction

Total hip arthroplasty (THA) involves the removal of the damaged joint and the replacement of an artificial component in a medical procedure. It is performed for people who have severe hip pain or loss of mobility due to osteoarthritis, rheumatoid arthritis, or other hip-related diseases. Most people who have THA are over 60 years of age, but younger people are also more susceptible to hip injuries today due to more intense and frequent physical activity. However, as the population ages, the number of patients requiring THA has increased and is expected to increase in the coming years[1]. Also, due to the increasing number of young people who are susceptible to hip injuries, the number of patients requiring THA at younger ages is also increasing[2]. Recent research has shown that the typical residual value of hip implants after 25 years in younger patients is about 15 to 20 percent lower than in older patients. It can be concluded that for younger individuals, the prosthetic component should be more resistant to wear and tear, and similar

in mechanical properties to the natural model, leading to long-term strength and durability. When considering the longevity of the femoral stem, the goal is to make THA as noninvasive as possible and to take into account the differences in mechanical and biological properties that lead to abnormal behavior in the affected area, such as protection against stress/strain caused by changes in the natural load pattern on the bone. Traditional femoral stems tend to reduce the load in the proximal region and increase it in the distal region, as the bone is stronger in the distal part[3]. This disadvantage is exacerbated by reducing the length of the stem to preserve the bone and prevent its weakening by increasing proximal load transfer, which preserves bone density. In the past years, short-stem THA has emerged as a common and popular choice for patients to preserve the THA implant with adequate bone mass for proportional hip correction[4]. The use of these short-stem prostheses in young patients aims to create favorable conditions for hip replacement during implantation due to bone and soft tissue grafting, as well as to prevent stress protection and bone loss due to greater physiological load transfer. One of the newest generations of prostheses, bone-based short-stem prostheses, is to preserve soft tissue as well as increase the stability and integrity of the primary bone[5].

Obesity, with a BMI ≥ 30 kg/m2, is a risk factor for hip osteoarthritis, and the number of patients undergoing hip replacement surgery for this reason is increasing [6]. It has also been shown to be a specific risk factor for complications such as infection and dislocation after hip replacement[7]. In this context, the only option that has been shown to be partially effective in obese patients is short-stem hip replacement, which has been highly rated in terms of operative characteristics, reconstructive surgery, and clinical outcomes such as pain, etc.[8-10].

The choice of material for most femoral stems is made of solid metals such as titanium, titanium alloys, cobalt-chromium, or stainless steel, which have a higher elastic modulus than native bone. Stress retention is the main cause of bone mineral density loss and the consequences of bone resorption and implant loosening after hip replacement[11, 12]. One of the materials used in most femoral stems is titanium. Titanium has high biocompatibility and the lowest Young's modulus among biometallic materials used, and it also exhibits corrosion resistance in the corrosive environment of the body, leading to its successful and widespread use in faceplates, microparts, endoprostheses, and dental implants[13-16].

One of the most common titanium alloys used in these devices is Ti6Al4V, which is a two-phase alloy with low density and very good corrosion resistance, good machinability and especially high mechanical strength[17-19]. Recent research proves that the main elements of this alloy can leave negative effects on the body. For example, aluminum, in addition to worsening the activity and function of enzymes and neurotransmitters, may lead to osteoporosis and its increase or even damage nerve cells.

This study analyzes the geometric optimization of a short stem using advanced engineering tools. Using a fixed material for the prosthesis, different geometric shapes were evaluated and the resulting grooves were compared. The results showed that the optimized designs using these materials can enhance the osseointegration and stability of femoral stem to a great extent. This design can play an important role in the development and production of lightweight, stress shielding, and high-performance prostheses.

2. Materials and Designs

2.1. Materials

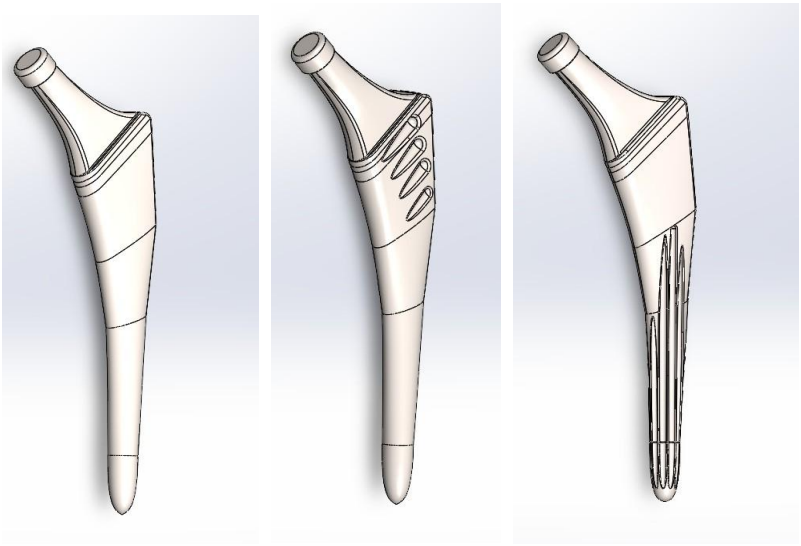
This study is based on a structured synthesis of 2 peer-reviewed articles published between 2020 and 2024, covering clinical, biomechanical, and materials science perspectives on total hip arthroplasty (THA). Selected sources include epidemiological analyses[1, 2], finite element modeling [3, 20], implant design reviews[4, 21, 22], and surface engineering studies of titanium alloys [13-18]. Articles were selected based on their relevance to short-stemmed femoral implants, titanium-based biomaterials, and obesity-related surgical outcomes. Data extraction focused on implant geometry, material composition, surface treatment techniques (e.g., micro-arc oxidation [14], laser modification [15, 23], nanostructured coatings [24]), and biomechanical performance indicators such as stress protection and load transfer efficiency. Finite element analysis (FEA) data were synthesized to compare short metaphyseal anchor rods with conventional long rods. Borchardt et al. [20] showed that rod stiffness and design significantly affect stress protection. These biomechanical parameters were normalized in the studies using dimensionless ratios to facilitate comparative interpretation. Clinical studies were reviewed to assess the rate of repair, infection risks, and fracture incidence, particularly in obese patients undergoing total hip arthroplasty (THA). Feng et al. [11] identified aseptic loosening as a major cause of implant failure, and Sonawala-

Dosabhoy et al. [12] proposed volume reduction strategies to reduce stress shielding. Material characterization data were extracted from surface engineering studies, and tensile strength, corrosion resistance, and osseointegration potential were evaluated. Further studies [15-17, 19, 24] provided insights into the coating morphology, mechanical behavior, and manufacturing techniques of titanium alloys.

The titanium alloy (Ti6Al4V) used for the designs was considered with the help of literature. All findings were extracted from published data and interpreted in a comparative framework to aid future implant design and patient-specific optimization strategies.

2.2. Designs

After selecting the most suitable material from among the engineering materials, considering the mechanical properties of the materials, a design for the stem was prepared. In the design of this prosthesis - especially in a field such as medical engineering - small and key points such as the edges and grooves of the prosthesis are important. This design is based on the dimensions of similar designs. An attempt has been made to use fillets throughout the design to soften the surfaces and have no edges. Three different designs of grooves are provided on the femoral stem, which can be seen (Fig 1). The first design without grooves has been considered, which also brings a new model of short stems. In the next two designs, an attempt has been made to create different grooves perpendicular to the stem axis and vertical grooves along the stem axis. The two designs with grooves indicate optimization in the geometric structure of the initial stem. Where optimization of mechanical performance and the weight of the structure is very important.



(a) (b) (c)

Figure 1. Different designs a,b, c in CAD software.

3. Results and Discussion

Finite element models of an intact right femur of one representative female patient from a larger cohort who underwent THA in our clinic were created (Fig 2). No patients were directly involved in this study. Separate Institutional Review Board approval was not necessary as available, approved imaging data from our university hospital was used [25].

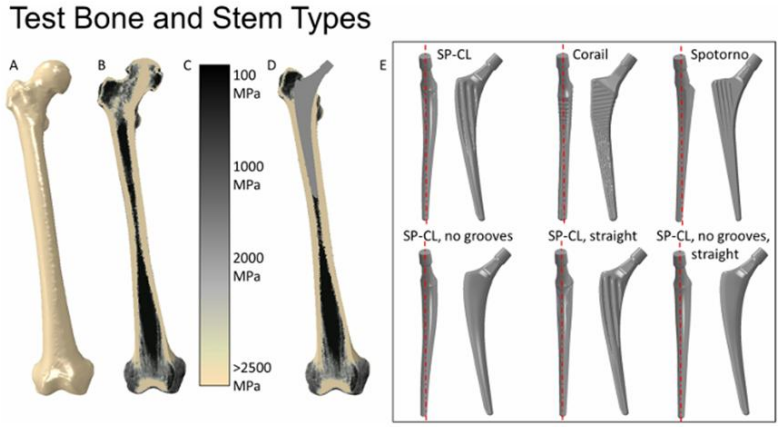


Figure 2. Overview of models: From left to right, (A) intact bone surface, (B) intact bone cut (coronal plane) with illustration of the material mapping approach, (C) legend showing Young's modulus of the tissue, (D) illustration of THA in bone cut. On the right, (E) Tested implants seen from medial and from anterior (line in medial view to illustrate anatomically curved vs. straight stems) [25].

The highest deviations to intact (Fig 3) are observed in Gruen zone 1 with over 120 microstrain root mean square error (RMSE) for all stem designs and over 60 microstrain RMSE in Gruen zones 2, 6, and 7. Gruen zones 4 and 5 show small deviations to intact of about 20 microstrain RMSE [25,26].

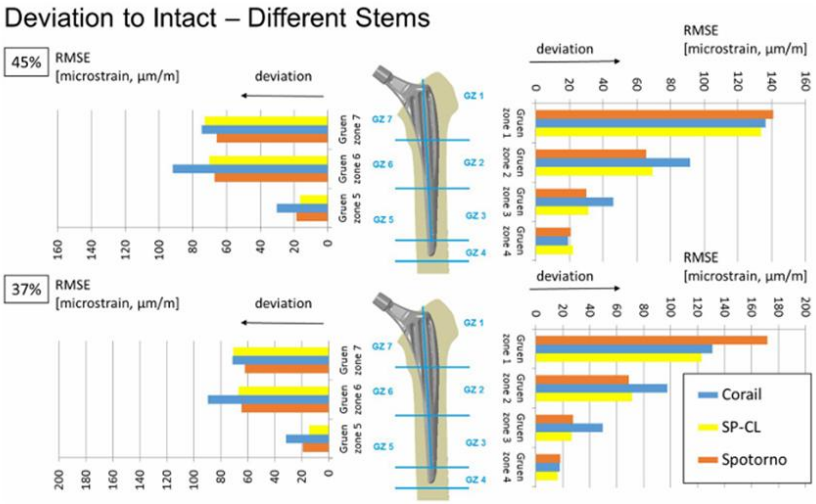


Figure 3. Deviation to intact (RMSE = root mean square error) per Gruen zone (GZ) at 45% (top) and 37% (bottom) of the gait cycle for different stem designs [25].

The load transfer from the stem to the bone is not homogeneous. Especially the straight stems with grooves or ribs show marked stress concentrations. The CLS Spotorno stem manifests a relatively focused proximal diaphyseal load transfer compared to the other tested implants with its reduced cross-sectional area below 40% of the length from proximally to distally and thus metaphyseal bracing [27]. In contrast, the CORAIL shows a more widely distributed, but not homogeneous load transfer to the bone, with a concentration even more distally than in the CLS Spotorno (Fig 4).

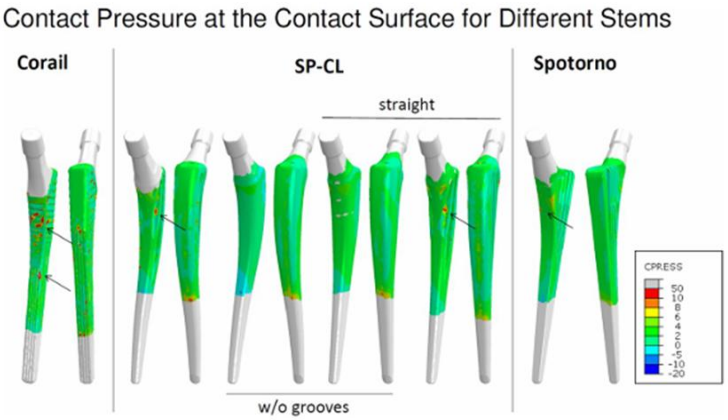


Figure 4. Load transfer at the bone-implant interface shown as contact pressure (MPa) at the implant surface at 45% of the gait cycle for different stem designs [25].

Small changes in stem placement would likely have little influence on the internal loading of the femur after bony on-growth has been achieved and thus small positioning errors result in generally small strain differences when compared to the overall change from the intact femur strain44. This is confirmed by computational results suggesting that the strain distribution in the femur may be similar at different stages of healing after THA, regard less of small alterations in implant positioning. However, the healing immediately after surgery will be affected differently because the sensitivity of micro-motion is characteristic of the implant geometry45 and implant place ment46. The sensitivity of stem design especially to initial micro-motion (vulnerability of on-growth) will have to be considered in future studies. In this study, we evaluated only implant geometry, however femur variability, especially Dorr femoral bone classification canal stovepipe shape versus champagne flute shape, should be included in future models of THA. Considering the range of anatomical parameters makes it possible to general ize or stratify the results to the entire population.

4. Conclusion

This study indicates that small changes in geometry of uncemented stems can change strain-shielding considerably up to 20% locally. Combinations of moderately low stem stiffness (slender titanium stem with deep grooves) and a large proximal contact area (anatomically curved stem in combination with large surfaces through ribs or grooves) lead to reduced strain-shielding, estimated through finite element analyses. Insights to long-term effects of the improved strain-shielding on bone mass can be gained by clinical studies and may eventually be explained by mathematical remodeling analyses. Both are parts of our ongoing research activities.

Also as a brief summary, our design can improve and enhance:

1) Less micromotions.
2) Decrease stress shielding and stress concentration by optimum coating materials.
3) Low deviation.
4) Increase contact stress or contact pressure for stability in femoral bone.

Finally, geometrical changes (grooves, cross sections, stem length, anatomic curvature) have a considerable effect on strain-shielding; up to 20%. Combinations of reduced stem stiffness with larger proximal contact area (anatomically curved, grooves) lead to less strain-shielding compared to clinically established implant designs.

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Effect of Layer Thickness on Contact Angle in Parts Produced with 3D SLA Method

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ÖZET

Bu çalışmada, stereolitografi (SLA) yöntemi ile fotopolimer reçine kullanılarak üretilen numunelerde, tabaka kalınlığının yüzey ıslanabilirliği üzerindeki etkisi temas açısı ölçümleri yoluyla araştırılmıştır. Numuneler beş farklı tabaka kalınlığında basılmıştır: 0,02 mm, 0,03 mm, 0,04 mm, 0,05 mm ve 0,06 mm. Her numunedeki temas açısı ölçümleri sırasıyla 63.8, 66.7, 72.6, 73.5 ve 74.1° olarak belirlenmiştir. Elde edilen veriler, temas açısının tabaka kalınlığının artmasıyla arttığını açıkça göstermektedir. Bu artış, yüzeyin daha hidrofobik hale geldiğini ve dolayısıyla ıslanabilirliğinin azaldığını göstermektedir. Yüzey pürüzlülüğünün tabaka kalınlığının artmasıyla birlikte artmasının, temas yüzeyini azaltarak su damlacıklarının yayılmasını sınırladığı düşünülmektedir. Sonuç olarak, SLA kullanılarak üretilen parçaların geometrik doğruluğu ve işlevsel yüzey özellikleri, tabaka kalınlığı gibi üretim parametreleri aracılığıyla hassas bir şekilde kontrol edilebilir. Bu, yüzey ıslanabilirliğinin kritik olduğu biyomalzemeler, mikroakışkan sistemler ve fonksiyonel kaplamalar gibi uygulamalar için önemli tasarım girdisi sağlar.

Anahtar Kelimeler : Stereolitografi (SLA), Katman Kalınlığı, Temas Açısı, Yüzey Islanabilirliği.

Effect of Layer Thickness on Contact Angle in Parts Produced with 3D SLA Method

ABSTRACT

This study investigates the effect of layer thickness on surface wettability in samples produced using photopolymer-based materials using stereolithography (SLA) through contact angle measurements. Samples were printed with five different layer thicknesses: 0.02 mm, 0.03 mm, 0.04 mm, 0.05 mm, and 0.06 mm. Contact angle measurements on each sample were determined to be 63.8, 66.7, 72.6, 73.5, and 74.1°, respectively. The obtained data clearly show that the contact angle increases with increasing layer thickness. This increase indicates that the surface becomes more hydrophobic, thus decreasing wettability. It is believed that increasing surface roughness with increasing layer thickness limits water droplet spread by reducing the contact surface. As a result, the geometric accuracy of parts produced using SLA and their functional surface properties can be precisely controlled through manufacturing parameters such as layer thickness. This offers important design input for applications in biomaterials, microfluidic systems, and functional coatings, where surface wettability is critical.

Keywords: Stereolithography (SLA), Layer Thickness, Contact Angle, Surface Wettability.

1. Introduction

Additive manufacturing technologies have gained widespread popularity in industrial applications in recent years because they enable the rapid and cost-effective production of more complex geometries compared to traditional manufacturing methods. Among these technologies, Stereolithography (SLA) is particularly preferred in areas such as biomaterials, microfluidic systems, and functional coatings due to its high precision and surface quality [1-3]. In the SLA method, three-dimensional objects are created by

curing photopolymer resin layer by layer, and the layer thickness used in this process plays a decisive role in production time and part properties [4, 5].

Surface wettability is a critical parameter that defines a surface's interaction with liquids and is particularly important in applications such as medical implants, electronic devices, and water-resistant coatings [6, 7]. In this context, the surface contact angle is considered a direct indicator of the degree of hydrophobicity or hydrophilicity. The surface morphology of parts produced with SLA varies depending on the layer thickness used, which can directly affect the contact angle by influencing how water droplets interact with the surface.

In this study, the effects of different layer thicknesses on the contact angle were experimentally investigated in samples produced using photopolymer resin using the SLA method. The research aimed to integrate manufacturing parameters into the design to optimize application-specific surface properties by controlling surface wettability. Thus, the design flexibility offered by SLA technology can be utilized more effectively for functional surface engineering.

2. Materials and Method

2. 1. Sample preparation

The samples were printed with different layer heights (0.02, 0.03, 0.04, 0.05, and 0.06 mm) on the Elegoo Saturn 3 SLA printer. During the printing process, only the layer thickness was changed; all other parameters were kept constant. Anycubic white resin with a wavelength of 405 nm was used for the study. Three samples for each thickness value were produced with dimensions of 10 mm x 10 mm x 10 mm. After printing, the samples were cleaned with IPA for 5 minutes in the Anycubic Clean and Wash device and then cured with a 405 nm wavelength. Curing was performed for 10 minutes for each sample.

2. 2. Surface morphology measurements

In order to evaluate surface wettability, contact angle measurements on the samples were carried out with the Attension brand contact angle meter device in Figure 1. The sessile drop method was used. Measurements were conducted at constant ambient temperature and relative humidity. Approximately 5 µL of pure water was carefully pipetted onto the surface of each sample. The contact angle was measured using image analysis software using the edge profile of the fixed drop after 10 seconds. Three measurements were taken for each sample, and the average contact angle value was calculated for each sample. To support the relationship between surface roughness and layer thickness, the surface roughness of the selected samples was examined with an optical profilometer. This allowed us to examine the relationship between surface roughness and contact angle.

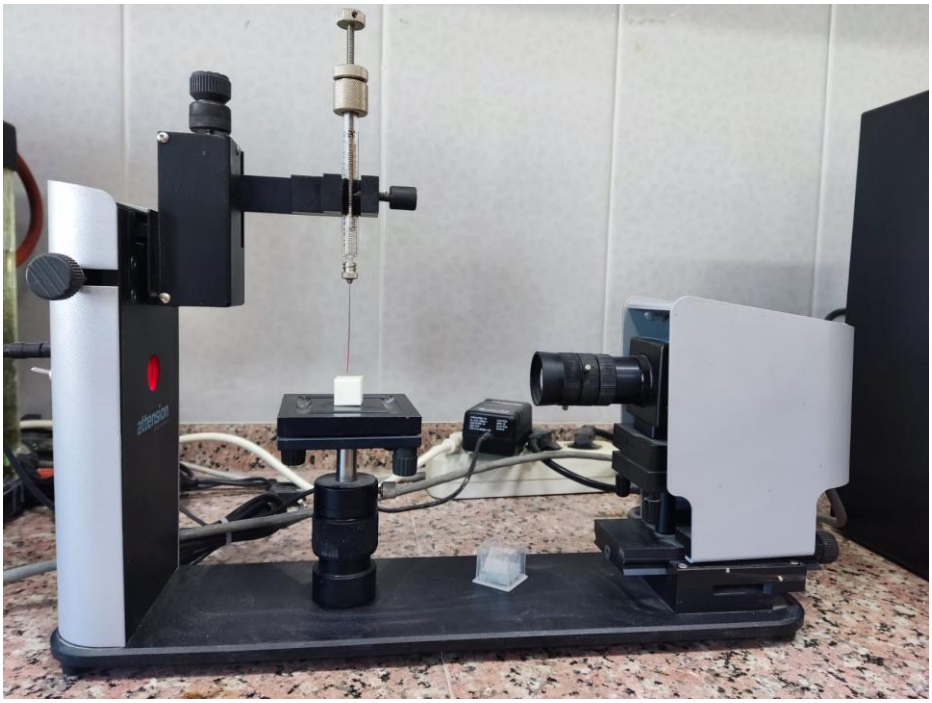

Figure 1. Contact angle meter

3. Results and Discussion

3.1. Contact angle results

The experimental data presented in Table 1 reveal that layer thickness plays a significant role in both surface morphology and wettability. Contact angle measurements were determined as 63.8°, 66.7°, 72.6°, 73.5°, and 74.1° for layer thicknesses of 0.02, 0.03, 0.04, 0.05, and 0.06 mm, respectively. This trend indicates that as layer thickness increases, the surface becomes more hydrophobic, and water droplets spread more limitedly. This suggests that the wettability of the surface decreases, and that the increase in contact angle is primarily related to transformations in the physical structure, not changes in surface energy.

Table 1. Contact angle and surface roughness results

Layer Heights (mm)	0.02	0.03	0.04	0.05	0.06
CA (°)	63.8	66.7	72.6	73.5	74.1
SR (μm)	0.35	0.45	0.52	0.59	0.65

Similarly, surface roughness (Sa) values were measured as 0.35 μm, 0.45 μm, 0.52 μm, 0.59 μm, and 0.65 μm, respectively, with increasing layer thickness. This increase indicates that surface irregularities and layer marks become more pronounced when printing with thicker layers. As layer thickness increases in parts produced using the SLA method, the surface profile formed during the printing process consists of

peaks and valleys, which increases surface roughness. Figure 2 shows the 3D surface profile of a sample with a 0.02 mm layer thickness. The peaks and valleys formed by the layer marks are clearly visible. In this context, as roughness increases, the interaction between the surface and the contacting liquid decreases, causing water droplets to rest at a larger angle on the surface.

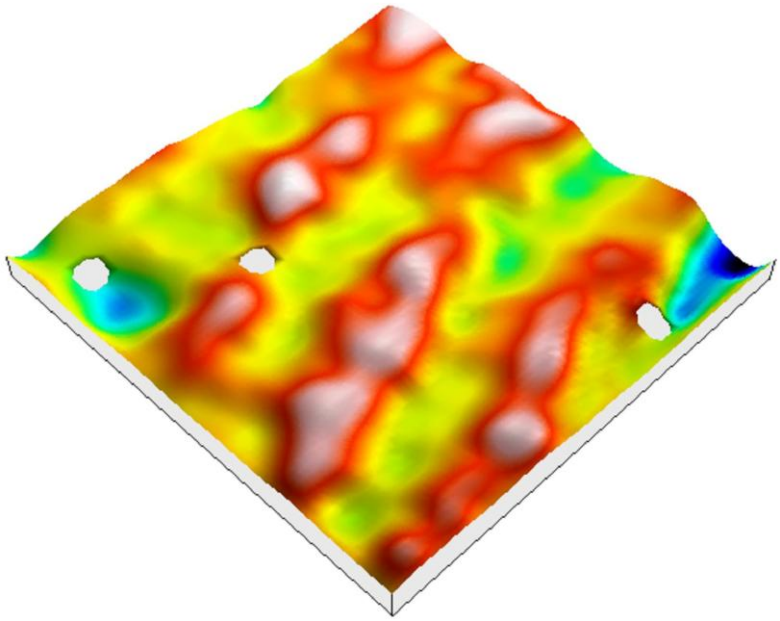

Figure 2. Surface profile of the sample with a layer thickness of 0.02 mm

When considered within the context of the Wenzel model, rough surfaces play a significant role in droplet formation by increasing the actual contact area of the liquid on the surface. This model states that increasing surface roughness will increase the contact angle if the surface is primarily hydrophobic. A similar trend was observed in this study, with a parallel increase in contact angle values as the roughness increases with increasing layer thickness.

Consequently, the layer thickness parameter directly affects not only production time but also surface quality. A key finding of this study is the need for careful optimization of production parameters in applications where surface wettability is critical. It has been demonstrated that in precision manufacturing techniques such as SLA, surface properties, and therefore material performance, can be manipulated as desired by controllable parameters such as layer thickness.

4. Conclusions

This study demonstrated the effects of layer thickness on surface wettability and surface roughness in samples produced using photopolymer resin using stereolithography (SLA). Contact angle and surface roughness values increased, respectively, in samples produced with different layer thicknesses. Increasing layer thickness increased surface roughness, making the surface more hydrophobic and thus increasing the contact angle. These findings demonstrate that manufacturing parameters play a decisive role in surface morphology and functional properties.

It appears that surface properties such as wettability, which directly affect the performance of SLA-produced parts, can be optimized through controllable manufacturing parameters such as layer thickness.

Integrating such parameters into the design process is particularly important in applications where surface contact is critical, such as biomaterials, microfluidic systems, and functional coatings.

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Effect of Heat Treatment Parameters on Microhardness in Hot Forming Process of AISI 4140 Steels

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ÖZET

AISI 4140 çelikleri, yüksek mukavemet ve aşınma direnci gibi üstün mekanik özellikleri nedeniyle otomotiv, savunma ve imalat endüstrilerinde yaygın olarak kullanılmaktadır. Sıcak şekillendirme ile şekillendirilmeleri sırasında uygulanan ısıl işlem parametreleri çeliğin mikro yapısını ve sertliğini önemli ölçüde etkiler. Bu çalışmada, sıcak şekillendirme prosesi sırasında uygulanan farklı ısıl işlem parametrelerinin (sıcaklık, süre ve tekrar sayısı) AISI 4140 çeliğinin mikro sertlik değerlerine etkileri sistematik olarak incelenmiştir. L9 ortogonal dizisi ile oluşturulan deney tasarımına göre, 4140 çelik numuneleri 1-3 ısıtma çevriminde 15, 30 ve 60 dakikalık sürelerle 900°C, 950°C ve 1000°C sıcaklıklara ısıtılmıştır. Sonuçlar; sıcaklık, ısıtma süresi ve tekrar sayısı arttıkça mikro sertliğin azaldığını göstermektedir. Mikrosertlik için etkili parametreler ve optimum sıcak işlem parametreleri belirlenmiştir. Çalışmanın sonuçları, sıcak şekillendirme koşullarının 4140 çeliğinin mikro sertliği üzerindeki etkisini ortaya koymakta ve endüstriyel proseslerde uygun sertlik değerlerinin korunması sonucu sıcak şekillendirme işlemi sırasında hurdaya ayrılan malzemelerin kurtarılmasını sağlayacağı düşünülmektedir.

Anahtar Kelimeler : AISI 4140, sıcak şekillendirme, ısıl işlem, mikro sertlik, tekrarlı ısıtma.

Effect of Heat Treatment Parameters on Microhardness in Hot Forming Process of AISI 4140 Steels

ABSTRACT

AISI 4140 steels are widely used in the automotive, defense, and manufacturing industries due to their superior mechanical properties such as high strength and wear resistance. The heat treatment parameters applied during hot forming significantly affect the microstructure and hardness of the steel. In this study, the effects of different heat treatment parameters (temperature, time, and number of cycles) applied during the hot forming process on the microhardness values of AISI 4140 steel were systematically investigated. According to the experimental design created with the L9 orthogonal array, 4140 steel samples were heated to 900°C, 950°C, and 1000°C for 15, 30, and 60 minutes in 1-3 heating cycles. The results show that microhardness decreases as temperature, heating time, and number of cycles increase. The effective parameters for microhardness and the optimum hot working parameters were determined. The results of the study reveal the effect of hot forming conditions on the microhardness of 4140 steel and it is thought that maintaining appropriate hardness values in industrial processes will enable the recovery of materials scrapped during the hot forming process.

Keywords: AISI 4140, hot forming, heat treatment, microhardness, reheating.

1. Introduction

AISI 4140 steels are widely used in many industrial fields, including the defense industry, automotive, aerospace, and machine manufacturing, due to their superior mechanical properties such as high strength, toughness, and wear resistance. In industry, they are frequently subjected to processes such as

hot forming, machining, and pressing, where their mechanical properties are modified through heat treatments. The mechanical properties of these steels can vary significantly depending on the applied heat treatment parameters (temperature, cooling rate, annealing time, etc.). In particular, the temperature range to which 4140 steels are exposed during hot working (generally between 800°C and 1200°C) is a critical region where microstructural transformations (austenitization, martensitic transformation, and ferrite-bainite formation) occur. These transformations directly affect the steel's mechanical properties such as hardness, tensile strength, toughness, and ductility [1-4].

Various studies have attempted to optimize hot forming parameters for AISI 4140 steel to achieve a balance between hardness, strength, and ductility. A study by Wang et al. (2013) investigated the austenite grain growth behavior of AISI 4140 alloy steel under various temperatures and holding times. Samples were heated to temperatures between 800 °C and 1100 °C and held for up to 480 seconds. The results showed that austenite grain size increased with both temperature and holding time. In particular, higher temperatures and longer holding times led to significant grain growth, which could negatively affect mechanical properties such as strength and toughness [5].

In another study by Zhang and Sisson (2015), the effects of austenitizing temperatures and holding times on the grain size and hardness of 4140 steel were investigated. The samples were heat treated at 900°C, 1000°C, and 1100°C with holding times of 1, 4, and 9 hours. Findings showed that higher austenitizing temperatures and longer holding times resulted in increased grain sizes and decreased hardness, indicating a decrease in strength and toughness [6].

Research by Lv et al. (2017) suggested that controlling the cooling rate could optimize the formation of martensite and bainite, thereby increasing both the hardness and toughness of the material. The study also emphasized that quenching at high temperatures should be avoided unless a specific hardness is required [7].

Sanij et al. (2012) investigated how single and double quenching and tempering processes affect the microstructure and mechanical properties of AISI 4140 steel. The authors found that double quenching and tempering can increase certain mechanical properties, such as strength and toughness, without significantly reducing ductility. However, they also noted that excessive or inappropriate heat treatment cycles can lead to adverse effects, including increased brittleness [8].
4140 steels are heated to a temperature between 900 and 1100°C for hot forming. Generally, in induction heating systems, the process begins after the desired temperature is reached. During mass production with hot forming, many malfunctions and errors can cause system downtime. Steel wedges are heated in induction furnaces of various sizes and dimensions, and if a sudden stop occurs, they must be removed from the furnace. Once the faults or errors are corrected, the wedges are returned to the furnace. However, these 4140 steel wedges can only be heated to the hot forming zone twice. When heated three or more times, the material's elongation decreases and the material becomes brittle. Especially in vital industries such as the defense industry, the mechanical properties of materials must be maintained during the manufacturing process. Therefore, it is crucial to investigate the hot working parameters and optimize the mechanical properties of 4140 steels after heating to the hot forming zone.

Within the scope of this study, changes in the microhardness of 4140 steels were experimentally investigated under different temperature, time, and cyclic heating parameters. In particular, the effects of hot forming temperature and the number of cycles, which significantly affect the mechanical properties of the steel after heat treatment, on the hardness of the steel were analyzed in detail. The values obtained from these experiments were used to determine which parameters influenced hardness.

2. Materials and Method

After polishing the surfaces of 20 mm diameter 4140 steel, they were subjected to heat treatment according to the parameters listed in Table 1. After heat treatment, only the surface was descaled and the surfaces were cleaned, and the Vickers hardness test was performed. Three tests were performed on each sample to determine the average hardness results. The hardness test results were analyzed using the Taguchi method, and the effective parameters were determined.

Table 1. Hot forming parameters

Exp. No	Temperature	Time	Number Of Cycles
1	950	20	1
2	950	40	2
3	950	60	3
4	1000	20	2
5	1000	40	3
6	1000	60	1
7	1050	20	3
8	1050	40	1
9	1050	60	2

3. Results and Discussion

3.1. Hardness results

The average hardness value of each parameter is given in Table 2. As a result of the experimental studies, it is seen that the increase in temperature, heating time and number of cycles significantly decreases the Vickers microhardness (Hv) of AISI 4140 steel. As time and number of cycles increase at 950°C, the hardness decreases from 287 Hv to 278 Hv and then to 265 Hv, respectively. Similarly, in experiments carried out at 1000°C, as heat treatment time and number of cycles increased, the hardness decreased from 269 Hv to 257 Hv and to a minimum of 251 Hv. The lowest hardness values were obtained at 1050°C; with time and cycle factors, the hardness decreased to 246 Hv, 242 Hv and finally to 235 Hv. These data show that each of the heat treatment parameters has a negative effect on hardness; That is, as temperature, time, and number of cycles increase, changes in the microstructure decrease hardness. The material softened significantly, particularly at 1050°C and at higher cycle/time combinations.

Table 2. Hardness results for each parameter

Exp. No	Temperature	Time	Number Of Cycles	Hardness (Hv)
1	950	20	1	287
2	950	40	2	278
3	950	60	3	265
4	1000	20	2	269
5	1000	40	3	257
6	1000	60	1	251
7	1050	20	3	242
8	1050	40	1	246
9	1050	60	2	235

3.2. Taguchi analysis

When Table 3 and Figure 1 showing the S/N ratios obtained using the Taguchi method are evaluated together, a significant decrease in hardness values is observed as the temperature increases. The graph clearly shows a sharp decrease in the S/N ratio from 950°C to 1050°C. This is further supported by the fact that the average S/N ratio difference between temperature levels is at its highest value. This demonstrates that temperature is the factor that causes the greatest change in the steel's microstructure and, consequently, the greatest loss in hardness.

When the time parameter is examined, a moderate decrease in the SN ratio is observed as time increases. While higher hardness values were obtained after 20 minutes of heating, decreased after 60 minutes. Table 3 and Figure 1 show that the average effect of time is less than that of temperature, but still significant. On the other hand, when the number of heating cycles is evaluated, very limited change in S/N ratios is observed. Although hardness values decrease slightly as the number of cycles increases, it is clear from Table 3 and Figure 1 that this effect is quite weak compared to the other two parameters.

When Figure 1 and Table 3 are evaluated together, temperature is the most influential parameter, time is moderately influential, and number of cycles is the least influential parameter.

Table 3. Response Table for S/N Ratios

Level	Temperature	Time	Cycle
1	48,83	48,48	48,32
2	48,26	48,30	48,30
3	47,64	47,96	48,11
Delta	1,20	0,52	0,21
Rank	1	2	3

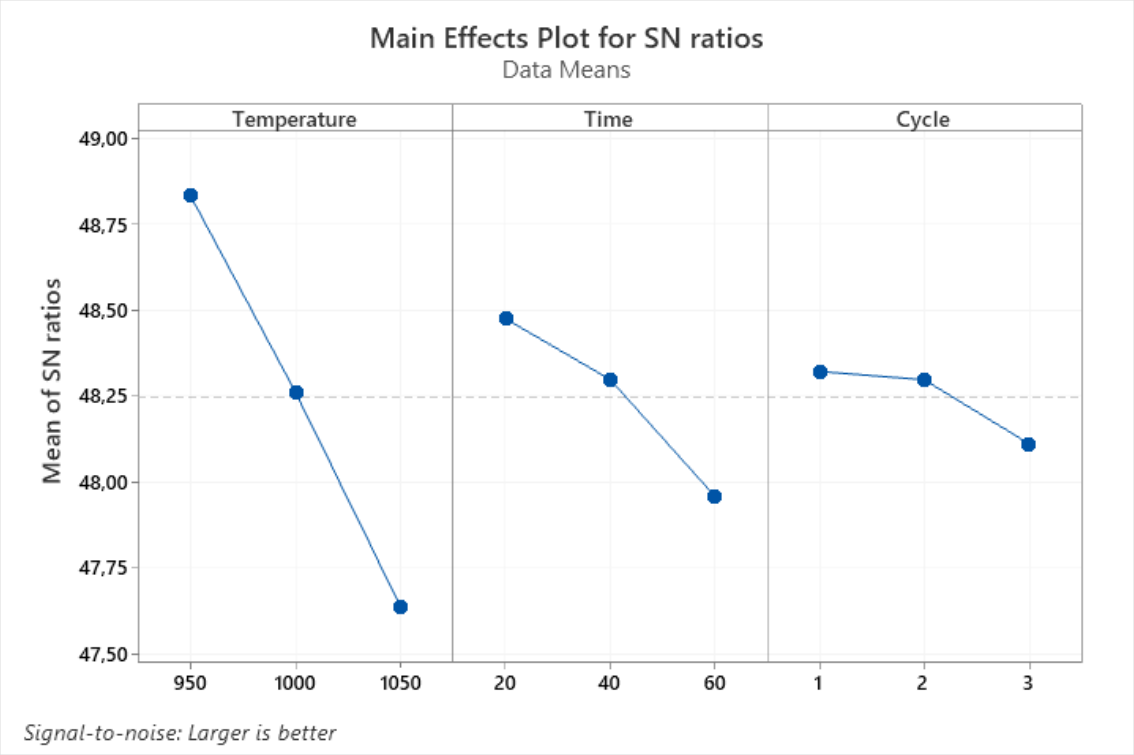

Figure 1. S/N graph for hardness (Hv)

3.3. Analysis of Variance (ANOVA) for hardness

According to the ANOVA analysis presented in Table 4, temperature is the most influential factor among the heat treatment parameters applied to AISI 4140 steel. The F-value calculated for temperature was 117.63 and the p-value was 0.008 ($p<0.05$). The temperature change resulted in a highly statistically significant change in the steel's hardness.

The F-value obtained for heating time was 23.27 and the p-value was 0.041. This value is less than 0.05, making it statistically significant. This indicates that the time parameter also has an effect on hardness, but its effect is less than that of temperature.

The number of heating cycles had the least impact. This factor had a p-value of 0.167. This p-value, being above 0.05, is not statistically significant. That is, it is concluded that the change in the number of cycles is not an effective parameter on steel hardness.

Table 4. Analysis of Variance for hardness

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Temperature	2	1908,22	954,111	117,63	0,008
Time	2	377,56	188,778	23,27	0,041
Cycle	2	80,89	40,444	4,99	0,167
Error	2	16,22	8,111		
Total	8	2382,89			

4. Conclusions

In this study, the effects of heat treatment parameters (temperature, time, and number of cycles) on microhardness before hot forming of AISI 4140 steel were systematically investigated. In experiments conducted using the L9 orthogonal experimental design, a significant decrease in the microhardness values of the steel was observed as the temperature, heating time, and number of cycles increased.

- Temperature was determined to be the most influential parameter on microhardness. High temperatures cause significant hardness losses.
- Heating time has a moderate impact on hardness, with prolonged heating resulting in greater softening.
- The number of heating cycles was determined to have the least impact on hardness and did not produce a statistically significant difference.
- The S/N ratio graphs and ANOVA obtained using the Taguchi method support these findings, demonstrating that optimal microhardness values can be achieved with lower temperatures, shorter times, and minimal heating cycles.

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Synthesis, Sintering Behavior, and Structural Characterization of Calcium Phosphate-Based Bioceramics for Bone Tissue Applications

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ABSTRACT

This study investigates the synthesis, shaping, and characterization of calcium-phosphate-based bioceramics, specifically hydroxyapatite (HA) and tricalcium phosphate (TCP), produced using two precursor systems: high-purity CaO and industrial marble powder. Calcium nitrate solutions were prepared by reacting CaO or $CaCO_3$-rich marble powder with nitric acid, followed by pH adjustment and precipitation using diammonium hydrogen phosphate. The obtained precipitates were centrifuged, washed, dried, and calcined at temperatures ranging from 750 to 1100 °C to obtain phase-pure HA and TCP powders. The powders were shaped by uniaxial pressing and sintered at 1200 °C. Mechanical strength, water absorption, apparent porosity, density, and X-ray diffraction (XRD) analyses were performed. Results indicate that CaO-derived powders produced highly crystalline HA at 750–850 °C and pure TCP at 1100 °C, while marble-derived precursors generated bioceramics with comparable phase structure. Sintered samples exhibited bending strengths between 129–326 kg/cm², porosity from 9–33%, and densities of 1.64–1.80 g/cm³. The findings demonstrate that marble powder—an inexpensive industrial waste—can be successfully used as an alternative raw material for biomedical-grade bioceramic production.

Keywords: Tricalcium phosphate (TCP), Calcium phosphate ceramics, Bioceramics, Sintering temperature, Phase transformation, X-ray diffraction (XRD)

Kemik Dokusu Uygulamaları için Kalsiyum Fosfat Bazlı Biyoseramiklerin Sentezi, Sinterleme Davranışı ve Yapısal Karakterizasyonu

ÖZET

Bu çalışmada, iki başlangıç maddesi (yüksek saflıkta CaO ve endüstriyel mermer tozu) kullanılarak üretilen kalsiyum fosfat esaslı biyoseramiklerin, özellikle hidroksiapatit (HA) ve trikalsiyum fosfatın (TCP) sentezi, şekillendirilmesi ve karakterizasyonu araştırılmıştır. Kalsiyum nitrat çözeltileri, CaO veya $CaCO_3$ açısından zengin mermer tozunun nitrik asitle reaksiyona sokulması, ardından pH ayarlanması ve diamonyum hidrojen fosfat kullanılarak çöktürülmesiyle hazırlanmıştır. Elde edilen çökeltiler santrifüj edilmiş, yıkanmış, kurutulmuş ve 750 ila 1100 °C arasındaki sıcaklıklarda kalsine edilerek faz saflığında HA ve TCP tozları elde edilmiştir. Tozlar tek eksenli presleme ile şekillendirilmiş ve 1200 °C'de sinterlenmiştir. Mekanik dayanım, su emilimi, görünür gözeneklilik, yoğunluk ve X-ışını kırınımı (XRD) analizleri yapılmıştır. Sonuçlar, CaO türevi tozların 750-850 °C'de yüksek kristalli HA ve 1100 °C'de saf TCP ürettiğini, mermer türevi öncüllerin ise benzer faz yapısına sahip biyoseramikler ürettiğini göstermektedir. Sinterlenmiş numuneler 129-326 kg/cm² arasında eğilme mukavemeti, %9-33 arasında gözeneklilik ve 1,64-1,80 g/cm³ yoğunluk sergilemiştir. Bulgular, ucuz bir endüstriyel atık olan mermer tozunun, biyomedikal sınıf biyoseramik üretimi için alternatif bir hammadde olarak başarıyla kullanılabileceğini göstermektedir.

Anahtar Kelimeler : Trikalsiyum fosfat (TCP), Kalsiyum fosfat seramikleri, Biyoseramikler, Sinterleme sıcaklığı, Faz dönüşümü, X-ışını kırınımı (XRD)

1. Introduction

Bioceramics such as hydroxyapatite (HA) and tricalcium phosphate (TCP) have gained significant importance due to their close chemical similarity to the mineral phase of bone and teeth (Rh Owen et al 2018, Champion 2013). Their biocompatibility, bioactivity, and structural resemblance to natural hard tissues make them highly suitable for orthopedic and dental implant applications (Nouri et al 2010, Jazayeri et al 2016). Historically, calcium-phosphate materials were first explored for bone substitution in the early 20th century and later commercialized following extensive research in the 1960s and 1970s (Dorozhkin 2013, Eliaz and Metoki 2017).

HA ($Ca_{10}(PO_4)_6(OH)_2$) is known for its chemical stability and strong interfacial bonding with bone tissue, whereas TCP ($Ca_3(PO_4)_2$) is bioresorbable and gradually replaced by new bone(Kareiva 2025, Dorozhkin 2022). Many biomedical applications utilize biphasic mixtures of HA and TCP to balance bioactivity and resorption rate (RH Owen et al 2018). Producing these phases in controlled stoichiometry requires precise synthesis routes, typically involving aqueous precipitation, hydrothermal processing, or solid-state reactions(Kargozar et al 2019, Biswal et al 2020).

In recent years, the use of industrial waste materials as calcium sources has attracted interest due to cost reduction and environmental considerations (Makinde et al 2007). Marble powder, rich in $CaCO_3$, presents a promising alternative precursor for HA/TCP synthesis. This study evaluates the feasibility of producing high-quality bioceramic powders using both pure CaO and marble waste, while comparing structural, physical, and mechanical properties of the resulting materials.

2. Materials and Methods

2.1. Materials

Two calcium sources were used:

High-purity CaO (Merck, 96%)

Industrial marble powder containing ~44.5% CaO, obtained from Afyon Reis Marble Factory

Other reagents included nitric acid (HNO_3), diammonium hydrogen phosphate ($(NH_4)_2HPO_4$), ammonium hydroxide (NH_4OH), and polyvinyl alcohol (PVA) as a binder.

2.2. Synthesis of HA and TCP Powders

CaO was dissolved in HNO_3 to form $Ca(NO_3)_2$ solution, and the pH was adjusted above 8 with NH_4OH. A separate $(NH_4)_2HPO_4$ solution was similarly prepared and added dropwise (2–5 mL/min) under stirring and heating. A fine precipitate formed, which was centrifuged, washed, and dried at 100 °C. Dried powders were calcined at 750 °C / 3 h, 850 °C / 3–5 h for HA 1100 °C / 12 h for TCP. Resulting powders were ground to 1–10 μm.

2.3. Powder Shaping and Sintering

Dried powders were mixed with 5 wt.% PVA and pressed uniaxially into 5×1×1 cm bars at 40 bar. Samples were dried and sintered following a stepped heating schedule up to 1200 °C.

2.4. Characterization

XRD analysis was performed using Shimadzu XRD-6000. Three-point bending strength was measured on sintered bars. Water absorption, apparent porosity, and bulk density were determined using standard boiling-water methods.

3. Results and Discussion

3.1. Phase Analysis

The results of bioceramic powders obtained using calcined marble powder and CaO are shown in Figure 1 and 2 The XRD pattern results of bioceramic powders obtained using calcined marble powder showed no HA (hydroxyapatite) formation; instead, peaks of dicalcium phosphate, an intermediate phase in the formation of HA, were observed. The bioceramic powder producing this result was formed after calcination at 1100°C. The XRD analysis results of bioceramic powders obtained using 96% pure CaO revealed the formation of a TCP (tricalcium phosphate) peak, which was identical to the standard TCP peaks. The TCP bioceramic powder results shown here were obtained after calcination at 1100°C for 12 hours (Takagi et al 1998, Ferreira et al 2003).

The XRD pattern of the powders synthesized using calcined marble waste shows a highly complex and multiphasic structure characterized by numerous low-to-medium intensity reflections distributed over a wide 2θ range. This behaviour is directly related to the chemical impurities inherently present in marble waste, such as MgO, SiO_2, Al_2O_3, and Fe_2O_3. These components disrupt the normal crystallization of calcium phosphate phases at high temperature and lead to the formation of various secondary phases, including calcium silicates (e.g., β-Ca_2SiO_4 and $Ca_3Si_2O_7$), residual calcite or dolomite decomposition products, and magnesium-containing oxides. Although some β-TCP peaks are still detectable, their intensities are significantly reduced, indicating that TCP is not the dominant phase in this system. The abundance of additional peaks confirms that the marble-derived calcium source results in extensive phase diversification and reduced crystallinity due to the presence of silica and magnesia impurities acting as structural disruptors(Aliyu et al 2023, (Gallinetti et al 2014).

The XRD pattern obtained from the powders synthesized using pure CaO exhibits sharp, high-intensity reflections, indicating a well-crystallized and compositionally controlled structure. The dominant diffraction peaks observed in the 29–34° 2θ range correspond closely to the characteristic reflections of β-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$). In particular, the peaks near 29.3°, 32.3°, and 34.4° match the fundamental β-TCP planes reported in the literature, confirming that β-TCP is the major crystalline phase formed at high temperature. A few minor reflections of lower intensity suggest the presence of small amounts of intermediate phosphate phases such as dicalcium phosphate (DCP) or calcium pyrophosphate ($Ca_2P_2O_7$). Overall, the blue pattern demonstrates that the use of pure CaO promotes a stable and predictable phase transformation pathway, yielding a predominantly β-TCP structure with high crystallinity (Caicedo et al 2020, Massit et al 2021).

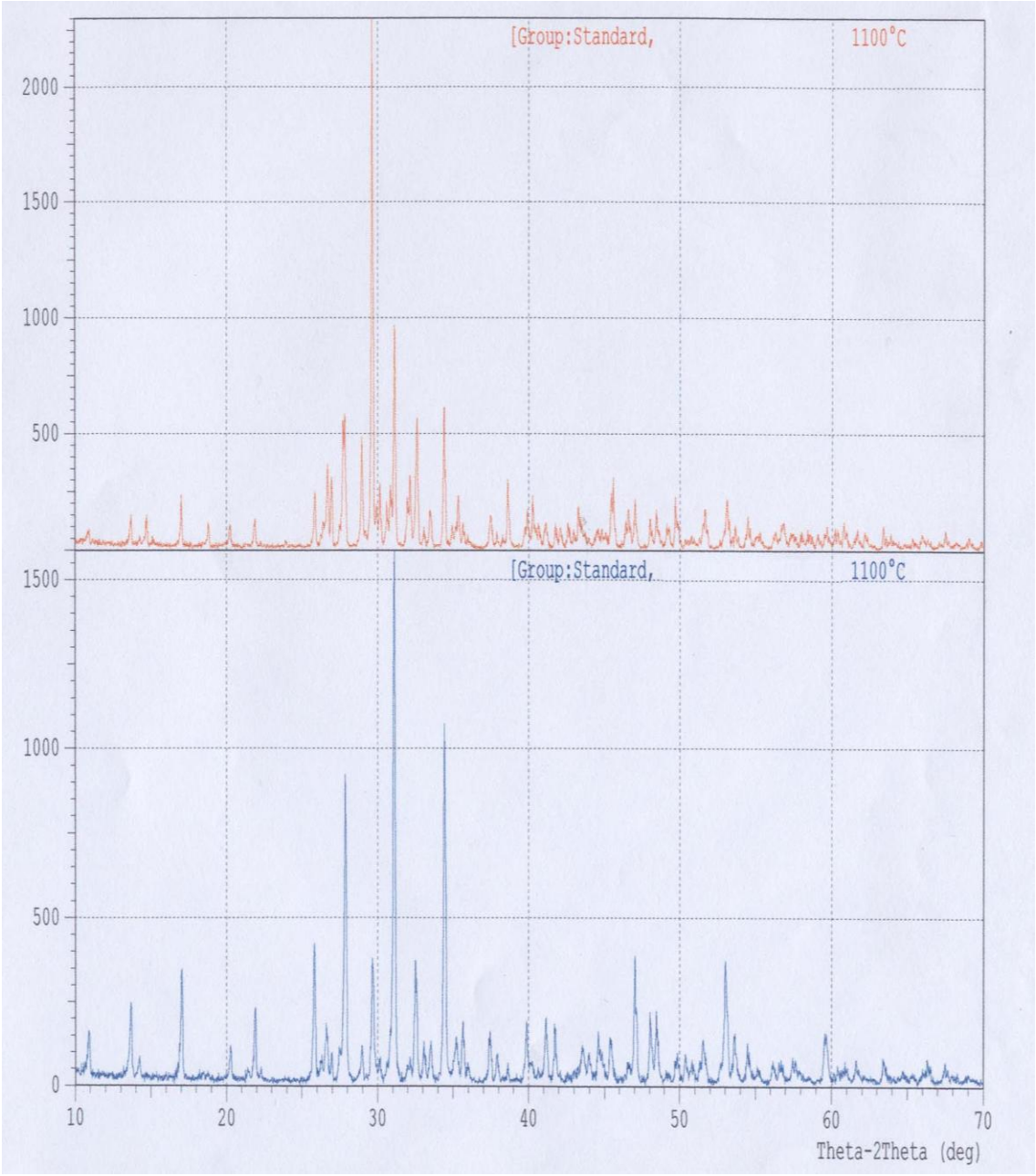

Figure 1. XRD diagram of bioceramic powders.

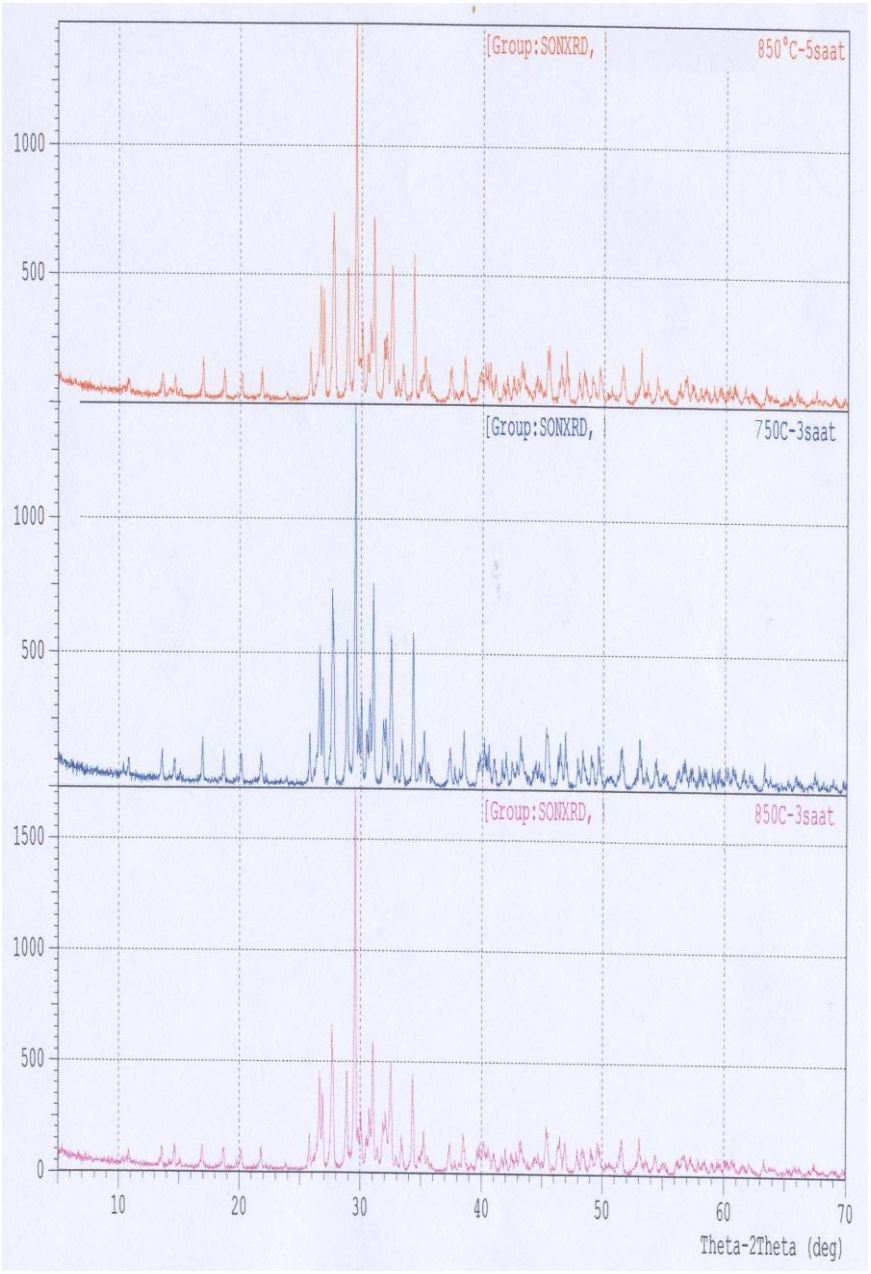

Figure 2. Effect of sintering temperature

The XRD pattern obtained at 750 °C for 3 hours shows a mixture of partially developed phosphate phases with moderate crystallinity. While the characteristic reflections of calcium phosphate—particularly those associated with β-tricalcium phosphate (β-TCP)—begin to appear, their intensities remain relatively low compared to higher-temperature samples. This indicates that the thermal energy supplied at 750 °C is insufficient to drive a complete transformation of precursor phases into a fully crystallized TCP structure. The presence of several broad or low-intensity peaks suggests that intermediate phases such as dicalcium phosphate (DCP) or partially decomposed carbonate residues may persist at this temperature. Overall, the sample treated at 750 °C represents an early stage of phase formation, where the crystal structure is still evolving and thermally activated diffusion is limited (Pena and Vallet 2003, (Ferreira et al 2003).

The sample treated at **850 °C for 3 hours** exhibits a significant improvement in crystallinity and peak definition compared to the 750 °C sample. At this elevated temperature, the majority of intermediate phosphate phases have undergone further transformation, leading to clearer and more intense β-TCP reflections, particularly in the 29–34° 2θ region. The sharper peaks indicate enhanced atomic ordering

and increased crystal domain size, consistent with more efficient solid-state diffusion at higher temperatures. However, the pattern also shows evidence of minor coexisting phases—likely silicate-, magnesium-, or carbonate-derived side phases—suggesting that although the primary transformation toward β-TCP is progressing, complete phase purification has not yet been achieved. This stage represents an intermediate degree of thermal maturation, where crystalline growth is pronounced but still not maximized (Nahar et al 2017 Bakan 2019).

The XRD pattern corresponding to **850 °C for 5 hours** demonstrates the most advanced degree of crystallization among the tested conditions. The peaks are sharper, narrower, and more intense than those observed in shorter-duration or lower-temperature treatments, confirming that prolonged exposure at 850 °C enables the system to achieve a more thermodynamically stable phase composition. The β-TCP reflections dominate the pattern, indicating that extended holding time facilitates the complete conversion of precursor phases, minimizes residual intermediates, and enhances lattice ordering. The reduction in background noise and the increase in peak symmetry strongly suggest improved grain growth and a higher degree of phase purity. This condition—high temperature combined with longer dwell time—provides the optimal environment for the formation and stabilization of well-crystallized β-TCP structures (Nahar et al 2017, Bakan 2019).

3.2. Mechanical Properties

Table 1. Three-Point Bend Test Results

Sample	Load (kg)	Strength (kg/cm2)
A Tricalcium phosphate	18,58	200,8
B Dicalcium phospshate powder calcined at 850°C for 5 hours	9,7	129,0
C 850°C for 3 hours	19,5	295,85
D 750°C for 3 hours	23,85	326,0

Three-point bending strengths of sintered ceramics ranged from 129–326 kg/cm² (Table 2.4). The highest strength corresponded to samples calcined at 750 °C and 850 °C for shorter durations, likely due to improved microstructural homogeneity and reduced crack density. TCP samples showed lower strength due to higher intrinsic brittleness (Yang et al 2010, Lin et al 2009).

3.3. Porosity, Density and Water absorption

Table 2. Physical Test Results

Sample	Water absorption (%)	Apparent porosity (%)	Bulk Density
A	20	33	1,645
B	8	15	1,65
C	7,5	13	1,75
D	5,75	9,65	1,80

Porosity values ranged from 9.6% to 33%, depending on calcination temperature. HA samples calcined at lower temperatures showed higher porosity, while TCP sintered at 1200 °C showed lower porosity.

Bulk densities increased with decreasing porosity, reaching 1.80 g/cm³ for the densest samples. These values are consistent with biomedical porous scaffold requirements, where interconnected porosity supports bone ingrowth (Champion 2013, Hung et al 2012).

4. Conclusion

Micron-sized, chemically homogeneous bioceramic powders of tricalcium phosphate (TCP) and dicalcium phosphate were synthesized by chemical precipitation using CaO and calcined marble powder as calcium sources. The primary objective was to produce submicron TCP ($Ca_3(PO_4)_2$) and hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$); however, XRD analyses revealed that HA could not be obtained under the applied conditions, and instead its intermediate phase, dicalcium phosphate ($Ca_2P_2O_7$), was formed. When marble powder was used, dicalcium phosphate appeared in multiple crystal structures, whereas CaO-based precursors converted to TCP only at high temperatures (≥1100 °C). TCP powders were successfully formed after 12 h calcination at 1100 °C, while marble-derived powders calcined under the same conditions produced only dicalcium phosphate. Lower calcination temperatures (750–850 °C) consistently yielded dicalcium phosphate as an intermediate HA phase. Sintered TCP specimens exhibited approximately 33% apparent porosity, 20% water absorption, and a bulk density of 1.645 g/cm³, while dicalcium phosphate samples showed temperature-dependent variations in porosity and water absorption, being lower for samples calcined at lower temperatures. Particle size analysis indicated significantly coarser grains in TCP ($D_{0.1}$ = 4.95 µm, $D_{0.5}$ = 19.07 µm, $D_{0.97}$ = 556.97 µm) compared to CaO-derived dicalcium phosphate ($D_{0.1}$ = 1.28 µm, $D_{0.5}$ = 6.45 µm, $D_{0.97}$ = 38.86 µm). Optical microscopy further confirmed the pore distribution in the sintered bodies. Overall, the study shows that HA formation was not achieved, while TCP and dicalcium phosphate phases predominated, suggesting that HA synthesis requires alternative Ca/P ratios and different calcination regimes, marble powder must be purified before use, and improved porosity control in TCP may be achieved by exploring different shaping methods, binder types, and binder contents.

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Influence of Different Electrolytes on the Rheological and Physical Properties of Floor Tile Bodies

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ABSTRACT

This study investigates the effects of three different deflocculants—sodium silicate (Na_2SiO_3), sodium tripolyphosphate (STPP), and Dolapix PC67—on the rheological behavior, casting performance, and final ceramic properties of a floor-tile slip formulation. Raw materials including kaolin, two types of clay, albit, and pegmatite were mixed according to a standard tile recipe and processed under controlled grinding, casting, drying, and firing conditions. For each deflocculant, optimum dosage was determined using Ford-cup viscosity measurements. Prepared samples were evaluated in terms of dry, firing, and total shrinkage, dry and fired strength, layer formation rate, water absorption, and porosity. The results indicate that Dolapix PC67 provides the lowest viscosity and most efficient casting behavior, while Na_2SiO_3 shows the lowest shrinkage values but exhibits the highest porosity and water absorption. STPP yields the highest dry strength. The study demonstrates that deflocculant type has a significant influence on suspension rheology and the physical–mechanical performance of ceramic bodies.

Keywords: Floor tiles, Ceramic body formulation, Electrolytes, Sodium silicate (Na_2SiO_3), Sodium tripolyphosphate (STPP), Dolapix PC67

Farklı Elektrolitlerin Yer Karosu Gövdelerinin Reolojik ve Fiziksel Özellikleri Üzerindeki Etkisi

ÖZET

Bu çalışmada, üç farklı deflokülantın (sodyum silikat (Na_2SiO_3), sodyum tripolifosfat (STPP) ve Dolapix PC67) bir yer karosu kayma formülasyonunun reolojik davranışı, döküm performansı ve son seramik özellikleri üzerindeki etkileri araştırılmıştır. Kaolin, iki tip kil, albit ve pegmatit içeren hammaddeler standart bir karo reçetesine göre karıştırılmış ve kontrollü öğütme, döküm, kurutma ve pişirme koşulları altında işlenmiştir. Her bir deflokülant için optimum dozaj, Ford-cup viskozite ölçümleri kullanılarak belirlenmiştir. Hazırlanan numuneler kuru, pişirme ve toplam büzülme, kuru ve pişirme dayanımı, tabaka oluşum hızı, su emilimi ve gözeneklilik açısından değerlendirilmiştir. Sonuçlar, Dolapix PC67'nin en düşük viskoziteyi ve en verimli döküm davranışını sağladığını, Na_2SiO_3'nin ise en düşük büzülme değerlerini gösterdiğini ancak en yüksek gözeneklilik ve su emilimini sergilediğini göstermiştir. STPP en yüksek kuru dayanımı sağlamaktadır. Çalışma, deflokülant tipinin süspansiyon reolojisi ve seramik gövdelerin fiziksel-mekanik performansı üzerinde önemli bir etkiye sahip olduğunu göstermektedir.

Anahtar Kelimeler : Zemin karoları, Seramik gövde formülasyonu, Elektrolitler, Sodyum silikat (Na_2SiO_3), Sodyum tripolifosfat (STPP), Dolapix PC67

1. INTRODUCTION

Deflocculants play a crucial role in ceramic slip preparation by modifying the rheological behavior of aqueous suspensions. The stability, viscosity, and casting performance of a ceramic slip strongly depend on the type and amount of deflocculant used. These additives improve particle dispersion by increasing zeta potential and reducing interparticle attraction, thus minimizing flocculation and enhancing flowability. Maintaining a stable viscosity is particularly important in industrial ceramic processes, as raw materials from different deposits may exhibit variations in mineralogy, particle size distribution, and chemical composition (Vitali and Giorgini 2019, Ercioğlu et al 2024, Barrachina et l 2015).

Slip casting is widely used for shaping both traditional and advanced ceramics, and the success of this method depends on the controlled formation of a solid layer on the mold surface. Parameters such as plasticity, shrinkage behavior, strength, porosity, and water absorption are closely related to the rheology of the slip. Improper dispersion leads to poor casting behavior, defects, cracking during drying, or undesired changes in shrinkage(Treccani 2023, Bauer et al 1998, Evans 2008).

In this study, ceramic slips prepared from standard floor-tile raw materials were modified with three different deflocculants—Na_2SiO_3, STPP, and Dolapix PC67. The objective was to compare their effects on rheology, casting behavior, and the resulting physical and mechanical properties of ceramic bodies. Optimum deflocculant dosages were determined experimentally, and the overall impact of each additive was systematically evaluated.

2. MATERIALS AND METHODS

2.1 Raw Materials

Kaolin (Uşak), two clays (Eti Sörhaz and Eczacıbaşı ESBK2), albit (Çine), and pegmatite (Çaltı) were used. Chemical compositions were determined using standard analytical techniques. Based on the tile formulation, the batch consisted of 50% plastic materials (clays + kaolin) and 50% non-plastic materials (albit + pegmatite).

2.2 Grinding and Slip Preparation

Each raw material was ground separately in a ball mill.

- Pegmatite was ground for 8 h and albit for 7 h to <74 µm.
- Clays were crushed and sieved through 298 µm.

Slip preparation involved mixing ground powders with water at a solid-to-liquid ratio of **65/35**, resulting in a slip with a density of **1640 g/L**. Three deflocculants—Na_2SiO_3, STPP, and Dolapix PC67—were added at dosages just below their determined optimum levels.

2.3 Determination of Optimum Deflocculant Content

Optimum dosage was determined using incremental addition of each deflocculant, Ford-cup viscosity measurements, plotting flow time versus deflocculant amount. Optimum dosages for 300 g slip were for **Na_2SiO_3:** 1.56 g, **STPP:** 1.20 g, **Dolapix PC67:** 1.08 g

2.4 Casting, Drying, and Firing

Slips were cast into plaster molds (gypsum/water ratio = 1.43). Specimens were dried at room temperature and then at 105°C, fired in a kiln at **1180°C for 2 hours**, with 15 minutes holding time.

2.5 Characterization Tests

The following tests were performed:

- **Shrinkage:** dry, firing, and total shrinkage measured via caliper.
- **Mechanical strength:** three-point bending tests on dry and fired samples.
- **Layer formation rate:** measuring wall thickness after 10, 20, 30, 40 min.
- **Water absorption:** boiling method.
- **Porosity:** Archimedes method.

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3. RESULTS AND DISCUSSION

3.1 Optimum Deflocculant Behavior

Dolapix PC67 exhibited the strongest deflocculating effect, achieving minimum viscosity with the lowest dosage. The ranking in terms of fluidization efficiency was:

Dolapix PC67 > STPP > Na_2SiO_3

This reflects the superior electrosteric stabilization ability of Dolapix PC67 (Nunes et al 1992, Biswas and Raichur 2010).

3.2 Shrinkage Behavior

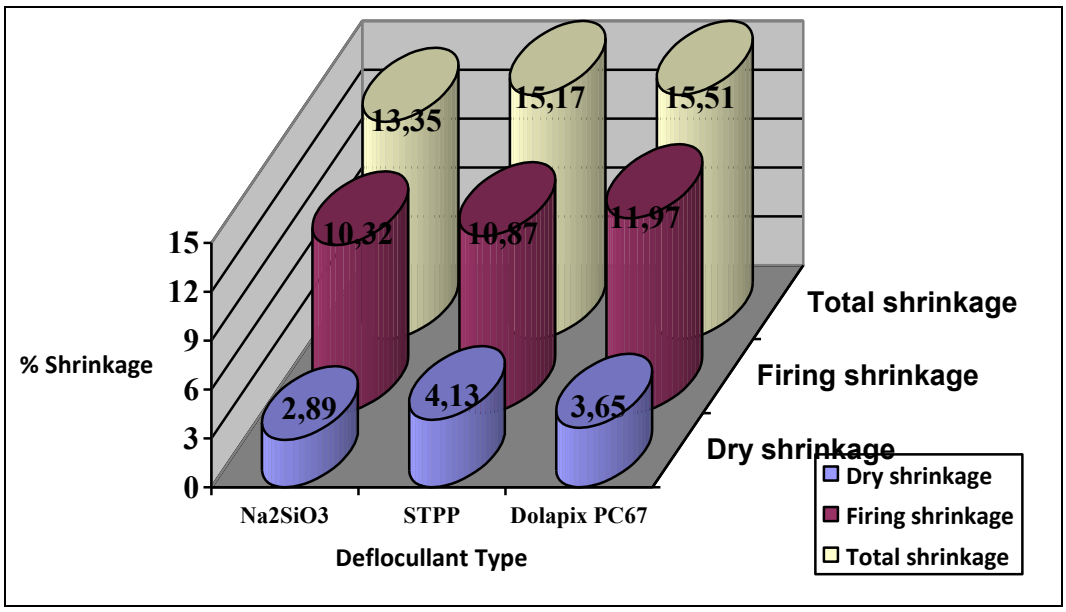

Figure Comparison of % dry, % firing and % total shrinkage values depending on the type of deflocculant

Average shrinkage values showed that:

- **Dry shrinkage:** STPP > Dolapix PC67 > Na_2SiO_3
- **Firing shrinkage:** Dolapix PC67 > STPP > Na_2SiO_3
- **Total shrinkage:** Dolapix PC67 > STPP > Na_2SiO_3

The graph compares the percentage of dry, firing, and total shrinkage for samples prepared with different deflocculant types (Na_2SiO_3, STPP, and Dolapix PC-67). Overall, the results indicate that the choice of deflocculant has a measurable effect on all shrinkage stages. Dry shrinkage values remain relatively low

for all samples, ranging from 2.89% to 4.13%, with STPP showing the highest dry shrinkage and Na_2SiO_3 the lowest. Firing shrinkage values show a more pronounced variation, with Dolapix PC-67 exhibiting the highest firing shrinkage (11.97%), followed by STPP (10.87%) and Na_2SiO_3 (10.32%). As expected, total shrinkage follows a similar trend because firing shrinkage constitutes the dominant contribution. Consequently, Dolapix PC-67 demonstrates the greatest overall shrinkage (15.51%), closely followed by STPP (15.17%), whereas Na_2SiO_3 results in the lowest total shrinkage (13.35%). These findings suggest that Na_2SiO_3 provides better dimensional stability during drying and firing, while STPP and PC-67 lead to increased densification and higher thermal shrinkage during sintering (Ercioğlu et al 2024, Jayaweera et al 2024). Na_2SiO_3 consistently produced the lowest shrinkage values, indicating a more stable body during both drying and firing.

3.3 Mechanical Strength

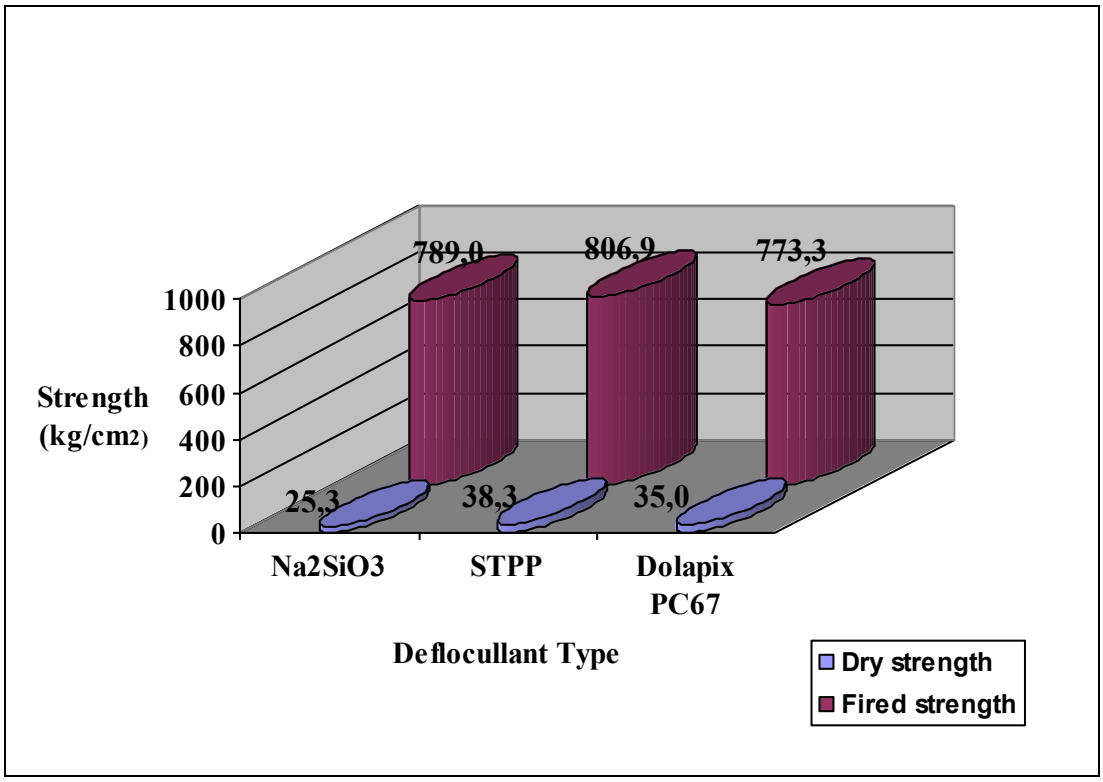

Figure Comparison of mechanical strength values depending on the type of deflocculant

- **Dry strength:** highest with **STPP** (38.3 kg/cm²).
- **Fired strength:** values were close for all three, with no significant difference.

The mechanical strength results reveal that both dry and fired strengths vary depending on the deflocculant used in the ceramic formulations. Among the samples, SDEF provides the highest dry strength (38.3 kgf/cm²), followed closely by Dolapix PC-67 (35.0 kgf/cm²), while Na_2SiO_3 exhibits the lowest dry strength (25.7 kgf/cm²). This suggests that STPP and Dolapix contribute more effectively to particle packing and green-body cohesion prior to firing. A similar trend is observed in the fired strength values, although the differences between the deflocculants are less pronounced. Dolapix PC-67 demonstrates the highest fired strength (806.9 kgf/cm²), followed by STPP (789.0 kgf/cm²), while Na_2SiO_3 again yields the lowest fired strength (773.3 kgf/cm²). These results indicate that Dolapix PC-67 enhances sintering efficiency and densification more effectively during firing, leading to improved mechanical integrity. Overall, STPP improves green-body strength, whereas Dolapix PC-67 maximizes fired strength, while Na_2SiO_3 produces comparatively weaker mechanical performance in both stages (Eygi and Ateşok

2008, Dikmen et al 2020, Fedorenko et al 2021, Ridha 2024, Ltifi et al 2011). STPP improved plastic bonding and resulted in better dry mechanical resistance.

3.4 Layer Formation Rate

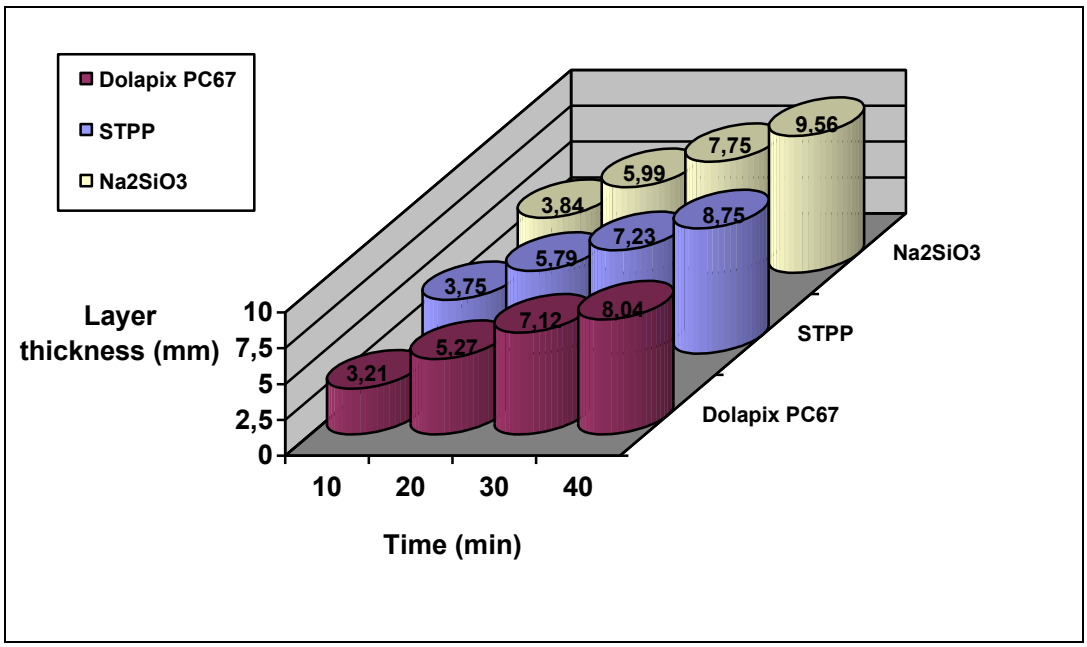

Figure Comparison of layer formation values depending on the type of deflocculant

The graph illustrates how layer thickness varies with time for three different deflocculants—Dolapix PC-67, STPP, and Na_2SiO_3—and reveals a consistent increase in deposited layer thickness as immersion time increases. Among the tested additives, Na_2SiO_3 produces the thickest layers at all time intervals, reaching 9.56 mm at 40 minutes, indicating its strong ability to promote rapid particle deposition and buildup. STPP provides intermediate layer formation, with thickness values rising from 3.75 mm at 10 minutes to 8.75 mm at 40 minutes, suggesting a balanced deflocculation effect that allows steady and controlled layer growth. In contrast, Dolapix PC-67 results in the thinnest layers, ranging from 3.21 mm to 8.04 mm, which implies that it enhances the stability and dispersion of particles in suspension, thereby reducing the rate of sedimentation and deposition. Overall, the data show that Na_2SiO_3 accelerates layer accumulation most effectively, STPP offers moderate deposition behavior, and Dolapix PC-67 yields the slowest layer formation due to its superior dispersing capability (Evcin 2011). Dolapix PC67 produced the fastest and thickest layer formation at all time intervals. Ranking:

Dolapix PC67 > STPP > Na_2SiO_3

Lower viscosity and better dispersion facilitated rapid deposition on plaster molds.

3.5 Water Absorption and Porosity

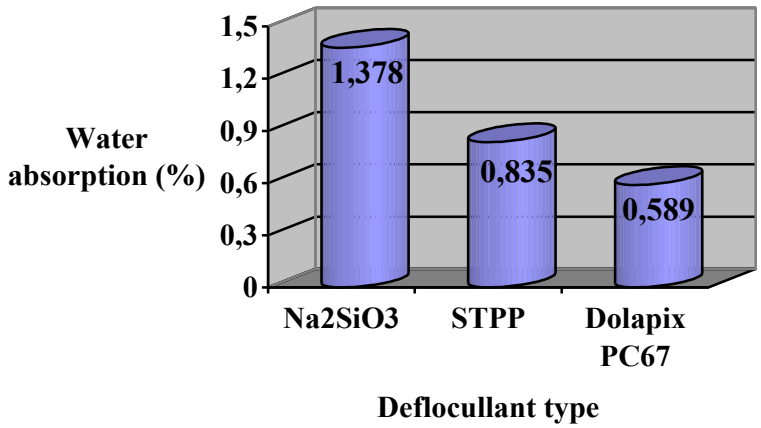

Figure Comparison of water absorption values depending on the type of deflocculant

The water absorption results show a clear dependence on the type of deflocculant used in the ceramic formulations. Na_2SiO_3 leads to the highest water absorption value (1.378%), indicating the presence of a more porous structure and lower overall densification after firing. In contrast, STPP exhibits a moderate absorption level (0.835%), suggesting improved particle packing and reduced porosity compared to Na_2SiO_3. Dolapix PC-67 provides the lowest water absorption (0.589%), demonstrating that it promotes the most efficient dispersion and densification among the tested additives. The reduced porosity associated with Dolapix PC-67 aligns with its previously observed effects on mechanical performance and sintering behaviour. Overall, the results indicate that Dolapix PC-67 enhances microstructural compactness, STPP offers intermediate performance, and Na_2SiO_3 results in the most porous ceramic body with the highest water uptake (Nunes et al 1992, Evcin 2011).

- Highest water absorption: **Na_2SiO_3**
- Lowest water absorption: **Dolapix PC67**

Porosity followed the same trend:

Na_2SiO_3 > STPP > Dolapix PC67

Dolapix PC67's improved packing and reduced flocculation produced denser ceramic bodies.

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4. CONCLUSION

This study demonstrates that deflocculant type has a significant influence on both the rheology of ceramic slips and the physical-mechanical properties of final tile bodies. Dolapix PC67 showed superior performance in reducing viscosity, increasing layer formation rates, and minimizing porosity and water absorption. STPP provided the highest dry strength, while sodium silicate produced the lowest shrinkage values but resulted in more porous and less dense bodies.

Overall, **Dolapix PC67** can be recommended as the most effective deflocculant for slip-cast floor-tile formulations, although industrial selection should also consider economic factors and production conditions.

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Sol-Gel Synthesis and Structural Characterization of Piezoelectric PZT Ceramic Powders

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ABSTRACT

Lead zirconate titanate (PZT), a technologically important piezoelectric ceramic, was synthesized using the sol–gel method in order to obtain chemically homogeneous powders with controlled microstructure. Lead acetate, zirconium oxychloride, and titanium isopropoxide were used as precursors, and the sol was prepared through sequential mixing, refluxing, and pH adjustment followed by aging, drying, and calcination at 700 °C. X-ray diffraction (XRD) analysis confirmed the successful formation of the perovskite PZT phase with minor TiO_2 traces. The results demonstrate that the sol–gel method offers an effective route for producing fine, reactive PZT powders with high chemical homogeneity, although the process remains relatively costly due to precursor and solvent requirements.

Keywords: PZT (lead zirconate titanate), Sol-gel method, Piezoelectric ceramics, Advanced ceramics

Piezoelektrik PZT Seramik Tozlarının Sol-Jel Sentezi ve Yapısal Karakterizasyonu

ÖZET

Teknolojik açıdan önemli bir piezoelektrik seramik olan kurşun zirkonat titanat (PZT), kontrollü mikro yapıya sahip kimyasal olarak homojen tozlar elde etmek amacıyla sol-jel yöntemi kullanılarak sentezlendi. Kurşun asetat, zirkonyum oksiklorür ve titanyum izopropoksit öncül olarak kullanıldı ve sol, ardışık karıştırma, geri akışlama ve pH ayarlaması, ardından yaşlandırma, kurutma ve 700 °C'de kalsinasyon yoluyla hazırlandı. X-ışını kırınımı (XRD) analizi, az miktarda TiO_2 içeren perovskit PZT fazının başarılı bir şekilde oluştuğunu doğruladı. Sonuçlar, sol-jel yönteminin, yüksek kimyasal homojenliğe sahip ince, reaktif PZT tozları üretmek için etkili bir yol sunduğunu, ancak öncül ve çözücü gereksinimleri nedeniyle sürecin nispeten maliyetli olduğunu göstermektedir.

Anahtar Kelimeler : PZT (kurşun zirkonat titanat), Sol-jel yöntemi, Piezoelektrik seramikler, İleri seramikler

1. INTRODUCTION

Piezoelectric ceramics play a central role in modern sensing, actuation, energy harvesting, and ultrasonic systems. Among these materials, lead zirconate titanate (PZT), with the general formula $Pb(Zr_{1-x}Ti_x)O_3$, is the most widely used due to its high piezoelectric coefficients, broad electromechanical coupling, thermal

stability, and ability to be compositionally tailored near the morphotropic phase boundary (MPB). The performance of PZT strongly depends on its phase purity, chemical uniformity, and microstructural control. Conventional solid-state synthesis often results in large particle sizes, incomplete reactions, and compositional inhomogeneities due to limited diffusion kinetics. Therefore, wet-chemical routes such as sol–gel, coprecipitation, hydrothermal synthesis, and spray pyrolysis have gained importance as they allow molecular-level mixing of precursors, lower reaction temperatures, and improved phase homogeneity (Hao et al 2019, Pohanka and Smith 2020, Zhao et al 2025, Tiwari et al 2021, Hidayat et al 2022, Shirke and Balivada 2024).

The sol–gel process, in particular, is capable of producing high-purity ceramic powders by using metal alkoxides or salts that undergo hydrolysis and polycondensation, forming a polymeric network. For PZT, this method enhances chemical uniformity of Pb-, Zr-, and Ti-containing species, suppresses undesired secondary phases, and enables fine microstructural control. In this study, PZT powder was synthesized via the sol–gel method using a sequential precursor addition route. The aim was to obtain homogeneous PZT powder, characterize its phase formation, and validate the efficiency of the sol–gel process using XRD analysis (Paramonova et al 2024, Garnica et al 2015, Paramonova et al 2025).

2. MATERIALS AND METHODS

2.1 Raw Materials

The precursors used were:

- Lead acetate trihydrate, $Pb(CH_3COO)_2 \cdot 3H_2O$ (Merck),
- Zirconium oxychloride octahydrate, $ZrOCl_2 \cdot 8H_2O$ (Merck),
- Titanium isopropoxide, $Ti(O–C_3H_7)_4$ (Fluka).

Acetic acid and isopropyl alcohol were used as solvent and pH regulators.

2.2 Sol Preparation

A solution of lead acetate in 500 mL isopropyl alcohol was refluxed at 90 °C for 1 h. Subsequently, a zirconium oxychloride solution in acetic acid was added and refluxed at 125 °C for 1 h. Titanium isopropoxide dissolved in isopropyl alcohol was then introduced, and the mixture was refluxed for an additional 4 h at 125 °C while adjusting the pH to 2. This process yielded a homogeneous PZT sol, which was aged at room temperature for 3 days after dilution with distilled water.

2.3 Drying and Calcination

The aged sol was dried at 60–100 °C to remove solvents and obtain precursor gel. The resulting solid was calcined at 700 °C for 2 h (1 °C/min heating rate) to induce crystallization of the PZT phase.

2.4 Characterization

Phase analysis of the synthesized powder was performed using X-ray diffraction (XRD) with a Shimadzu LabX XRD-6000 diffractometer. Powder samples were prepared as thin layers on glass slides. Diffraction peaks were compared with reference cards to identify crystalline phases.

3. RESULTS AND DISCUSSION

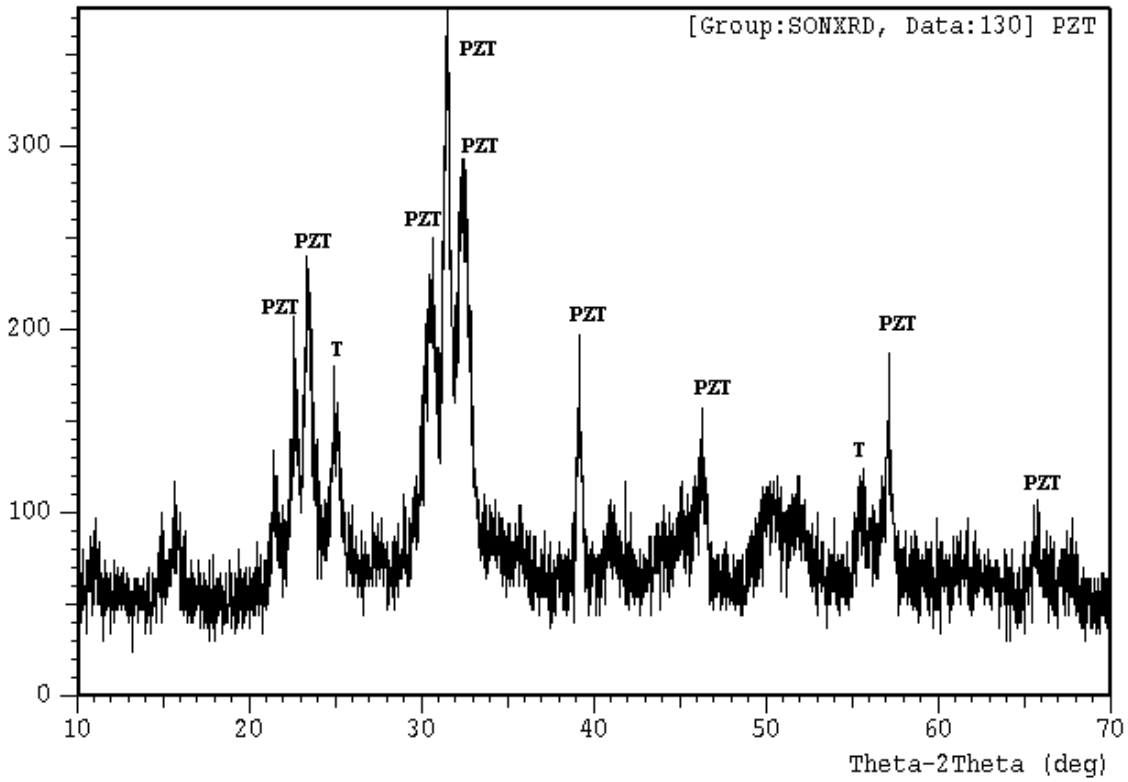

Figure 1. XRD analysis of PZT powders

XRD analysis revealed that the synthesized powder predominantly consisted of PZT with characteristic perovskite reflections. A strong diffraction peak at approximately 2θ ≈ 31.5°, corresponding to the (100) family of planes, confirmed successful crystallization of $Pb(Zr,Ti)O_3$. Minor TiO_2 reflections were also detected, indicating that a small portion of titanium precursor may not have fully reacted during calcination. The presence of sharp, well-defined peaks demonstrates that the sol–gel–derived powder achieved sufficient crystallinity at the relatively low temperature of 700 °C, consistent with the enhanced chemical reactivity typical of sol–gel–based precursors.

The crystallite size of the PZT powders was estimated using the Scherrer equation,

$$D = {}^{K.\lambda}/_{\beta.Cos\theta}$$

where K is the shape factor, λ is the Cu Kα wavelength (1.5406 Å), β is the full width at half maximum (FWHM) of the diffraction peak (in radians) after instrumental broadening correction, and θ is the Bragg angle. The most intense perovskite PZT reflection located around 2θ ≈ 31,5° was selected for this calculation. After inserting the experimentally measured FWHM value into the Scherrer equation, the resulting crystallite size was found to be about D ≈ 8,63 nm, confirming that the synthesized PZT powders are composed of fine, well-crystallized domains rather than coarse grains.

A Rietveld refinement of the XRD pattern was performed using a standard perovskite PZT structural model in order to obtain detailed information on the crystal structure and phase purity. The refinement yielded good agreement between the calculated and experimental patterns, with reliability factors (R_{wp}, R_p) and χ^2 values within the acceptable range for ceramic materials. All major reflections could be satisfactorily indexed to the PZT perovskite phase, and no significant secondary phases such as pyrochlore were detected, indicating high phase purity. The refined lattice parameters are consistent with a PZT composition close to the morphotropic phase boundary, where a coexistence of tetragonal and rhombohedral distortions is expected. This mixed-phase character, together with the nanometric

crystallite size obtained from the Scherrer analysis, suggests that the synthesized PZT powders possess a microstructure favorable for enhanced ferroelectric and piezoelectric properties.

Compared with conventional solid-state reactions, the sol–gel route enabled better precursor mixing and reduced the formation of unwanted secondary phases such as PbO-rich or ZrO_2-rich domains. The process also avoided the particle agglomeration and diffusion limitations seen in ceramic–oxide mixing routes. However, the need for high-purity alkoxides, controlled reflux conditions, and expensive organic solvents increases the processing cost. Despite this, the method offers superior chemical homogeneity, ease of stoichiometry control, and the capability to tailor microstructure for advanced applications such as actuators, ultrasonic transducers, sensors, and microelectromechanical systems (MEMS) (Paramonova et al 2024, Hidayatt al 2022).

4. CONCLUSION

PZT powder was successfully synthesized using the sol–gel method, and XRD analysis confirmed the formation of the desired perovskite phase. The process yielded chemically homogeneous and crystalline PZT at a comparatively low calcination temperature of 700 °C. Sol–gel synthesis proved to be an effective route for preparing fine, reactive ceramic powders suitable for high-performance piezoelectric applications. Although the method is costlier than traditional solid-state processing, its advantages in purity, homogeneity, and microstructural control make it a strong candidate for producing next-generation piezoelectric materials.

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Proton-Conducting Biopolymer Electrolytes from Sugar Palm-Derived Carboxymethyl Cellulose and Ammonium Thiocyanate

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ABSTRACT

A novel biodegradable biopolymer electrolyte (BPE) was developed using carboxymethyl cellulose (CMC) derived from sugar palm fiber. The BPE films were prepared by incorporating various weight percentages of ammonium thiocyanate (NH_4SCN) as a charge carrier via the solution casting technique. The structural, electrical, and electrochemical properties of the films were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Electrochemical Impedance Spectroscopy (EIS), Transference Number Measurements (TNM), and Linear Sweep Voltammetry (LSV). The highest ionic conductivity at ambient temperature was achieved with the sample containing 30 wt% NH_4SCN. X-ray Diffraction (XRD) analysis confirmed that reduced crystallinity contributed to enhanced ionic conductivity. FTIR and TNM results indicated that proton (H^+) conduction dominated due to interactions between CMC and the ammonium salt. The LSV analysis showed an electrochemical stability window of approximately 2.2 V, suggesting the potential of this biopolymer electrolyte for practical applications in electrochemical devices.

Keywords : Carboxymethyl Cellulose; Biopolymer Electrolyte; Sugar Palm Fiber; Ionic Conductivity; Proton Conductor

Şeker Palmiyesinden Elde Edilen Karboksimetil Selüloz ve Amonyum Tiyosiyanattan Proton İletken Biyopolimer Elektrolitler

ÖZET

Şeker palmiyesi lifinden elde edilen karboksimetil selüloz (CMC) kullanılarak yeni bir biyolojik olarak parçalanabilir biyopolimer elektrolit (BPE) geliştirildi. BPE filmleri, çözelti döküm tekniği ile yük taşıyıcı olarak çeşitli ağırlık yüzdelerinde amonyum tiyosiyanat (NH_4SCN) eklenerek hazırlandı. Filmlerin yapısal, elektriksel ve elektrokimyasal özellikleri Fourier Dönüşümlü Kızılötesi Spektroskopisi (FTIR), Elektrokimyasal Empedans Spektroskopisi (EIS), Transferans Sayısı Ölçümleri (TNM) ve Doğrusal Tarama Voltametrisi (LSV) kullanılarak karakterize edildi. Ortam sıcaklığında en yüksek iyonik iletkenlik, %30 ağırlıkça NH_4SCN içeren numuneyle elde edildi. X-ışını Kırınımı (XRD) analizi, azalmış kristalinitenin artan iyonik iletkenliğe katkıda bulunduğunu doğruladı. FTIR ve TNM sonuçları, CMC ve amonyum tuzu arasındaki etkileşimler nedeniyle proton (H^+) iletiminin baskın olduğunu gösterdi. LSV analizi yaklaşık 2,2 V'luk bir elektrokimyasal kararlılık penceresi gösterdi ve bu biyopolimer elektrolitin elektrokimyasal cihazlarda pratik uygulamalar için potansiyeli olduğunu gösterdi.

Anahtar Kelimeler: Karboksimetil Selüloz; Biyopolimer Elektrolit; Şeker Palmiyesi Lifi; İyonik İletkenlik; Proton İletkeni

1. Introduction

The dependency on fossil fuels to generate electricity has increased the concentration of greenhouse gases such as carbon dioxide, methane and nitrous oxide [1]. The emission of these gases leads to global warming by trapping heat in the atmosphere and raising the Earth's surface temperature. One of the contributors, fossil-based energy storage, must be controlled to reduce the consumption of fossil fuels, hence lowering the global warming effect. Fossil fuels have been used to fabricate synthetic polymers, which are the vital components in electrolytes of energy storage. This is a concern because of the rising production of synthetic polymers from 2 million tons in 1950 to around 381 million tons in 2015 [2, 3]. To address the huge leap in the production of synthetic polymers, ongoing efforts are being made to synthesize biopolymers from natural resources. This approach leverages the abundance of these materials in nature and promotes environmental sustainability. Biopolymers present promising opportunities to serve as alternatives to some petrochemicals, contributing to a more sustainable future [4]. Several resources of biopolymers have been discovered to diverse the compatibility of host polymers with the charge carrier such as chitin, chitosan, starch, carrageenan and cellulose [5-8]. Among these resources, cellulose and its derivatives have been studied extensively, owing to their availability in nature, low-cost and green materials [9, 10]. Carboxymethyl cellulose (CMC) is a cellulose derivative identified as a natural-based host polymer for fabrication of solid electrolytes in solid-state energy storage potential applications [8, 11]. Focusing on potential application of solid-state energy storage, Rani et al. [8] attempted to synthesize CMC from palm oil empty fruit bunch for fabrication of solid electrolyte and achieved conductivity exceeding 10^{-4} S cm^{-1} and a stable electrochemical window when doped with 20 wt% of magnesium salt. The result indicates that CMC as a host polymer is capable of developing solid electrolyte for potential application in solid-state energy storage.

Solid-state energy storage, which utilizes solid electrolytes, promises a bright future for the development of batteries in electric vehicles to replace conventional liquid-based batteries [12, 13]. Offering several advantages such as smaller size, having higher capacity and being non-flammable, solid-state batteries have been extensively developed by giant companies (Toyota, Nissan and Panasonic) for manufacturing electric vehicles and drones [14-16]. At present, lithium-based solid-state batteries have attracted huge attention in this field due to the Li+ having a small size of ion radii; hence, easier to dissociate within the solid electrolytes, which contributes to higher ionic conductivity [17]. However, the consumption of Li+ as a charge carrier has depleted the source of lithium and researchers has predicted the demand for lithium will become six times the potential of its mineral deposits [18]. Hence, proton (H+) as a charge carrier is being recognized as a potential candidate to minimize the consumption of Li+ in developing low energy density proton batteries. This development is due to the availability of cost-effective proton conductors, which are also environmentally friendly [19].

Ammonium salts, such as ammonium thiocyanate (NH_4SCN), can be good proton donors within polymer systems and enhance ionic conductivity [20]. The presence of loosely bonded H+ ions attached to the nitrogen atom facilitates their dissociation in the polymer matrix through a hopping mechanism, which is essential for ionic conduction [21]. Moreover, NH_4SCN has low lattice energy (605 kJ mol^{-1}), which requires less energy to break the bond and diffuse the ions into the host polymer backbone [22, 23].

Therefore, the present work focuses on developing proton-based biopolymer electrolytes using CMC from sugar palm fiber as the host polymer and NH_4SCN as the charge carrier. The effect of NH_4SCN towards the host polymer will be characterized in terms of structural, thermal and electrical properties using Fourier Transform Infrared spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Electrical Impedance Spectroscopy (EIS), Transference Number Measurement (TNM) and Linear Sweep Voltammetry (LSV) techniques, respectively.

2. Experimental

2.1. Biopolymer electrolyte films preparation

The solution cast technique was employed to fabricate films using CMC derived from sugar palm fiber as a host polymer and NH_4SCN salt (Supelco) as a dopant with various amounts of weight percentage (wt%). A pristine CMC (without dopant) film was prepared as a reference sample. For preparation of biopolymer electrolyte films, CMC was mixed with NH_4SCN in 80 ml of 1% (v/v) acetic acid (Chemiz) and stir using magnetic stirrer at 50°C until homogenous solution obtained. The final clear solution was casted onto Petri dishes and dried at ambient temperature before transferred into the desiccator for further drying process. Once the drying process was complete, the sample was carefully peeled for the next stage of analysis. The composition and the name of the biopolymer electrolyte films are tabulated in Table 1.

Table 1. The composition of the biopolymer electrolyte films

Composition (wt%) CMC : NH_4SCN	Sample
100:0	CAT0
90:10	CAT10
80:20	CAT20
70:30	CAT30
60:40	CAT40

2.3. Characterization of BPE films

2.3.1. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectroscopy was collected using a spectrophotometer (Bruker Invenio R, Germany) to investigate the interaction between CMC and NH_4SCN in BPE films by observing the changes in the functional group of CMC after doped with NH_4SCN. The sample was placed on the top of the diamond surface with a pressure applied to the sample, and the infrared light was transmitted through the sample. The spectra were measured in the transmittance mode from an accumulation of 32 scans at 4 cm^{-1} resolution over 4000–400 cm^{-1} range.

2.3.2. X-Ray Diffraction Analysis (XRD)

The crystallinity structure of biopolymer electrolyte films were analyzed using an X-ray diffractometer (PW 3040/60 MPD X'PERT High Pro Panalytical, Netherlands). The samples were prepared by pressing the powders into the flattened sheet. The X-Ray patterns were taken by using radiation source CuKα and the patterns were recorded at 2θ from 10° to 80°.

2.3.3. Thermo Gravimetric Analysis (TGA)

2.3.4. Electrochemical Impedance Spectroscopy (EIS)

The ionic conductivity of the films was determined via Electrochemical Impedance Spectroscopy (EIS) using a CS Single Channel Potentiostat/Galvanostat in a frequency range of 10 Hz to 1 MHz. The films were appropriately cut into a suitable size and sandwiched between blocking stainless steel electrodes with a diameter of 2 cm which were connected to a computer.

2.3.5. Transference Number Measurement (TNM)

Transference Number Measurement (TNM) was performed to study the ion diffusion contributed to the conductivity of the highest conducting BPE film. Ionic transference number measurement was conducted using a direct current polarization technique by monitoring the polarization current as a function of time. The current decayed gradually with time and approached the steady state (saturated). The film was sandwiched between two stainless steel blocking electrodes connected to a 2.5 V voltage source.

2.3.6. Linear Sweep Voltammetry (LSV)

The electrochemical stability window of the film was determined through Linear Sweep Voltammetry (LSV) technique for the highest conducting sample of biopolymer electrolyte films using CS Single Channel Potentiostat/Galvanostat. The film was sandwiched between two stainless steel blocking electrodes at a scanning rate of 100 mV/s from 0 V to 3.0 V.

3. Results and Discussion

3.1. Fourier transform infrared (FTIR) spectroscopy

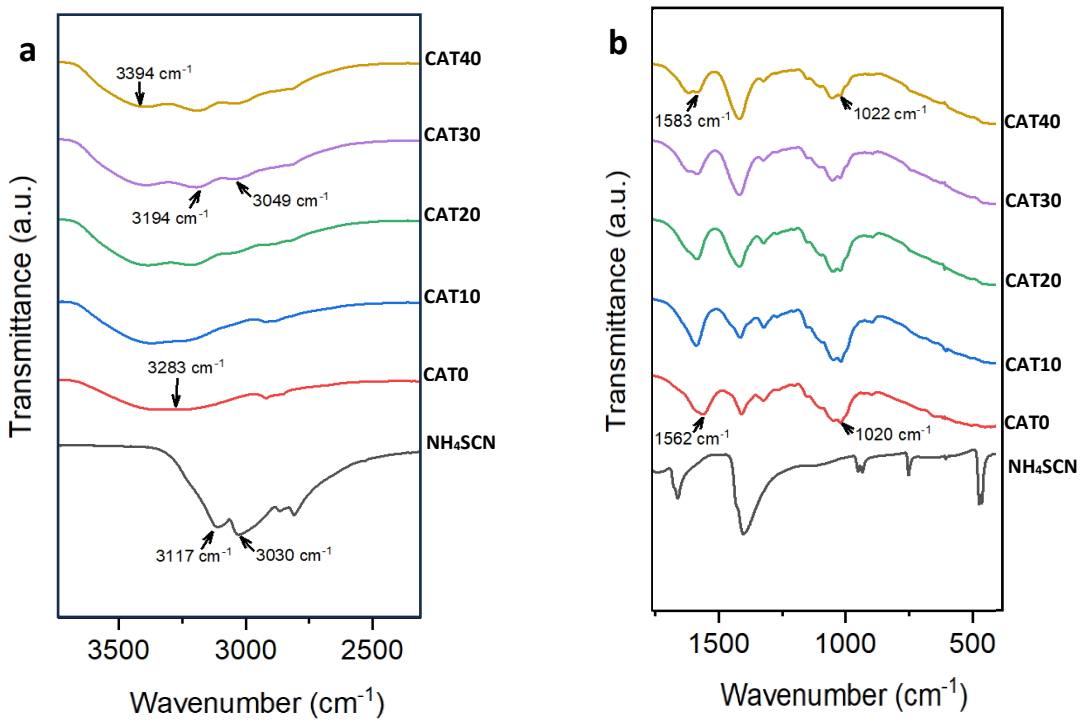

Fig. 1 FTIR spectra of BPE films with different concentrations of NH4SCN in the range of a) 2500-3500 cm^{-1} and b) 500-1750 cm^{-1}

The interaction between CMC and NH_4SCN salt can be observed using FTIR spectroscopy. Fig. 1 depicts the FTIR spectra of BPE films with various concentrations of salt in the region of 2500 to 3500 cm^{-1} and 500 to 1750 cm^{-1}. These wavenumber regions are chosen as most of the interaction between CMC and NH_4SCN happens in this range. In the FTIR spectra of NH_4SCN as shown in Fig. 1a), two peaks located at wavenumbers of 3117 cm^{-1} and 3030 cm^{-1} indicate the presence of NH^{4+} with asymmetry and symmetry vibration, respectively. The appearance of these two peaks is similar as stated by National Institute of Standards and Technology [24]. When a lower concentration of NH_4SCN is added into CMC, these peaks started to disappear, which can be spotted on CAT10 and CAT20 samples. However, the peaks reappeared in CAT30 and shifted to higher wavenumber from 3117 cm^{-1} to 3194 cm^{-1} and 3030 cm^{-1} to 3049 cm^{-1}. This

phenomenon can be attributed to the interaction of more H^+ ions from NH^{4+} with the oxygen from the hydroxyl group of the host polymer, which increases ionic conductivity [25]. On the addition of 40 wt% of salt, these peaks in CAT40 shifted back to lower wavenumber at 3190 cm^{-1} and 3042 cm^{-1} as more salt leads to ions reassociation and decreases the ionic conductivity [26].

The aforementioned band shifting is supported by the interaction of CMC hydroxyl group (OH) with salt which located at 3283 cm^{-1}on CAT0. The broad peak which is centered at 3283 cm^{-1} corresponds to the OH group of CMC. Upon the addition of 10 wt% of NH4SCN, the position of this peak shifted to a higher wavenumber at 3372 cm^{-1} as observed on CAT10. This peak continued to shift to 3387 cm^{-1}, 3390 cm^{-1} and 3394 cm^{-1} as spotted on CAT20, CAT30 and CAT40, respectively. This finding confirms the interaction of the cation H^+ substructure of NH4SCN with the oxygen atoms of the OH group in CMC as similar result also reported by Rani et al. [8].

Another location of the interaction of CMC with NH4SCN is believed to occur at carboxyl group (C=O) in the host polymer backbone, which contains carboxylate anion (COO^-) and ($C\text{-}O^-$) due to the presence of lone pair electrons attracting the salt molecules [8, 27]. As shown in Fig. 1b), the location of (C=O) and (COO^-) can be identified at the wavelengths of 1562 cm^{-1} and 1020 cm^{-1}, respectively, on CAT0 FTIR spectra. This peak at 1562 cm^{-1} shifted to a higher wavenumber when the sample was doped with higher concentrations of salt, eventually reaching 1583 cm^{-1} on the CAT40 sample. The interaction between hydrogen ions from salt and the ether group within CMC might contribute to this peak shifting. As the lone pairs of electrons on the oxygen atom exhibit an affinity for hydrogen ions, it allows them to adhere to the host polymer backbone [28]. The complexation of NH_4SCN with CMC also can be observed on ($C\text{-}O^-$). The peak at 1020 cm^{-1} slightly shift to higher wavenumber at 1022 cm-1 when the salt concentration increased. The decreased in this peak also noticed which indicates that a complexation has taken place between CMC and NH_4SCN salt [29]. This result comparable with finding reported by Samsudin et al., where ($C\text{-}O^-$) located at 1060 cm^{-1} slightly shifted when incorporated with NH_4Br due to the interaction of CMC with H+ [30]. Hence, all the peaks shifting which occurs at the location of NH^{4+}, OH group, (C=O) and ($C\text{-}O^-$) shows the complexation of H^+ from NH_4SCN with CMC functional groups which might affect the ionic conductivity that will be discussed on ionic conductivity analysis section.

3.2. XRD Spectroscopy Analysis

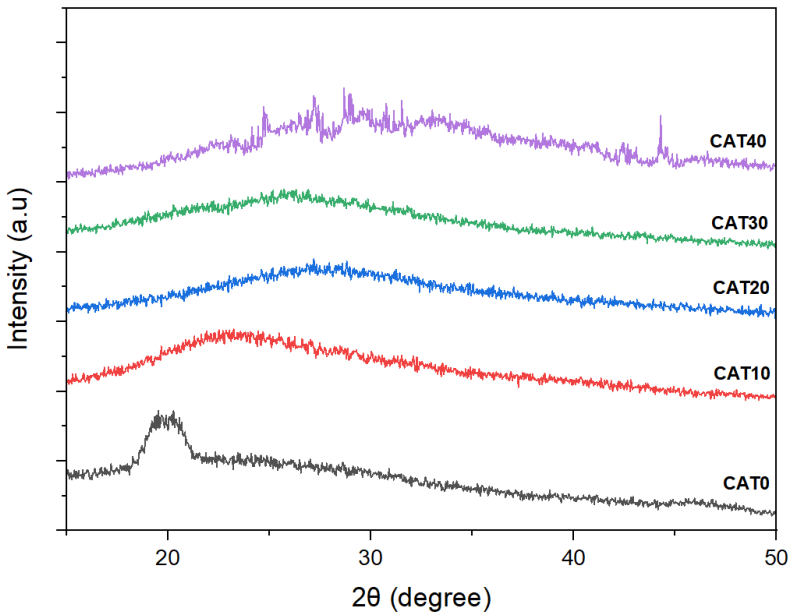

Fig. 2 X-ray diffraction patterns of BPE films with different concentrations of NH4SCN

Fig. 2 shows the X-ray diffraction patterns of CMC BPE film doped with different concentration of NH_4SCN salt. The XRD pattern of CMC which can be spotted on CAT0 sample, consists of a broad amorphous peak centered at 2θ = 20°, indicating the existence of carboxymethyl cellulose crystals. The formation of this amorphous peak in this work is same as previous study reported by previous studies [31-33]. As shown in Fig. 2, the peak changes in the doped samples (CAT10, CAT20, CAT30 & CAT40). The amorphous peak intensity decreases and becomes wider when the salt concentration increases, showing the increase of amorphousness of BPE films. By comparing all the doped sample, it can be observed that CAT30 is highly amorphous which is doped with 30 wt% of NH_4SCN. The highly amorphous sample due to the increment of H+ ion from the dissociation of NH_4SCN salt and more interaction of H+ ion with the host polymer backbone results in softer BPE film [34, 35]. However, upon the addition of 40 wt% of NH_4SCN on CAT40 sample, the appearance of crystalline peak located at 2θ = 24.7°, 28.7°, 30.8°, 31.5° and 44.2° can be spotted, which is believed belong to the agglomeration of NH_4SCN salt. This new crystalline phase might be due to the excessive amount of salt doped on the host polymer which reduces the distance between cation (NH^{4+}) and anion (SCN-) hence, allows them to recombine again becoming NH_4SCN [36]. The formed crystalline peaks of NH_4SCN are comparable with another study reported by Zainuddin et al. [37]. The dissociation and recombination of salt in the host polymer would affect the ion mobility which contributes to the ionic conductivity value that will be discussed in the ionic conductivity analysis part.

3.3. Ionic Conductivity Analysis

Ionic conductivity (σ) of BPE films were calculated using Eq. (1) by obtaining bulk resistance (R_b) from Nyquist plot in the impedance measurement.

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where t is the thickness of BPE films and A is the electrode-electrolyte contact area. The effect of NH_4SCN concentration on ionic conductivity of BPE films at room temperature is shown in Fig. 3. The ionic conductivity of pristine CMC increases from 5.34×10^{-6} S cm^{-1} to 5.27×10^{-5} S cm^{-1} when doped with 10 wt% of NH_4SCN. The conductivity is further increased up to the maximum value which is 6.99×10^{-3} S cm^{-1} when doped with 30 wt% of NH4SCN. This phenomenon is attributed to the number of mobile ions in BPE films. As the salt concentration increases, the mobility of ions increases due to the salt dissociating into ions through coordination with active sites in the polymer host. The ion hopping becomes favourable owing to the decrease in activation energy [36]. However, when the doping concentration exceeds 30 wt%, the conductivity of BPE films decreases to 2.97×10^{-4} S cm^{-1} because the ability of ions from salt to recombine and form neutral ion pairs as the distance between dissociated ions becomes smaller when the doping concentration is higher [38]. As a result, the presence of ion triplets, ion pairs, and ion aggregation will reduce conductivity due to the decrease in the number density and mobility of ions [39]. The trend of ionic conductivity, which is attributed to the behaviour of H^+ ions confirms the earlier discussions of FTIR and XRD analysis. Table 2 lists the highest conducting at room temperature of biopolymer-ammonium salt electrolyte system in another research. According to Ma et al. [40], the minimum value of ionic conductivity for any practical applications in electrochemical devices should be at least $\geq10^{-4}$ S cm^{-1} at room temperature. Hence, the highest conducting sample obtained in this work fulfil that requirement. In addition, the comparable value with another biopolymer-ammonium salt system as shown in Table 2 indicates that CMC from sugar palm fiber doped with NH_4SCN is a good combination to be a proton-conducting biopolymer electrolyte.

The temperature-dependent ionic conductivity was performed to determine the conduction mechanism of BPE films. The study of the temperature-dependent ionic conductivity was conducted in the temperature range of 303–353 K. Fig. 4a) shows the temperature-dependent ionic conductivity of BPE films with different concentrations of NH_4SCN. The Arrhenius behaviour is suggested based on the linear variation of log σ versus 1000/T. The Arrhenius equation can be expressed by:

$$\sigma = \sigma_0 exp^{E_a/kT} \quad (2)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature. Based on Fig. 4a), an increasing trend of ionic conductivity with increasing of temperature and the regression value near to unity (R2~1) for all samples confirming the Arrhenius behaviour. The activation energy for the thermally activated conduction process was calculated from the slope of the best linear fit of Fig. 4a) and the result is shown in Fig. 4b). Based on the result, the highest conducting sample which consists of 30 wt% of NH_4SCN exhibited the lowest activation energy (0.13 eV) and the lowest conducting sample has the highest activation energy (0.33 eV). This concludes that the highest conducting sample only needs a low activation energy to move ions from one coordinating site to another coordinating site in the host polymer [41]. The obtained result is comparable to another study by Monish et al. [29] where an increased concentration of NH_4SCN in the host polymer results in lower activation energy.

In polymer electrolytes, two types of conduction mechanisms widely reported in previous studies which is Vogel–Tammann–Fulcher (VTF) and Arrhenius behaviour. VTF type conduction mechanism occurs in an amorphous region which is above the glass transition temperature (Tg) due to the segmental motion of polymer. While Arrhenius type mostly occurs in crystalline region. As polymer electrolytes are mostly semi-crystalline material, the appearance of crystalline region, which is below melting point (Tm) inhibits the segmental motion of polymer. Above Tm, the crystalline region completely dissapear and expected VTF behaviour of ionic conduction in polymer electrolytes. According to previous research, the Tg of pure CMC is lower than Tm, which is 75°C and 173°C, respectively [42, 43]. Since the temperature range used to study temperature-dependent conductivity is lower than Tm of pure CMC, which is between 303K (30°C) to 353K (80°C) so, the conduction mechanism of the BPE films obeys Arrhenius behaviour [38].

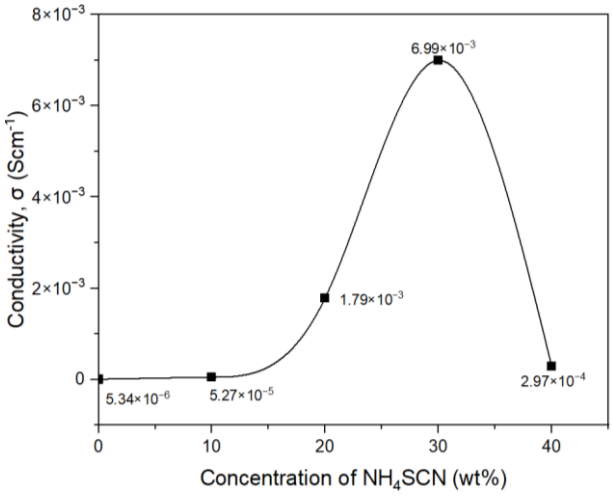

Fig. 3 Effect of NH4SCN concentration on ionic conductivity of BPE films at room temperature

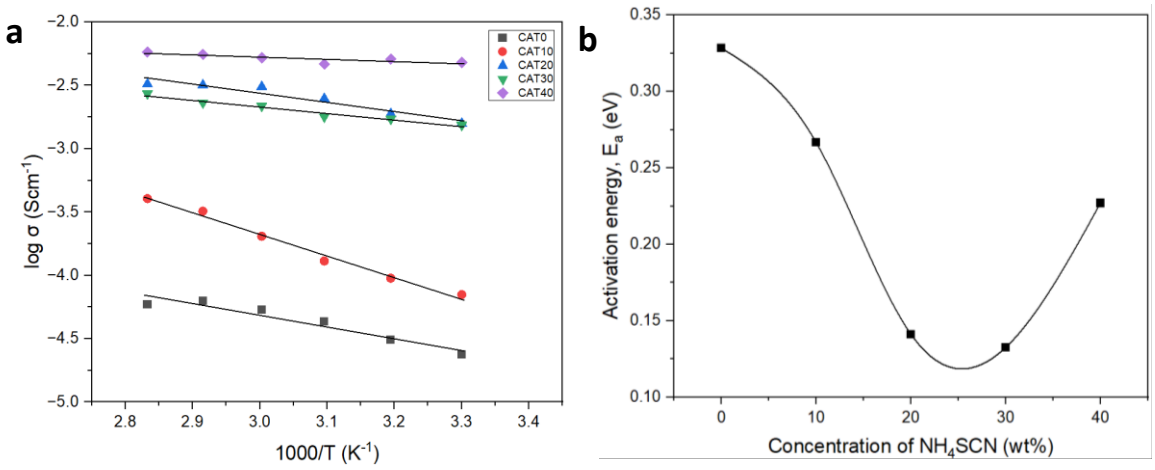

Fig. 4 a) Temperature dependence of ionic conductivity of BPE films and b) Activation energy vs concentration of NH_4SCN

Table 2 Ionic conductivity at room temperature obtained from literatures in comparison to the present work.

Biopolymer-ammonium salt system	Ionic conductivity, $\sigma/(\mathrm{S\ cm^{-1}})$	References
PVA-NH_4NO_3	5.17×10^{-5}	[44]
CS-PS-NH_4BF_4	3.07×10^{-8}	[45]
Cornstarch-PVP-NH_4Br	1.31×10^{-4}	[46]
Agar-NH_4Cl	4×10^{-3}	[47]
CMC-NH_4SCN	6.99×10^{-3}	Present work

3.4. Transference Number Measurement (TNM)

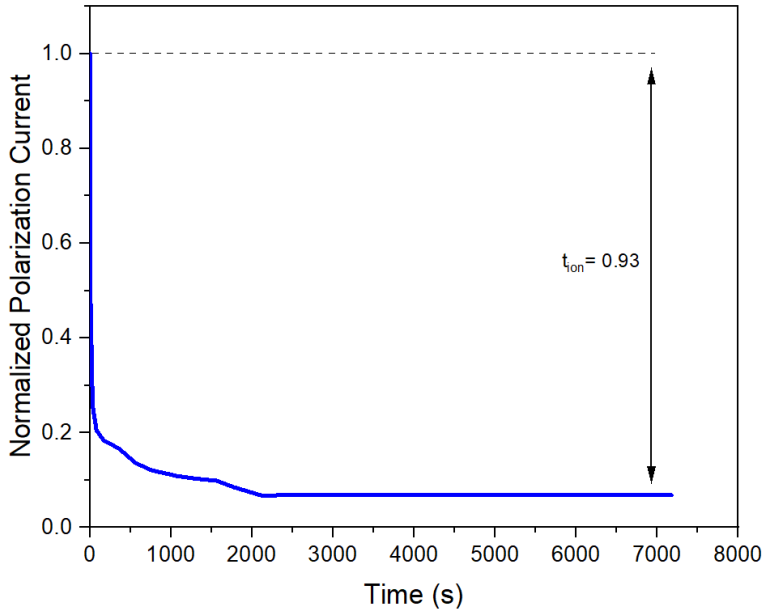

Fig. 5 Normalized polarization current versus time for sample CAT30

Transference Number Measurement (TNM) was performed to study the ion diffusion contributed to the conductivity of the highest conducting BPE film. Fig. 5 shows the plot of normalized polarization current versus time for the highest-conducting sample which is CAT30. From the plot, the transference number of ion (t_{ion}) and transference number of electron (t_{ele}) can be calculated using these equations:

$$t_{ion} = \frac{(I_i - I_s)}{I_i} \quad (3)$$

$$t_{ele} = \frac{I_s}{I_i} \quad (4)$$

where I_i, is the initial current and I_s is the steady-state current. Based on Fig. 5, the initial total current gradually decreases over time due to the depletion of ionic species in the electrolyte. This process continues until the current stabilizes at a constant value when the electrolyte is fully depleted. In a steady state, the cell is polarized, allowing current to flow due to the migration of electrons across the electrolyte and its interfaces. This phenomenon occurs because the ionic currents through an ion-blocking electrode

decrease rapidly over time when the electrolyte is predominantly ionic. The value of tion and tele for the highest-conducting sample (CAT30) is found to be 0.93 and 0.07, respectively. The results obtained indicate that the ion which contributes to the ionic conductivity mainly due to the H+ ions from NH4SCN salt, showing this sample almost exhibits a perfect ionic conductor. Another valid reason which might support the contribution of H^+ ions in ionic conductivity is from the bonding between hydrogen atoms and nitrogen atom in NH^{4+}. The tetrahedral structure of the NH^{4+} ion consists of four hydrogen atoms that are bonded with different strengths. One hydrogen atom is connected through a strong bond, two are connected by moderate bonds, and the last hydrogen atom exhibits a weaker bond to the nitrogen ion (N^+). This loosely bound hydrogen atom can easily migrate between different coordination sites of the host polymer. When the optimum concentration of NH_4SCN in the host polymer is achieved, more H+ ions will be supplied when subjected to an electric field [48]. Hence, it can be concluded that the sample is primarily due to the presence of protons (H^+), as indicated by a t_{ion} value of approximately 1. This observation is consistent with the findings reported by Venkatesh et al. [49], thereby supporting the validity of the analysis.

3.5. Linear Sweep Voltammetry (LSV)

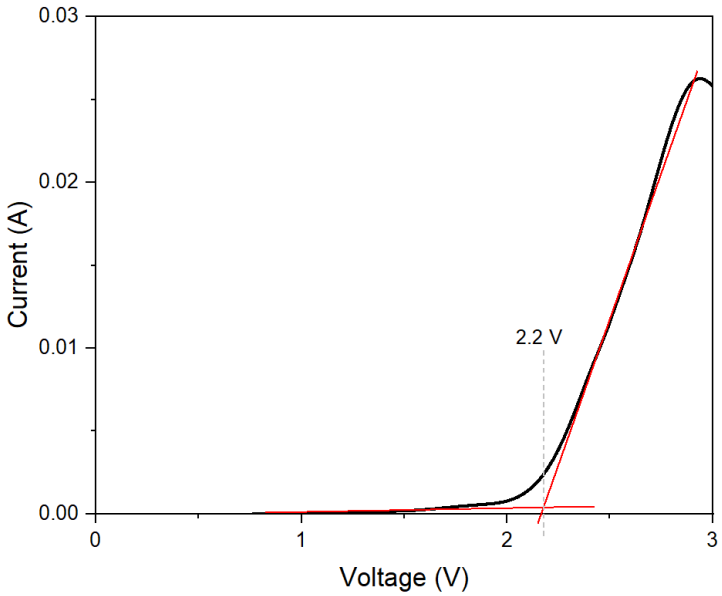

Fig. 6 Linear sweep voltammetry for sample CAT30

The electrochemical stability of the highest conducting sample (CAT30) was employed using Linear Sweep Voltammetry (LSV), which is the vital parameter in order to determine the suitability of this electrolyte films for potential application in an energy storage device such as a battery. Fig. 6 illustrates the I-V curve generated by LSV for CAT30 sample. From this curve, there is no obvious current from open circuit voltage up to 1.58 V, showing that no electrochemical reaction occurs and the sample remains stable in this voltage range. The sample started to break down at 2.2 V, which caused a sharp increase in current. The voltage at which the current rises rapidly through the electrolyte is referred to as the decomposition voltage. This observation indicates that this sample can withstand electrochemically up to 2.2 V and compatible to be used as an electrolyte in a proton battery since the standard decomposition voltage of a protonic battery is about ~1 V [50]. Table 3 shows the comparison of decomposition voltage for various biopolymer-ammonium salt system from previous studies.

Table 3 Decomposition voltage obtained from literatures in comparison to the present work.

Biopolymer-ammonium salt system	Decomposition voltage (V)	References
PVA-CS-NH_4I	1.33	[51]

PVA-MC-NH_4I	1.6	[52]
CMC-PVA-NH_4Br	1.55	[53]
PVA-CS-NH_4SCN	2.25	[34]
CMC-NH_4SCN	2.2	Present work

4. Conclusion

The biopolymer electrolyte based on CMC from sugar palm fiber incorporated with NH_4SCN has been successfully prepared using solution cast technique. The effect of NH_4SCN towards CMC on the structural, electrical, and electrochemical properties has been investigated using FTIR, XRD, EIS, TNM and LSV. The findings reveal that the formulation containing 30 wt% of NH_4SCN demonstrates the highest conductivity at ambient temperature which is 6.99×10^{-3} S cm^{-1}. This result is supported by FTIR and TNM analysis. FTIR highlights about the interaction between ions from NH_4SCN with functional group of CMC based on the shifting of NH^{4+}, OH group, (C=O) and ($C\text{-}O^-$). TNM shows the conductivity mostly from the movement of ions (H^+) within CMC matrix with the value of t_{ion} is 0.93, suggesting substantial ionic conduction. All BPE films exhibit Arrhenius behaviour, with activation energy computed from the Arrhenius plot revealing that the highest-conducting sample possesses the lowest activation energy of 0.13 eV. XRD analysis further demonstrates that the incorporation of NH4SCN enhances the amorphous characteristics of the BPE films by disrupting the polymer backbone structure. Furthermore, LSV testing confirms the high electrochemical stability of the most conductive sample, withstanding voltages up to 2.2 V. These results indicate that the CMC-NH4SCN system holds significant promise as an electrolyte for proton batteries for future practical applications in energy storage technology.

Acknowledge

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Mechanical Properties of PLA 3D Printed Parts for Passive Safety Increase in Vehicles

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ABSTRACT

Polymers are applied as a material in the production of decorative details, e.g. emblems, trademarks, decorative stripes, etc. Investigations of the mechanical properties of polymeric materials are necessary for developing optimal methods and applications for treatment of these materials for examples for using for 3D printing and their further application e.g. to increase passive safety in vehicles. Knowing the properties is very important for the reason to know the strength of a construction as well as for prediction of its lifetime. The properties are also important for providing solutions for possible troubleshooting during exploitation of a printed part or in a case when something needs to be changed. As the testing material there was used the PLA polymer (Polylactic acid) in a defined temperature range. Fully dense PLA blocks were manufactured and tested. For manufacturing of the elements four printing directions were used in one variant of the internal structure of the printed bulk elements, printed in a single direction via the fusion deposition method (FDM). For investigations and analysis of the material properties beside the thermal analysis also the mechanical strength and plasticity ware measured.

As a result of the investigations a correlation between the direction during printing, strength of the material itself as well as the printed construction and mechanical properties characteristics was obtained, determining the optimal application conditions in case of thermal behaviour of the material and structural stiffness of the printed structures. Based on these investigation results this work provides useful information essential for the polymer industry as well as user of polymer based products manufactured using 3D printing.

Keywords : Mechanical properties; 3D printing; Safety, PLA, ABS

1. Introduction

The popularity of polymer materials has certainly been determined by the relatively low cost of manufacture and good performance. Their advantage is low density, corrosion resistance and ease with which they are processed [1]. They are also characterized by low processing costs of large series of finished products compared to other material groups and the possibility of multiple processing [2]. These materials suppress noise and vibration, improve interior comfort and aesthetics, and serve to increase passive safety in vehicles.

In recent day the 3D printing has increasingly gain its popularity. This technique belongs beside the stereo-lithography (STL), inkjet printing (IP); selective laser sintering (SLS); or fused deposition modelling (FDM) to the additive manufacturing which allows automatic production of products with complex shape as well as with significant manufacturing cost reduction in relation to traditional techniques. The amount of produced elements has also growth in volume and scope, because due to the relatively inexpensive material (ABS, PLA) as well as 3D-printing devices. In this paper for testing the PLA material, also known as polyactic acid was used. This is a widely used material in diverse industry branches [3]. Other like ABS, the PLA material is biodegradable and does not produce harmful nanoparticles during printing process. Elements print-outs from this material are characterized by a relatively matt surface and low shrinkage during cooling. This is the reason why prints made from this material do not reveal remarkable cracking susceptibility during printing. So, the cooling systems of the filament and the nozzle does not to be deactivate, because of harmful particle as in case of the ABS material . The working temperature range for the PLA used in the study (Devil Design, thickness 1.75 mm) is in the range of 230-240 °C concerning the printing head and 25°C concerning the working table [4-6]. This material was also used for 3D-prnting investigations due to its relatively high mechanical properties, higher than in case of other polymer material, as reported by other authors (Table 1) [3, 7-9].

The PLA material can be also easily recyclable, which id a steadily growing research topic, this is the other reason for choosing this material [10].

Table 1. Mechanical properties of selected polymeric materials [3, 5]

Ultimate tensile strength, MPa			
Raster angle	PLA	ABS	Polycarbonate
90°	54	26	19
0°	58	34	59.7

This used FDM manufacturing method has become more and more important due to the reason of new properties and characteristics of the produced parts as well as because of other type of thermal processes occurred during production, and real conditions usage, where e.g. the UV radiation induces irreversible changes in polyethylene leading to deterioration of polymer mechanical properties i.e. a decrease of storage modulus and mechanical loss tangent values [11, 12]. Very important issue is that the properties of the material used for production of 3D printed parts are not the same in comparison to the bulk material properties of the materials used for printing. The characteristic of 3D printing reveals varying raster and build orientations, possibly to apply for printing of PLA constructions as well as results in anisotropy of the printed parts. For this reason also different printing directions were selected. Because of the anisotropy, tensile strength of the material cannot be used to determine the shear properties [13-15]. The specimens were manufactured as uniaxial blocks by depositing the melted PLA filament layer over layer in a single direction at the print raster orientation of [+45°/-45°] layups, and build four orientations (flat – x axes, flat y-axes, on-edge (45°), and up-right) to determine the directional properties.

The paper presents the investigation results and experimental printing techniques for the thermal and mechanical characterization of polylactic acid (PLA) 3D printed parts to determine the wear resistance, thermal and mechanical properties as well as anisotropy of their tensile properties. This research fill some gap in the literature, especially concerning the relationship between mechanical properties and thermal characteristics of the thermoplastic PLA material in different 3D printing conditions. Of course the presented results can be extended in future works concerning also the issues relevant to 3D printed polymeric materials like thin-walled structures, polymeric foams [16-18]. In some terms concerning the obtained surface, the prepared polymeric 3D printed material can be even used for further innovations concerning th application of any surface treatment method, for example LST (Laser Surface Treatment) [19].

Results show that there were measurable differences in the tested properties concerning strength or thermal properties between build orientations and significant differences in wear strength. The PLA samples exhibited also strong anisotropy as a function of build orientation compared to the ABS samples.

2. Materials and Method

For printing of the samples the printer is the 3D printing device XYZprinting Da Vinci 1.0 PRO, which has an external filament transfer system that ensures proper feeding to the head without loading it. It is the most versatile 3D printer in its class, giving the possibility of very high quality print. It is equipped with side walls and a front door made of Plexiglas, this helps to maintain a constant temperature during printing in the working area. The printer is equipped with a print bed with a heating plate. The maximum constant working temperature is 65°C, depending on the room temperature. The temperature of the printing nozzle was set as 220°C, according to the datasheet for the PLA material. Printing parameters used in process are shown in Table 2.

Table 2. Process parameters using for printing

Parameters	Value
Hatch spacing (H, mm)	1
Layer thickness (l, mm)	0.5
Printing or pulling speed (V, mm/min)	100
Temperature of liquefier (T, °C)	210
Feed rate of filament (E, mm/min)	100
Diameter of nozzle (mm)	2

For creation of the 3D model used for printing of the sample was used the Autodesk Inventor 2016 engineering graphics program. The files with the extension were generated in the FreeCad program. For testing of the mechanical and thermal properties samples of the following dimensions: were printed out 20mm×10mm with a length of 200 mm.

For printing of one sample 19.45 m of the black filament was used, the duration was established as 5 h 53 min.

For investigation also four diverse printing directions were applied:

1. horizontal (flat) position – wide side,
2. horizontal (flat) position – high side,
3. vertical position,
4. diagonal (edge) position – with the angle of 45°.

The filling density was set as 100%, as well as a single layer thickness of 0.28 mm was chose.

In order to ensure that the sample adheres properly to the table surface, a margin surrounding the first layer of 15mm around each sample was applied is used for both materials.

For the PLA printed sample, the fan cooling fan speed was set to 100%. The temperature of the heating table was set in the program at 60°C, while the temperature of the nozzle heater was set at 220°C. The measured printing time with the applied settings was determined as 75 minutes, and the material used was estimated at 15 grams, which is the equivalent of 5,5 meters of filament thread with a diameter of 1.75 mm.

3. Results and Discussion

Based on the macrostructure investigations is was found that the produced material in all variants is characterised by a shiny relatively homogenous surface without any beaks or holes (Fig. 2a).

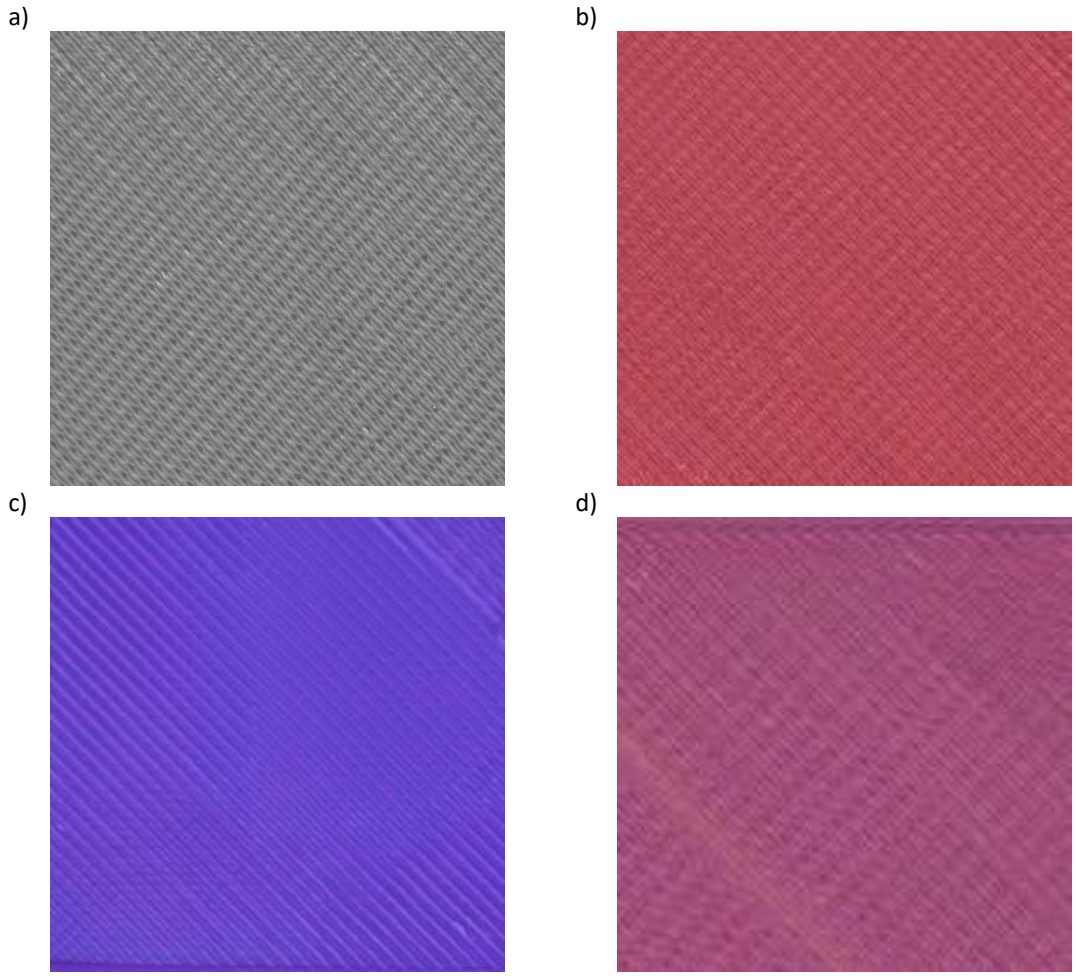

Figure 1. 3D printed samples on form of roads a), microstructure of the cross-section of the printed roads b)

Wear resistance measurements (Table 3) were performed to present the influence of the printing directions on the mass loss of the samples.

Table 3. Wear resistance

Mass loss measured as the wear resistance, [g]			
horizontal (flat) position – wide side	horizontal (flat) position – high side	Vertical position	diagonal (edge) position – with the angle of 45°
0,012	0,005	0,341	0,534

Flexural strength was measured to investigate the influence of 3D printing directions and manufacturing process on the mechanical properties of the produced samples. The results are presented in table 2. An

average flexural deflection was obtained in the range of 3-4 mm. The deflexion strength strongly depends on the printing direction. The results of deflexion measurement of the printed samples are shown in table 4 and of fig. 2.

Table 4. Deflexion values measurement of the printed samples

Deflection of the samples, mm				
Printing direction	horizontal (flat) position – wide side	horizontal (flat) position – high side	Vertical position	diagonal (edge) position – with the angle of 45°
Load, 10 N	9,3	8,9	10,3	4,5
Load, 7,5 N	6,3	6,0	7,6	4,6
Load 5 N	2,8	2,4	2,6	2,0

Mechanical properties measurement were carried out concerning the tensile strength, compressing strength, distortion and deflection. The samples were mounted in stable fixing position and a load of 5N, 7,5 N and 10 N was applied on the end of the sample. The elastic-plastic material response in form of deflection high was measured with results presented in table 5. The reaction of the material was found to be orthotropic and characterised by a strong tension/compression asymmetry.

Table 5. Strength test results

Sample	Force max [N]	Elongation for F_{max}, [mm]	Description
1	2430	4,45	Horizontal position (flat) – wide wall
2	824	1,18	Horizontal position (flat) – small wall
3	2546	4,27	Vertical position
4	1730	5,11	Diagonal position – angle 45°

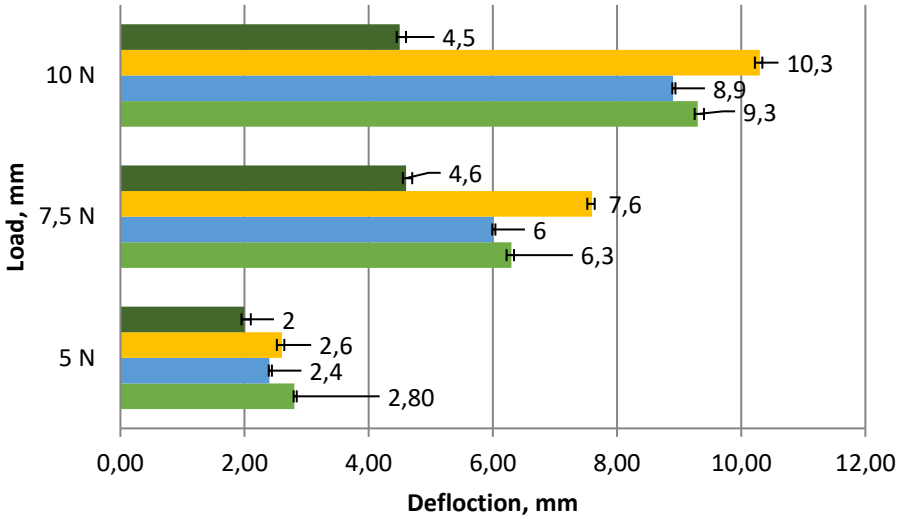

Figure 2. Deflection of the investigated 3D printed samples

4. Conclusions

Based on the carried out investigations the following conclusions were made:

1. The measured deflection of the investigated 3D printed samples achieves the lowest value for the 45 degree printed sample for all applied loads.
2. The lowest mass loss of 0,005 was obtained for the horizontal (flat) position – high side printed material
3. Also the lowest value of elongation (1,18 mm) was measured for the Horizontal position (flat) – small wall sample

In general the diagonal (edge) position – with the angle of 45° gives the highest strength and stability of the printed material and determines these samples with the highest energy absorption among all investigated variants of materials.

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Microstructural Refinement of TIG Weld Metal in Ti-6Al-4V Alloy Through Heat Treatment at 1000°C

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ABSTRACT

In this study, the effect of heat treatment at 1000 °C on TIG-welded Ti-6Al-4V alloy was investigated. Semi-cylindrical samples were welded in four passes using an ERTi-2 ELI filler metal in a single-flare V-groove configuration. After welding, the optimized sample (welded at 120A) was heat-treated. Macroscopic observations revealed a more uniform macrostructure in the fusion zone and heat-affected zone. Microstructural examinations using optical microscopy and SEM showed a reduction in cracks and porosity in the heat-treated sample. Furthermore, the microstructure of the heat-treated sample consisted of layered α+β phases, whereas the untreated samples exhibited undesirable Widmanstätten and martensitic structures. SEM-WDX analysis also confirmed a more uniform distribution of aluminum, titanium, and vanadium in the heat-treated sample compared to the untreated weld metals

Keywords : Tig Welding, Heat Treatment, Ti6Al4V.

1. Introduction

Titanium alloys are widely used in advanced industries, although they are among the most expensive[1]. These alloys have attracted the attention of researchers due to their high biocompatibility, thermal stability, non-ferromagnetic nature, and excellent strength-to-weight ratio[2, 3]. The widespread application of these alloys is attributed to their structural diversity, as they can be found in three primary forms: alpha, beta, and a combination of alpha and beta phases[4]. This structural diversity results in various mechanical and physical properties, allowing for selecting suitable alloys based on specific applications. For example, alpha-phase titanium alloys exhibit high weldability and desirable corrosion resistance, making them suitable for chemical and corrosion-related industries. Because of their high strength and good formability, beta-phase alloys are widely used in the medical and automotive industries[5]. Titanium alloys with a combination of alpha and beta phases possess balanced properties from both phases, enabling their application in various fields such as aerospace and medical equipment[6, 7].

Titanium alloys are highly sensitive, particularly because of their strong reactivity with elements such as oxygen and nitrogen at elevated temperatures. This reactivity leads to the deterioration of their properties, making titanium welding one of the major challenges in various industries[8]. Given that TIG welding with argon shielding gas is known as one of the high-protection methods for welding metals, its use in welding titanium is recommended. This method prevents the molten titanium from coming into

contact with atmospheric oxygen and nitrogen, thereby minimizing the loss of physical and mechanical properties in the welded metal[9, 10]. However, TIG welding of titanium alloys is not without flaws.
One of the main problems in TIG welding of titanium alloys is the oxidation of the weld metal. According to study Karpagaraj & Sankaranarayanasamy [11] , the use of secondary argon shielding gas in TIG welding prevented oxidation of the alloy, which contributed to the improvement of mechanical and metallurgical properties. Another defect in TIG welding is the formation of porosity. The study by Yi et al. [12] showed that TIG welding of Ti6Al4V alloy resulted in porosity in the weld metal, which led to a decrease in the mechanical properties of the alloy. Another issue with this welding process is the microstructural changes caused by high heat input and rapid solidification. According to study Cui et al. [13], the mechanical properties of the weld metal obtained from TIG welding of Ti6Al4V alloy were inferior to those of the base metal. This degradation in mechanical properties was due to microstructural changes in the weld metal and the formation of martensitic and Widmanstätten structures. In addition, Mehdi et al. [14] demonstrated that TIG welding of Ti6Al4V alloy caused the weld metal to become more brittle, with increased hardness and higher residual stresses than the base metal. These issues were also attributed to microstructural changes and martensite formation in the weld metal. To solve microstructural issues and improve mechanical properties, suitable heat treatments are applied. The Study by Yang et al., [7] showed that post-weld heat treatment after TIG welding improved the microstructure. In addition to microstructural improvement, heat treatment reduced residual stresses, increased fatigue life, and enhanced yield strength.
The present study investigated the effect of welding current and heat treatment on TIG-welded Ti6Al4V alloy. Additionally, secondary argon shielding gas was used to prevent oxidation of the weld metal. In this study, the samples were welded at currents of 85 and 120 amperes, and in the optimized condition, the sample welded at 120 amperes underwent heat treatment at 1000 °C. Microstructural examinations of the weld and base metal were performed using Optical Microscopy (OM) and Scanning Electron Microscopy (SEM).

2. Materials and Method

2.1. Sample Preparation, Welding Process, and Heat Treatment

The base metal used in this study was Ti-6Al-4V titanium alloy, which was prepared as cylindrical bars with a diameter of 16 mm. After being cut in half, the samples were divided into two semi-cylinders with a diameter of 8 mm. The chemical composition obtained from spectrometry of the alloy is presented in Table 1.

Table 1.Chemical Composition Of Ti6Al4V

Element	C	Fe	H	N	O	Al	V	Ti
Persent	0.08	0.25	0.01	0.05	0.20	6.23	3.70	Balance

Before the welding process, surface cleaning was necessary to remove contaminants and prevent the formation of oxide layers. This step was carried out mechanically using a wire brush without additional heat, and the surfaces were subsequently cleaned with alcohol.
Considering the shape and dimensions of the workpiece, a Single-Flare-V-Groove joint was used, as shown in Figure 1. The welding operation was performed using the Tungsten Inert Gas (TIG) arc welding method with direct current and electrode negative polarity (DCEN). In this mode, the majority of the arc energy is focused on the workpiece, ensuring efficient melting of the joint region. The welding was carried out in four passes, with no filler metal used in the first pass. The sequence of the welding passes followed the arrangement shown in Figure 1.

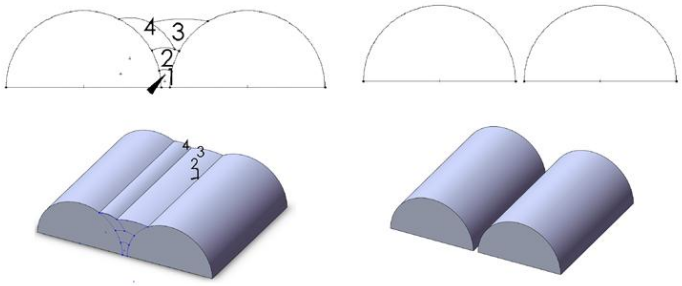

Figure 1. A schematic of the joint design and welding passes

High-purity argon gas was used to protect the weld pool. Additionally, a secondary argon shielding gas was applied as a backing flow to protect the underside of the weld and prevent oxidation during cooling. To achieve uniform and complete protection, a chamber was designed to provide stable shielding gas conditions (Figure 2).

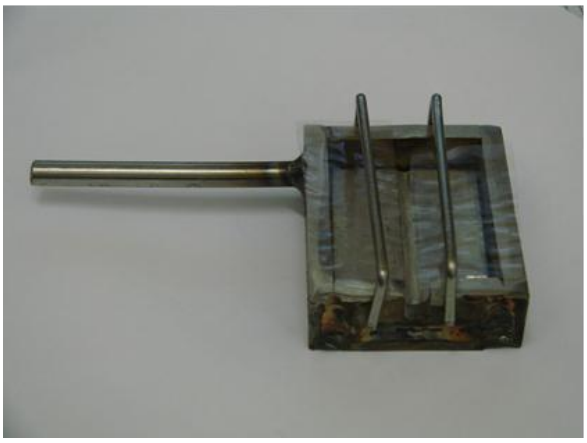

Figure 2. Sample fixture

In this process, a thoriated tungsten electrode and an ERTi-2 ELI filler wire were used. Heat treatment of the samples was carried out in a furnace with a controlled atmosphere and argon shielding gas. For this purpose, the welded samples were placed in the furnace at 1000°C for one hour. After one hour, they were transferred to a cooler section of the furnace and removed after another half hour. The samples were then prepared for metallographic analysis.

2.2. Metallography

For microstructural examination, the samples were cross-sectioned and cold-mounted. They were then polished with sandpapers ranging from grits 100 to 1200, then polished with alumina suspension. To reveal the microstructure, an etching solution made of 2 mL HF, 8 mL HNO_3, and 90 mL water was used. The microstructural analysis was conducted using an Olympus BH-2 optical microscope and a Philips XL30 scanning electron microscope.

2.3. WDX

To investigate the elemental distribution of titanium, aluminum, and vanadium, WDX analyses were performed on samples welded at 80 A and 120 A, as well as on heat-treated specimens. Before entering the SEM and undergoing Wavelength Dispersive X-ray Spectroscopy (WDX) analysis, the samples were coated with a thin layer of gold using a sputtering method.

3. Results and Discussion

3.1. Macrostructural Analysis

Figure 3 illustrates that increasing the welding current from 80 A to 120 A leads to coarser grain structures due to higher heat input, which extends the thermal cycle and allows more time for grain growth, thereby enhancing weldability[15].

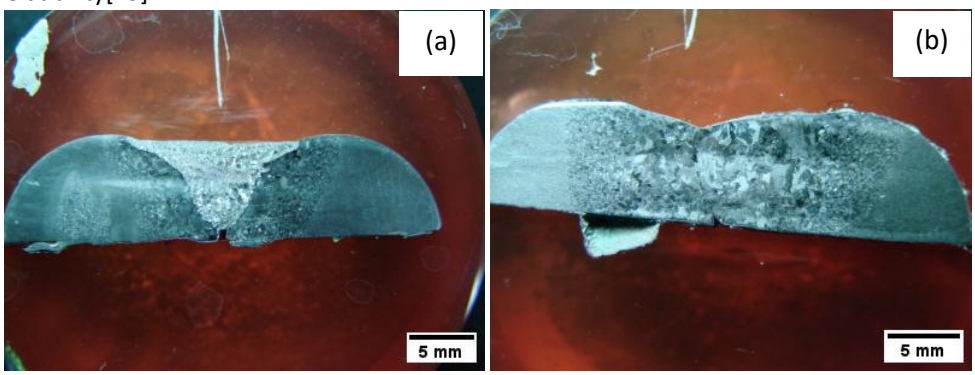

Figure 3. Macrostructure of weld metals (a) 80A (b)120A

3.1.1. Effect of Heat Treatment on Macrostructure

Figure 4 shows the effect of heat treatment at 1000°C on the macrostructure of the weld metals. As shown, the 80-ampere sample developed a more uniform coarse structure after heat treatment (Figure 4a). This effect was even more pronounced in the 120-ampere sample, due to its higher current than the 80-ampere sample (Figure 4b). Therefore, it can be concluded that the increase in heat input from 80 to 120 amperes resulted in a more uniform coarse structure. Aditionally, post-weld heat treatment at 1000 °C improved the uniformity of the coarse grain structure in the weld metal produced at 120 amperes. Improved weldability and the development of more uniform structures could positively influence the mechanical and physical properties[16, 17]. Further analysis was deferred to the subsequent stages of metallographic microstructure examination.

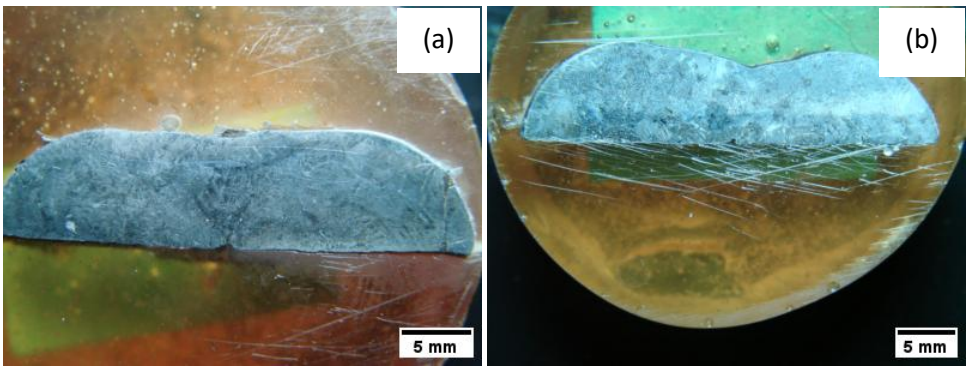

Figure 4. Macrostructure of weld metals heat treated at 1000 °C (a)80A (b)120A

3.2. Microstructural Analysis

Figure 5 shows the microstructure of the base metal and weld metals of the Ti6Al4V alloy. The base metal has a uniform alpha-beta structure (Figure 5a). Using an 80-ampere current, in addition to phase changes compared to the base metal, led to the formation of discontinuities and incomplete mixing in the molten

regions (Figure 5b). To examine the element distribution in the weld metal and base metal, WDX analysis was performed on the three main elements of this alloy (titanium, aluminum, and vanadium).

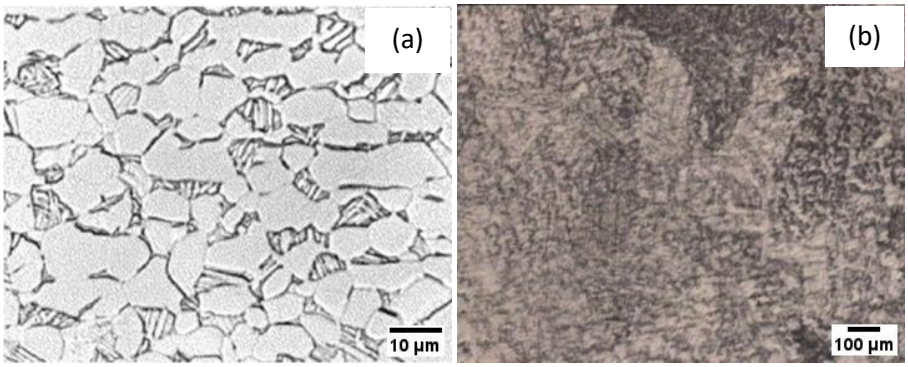

Figure 5. Optical microstructure (a) base metal (b)weld metal with 80A

As shown in Figure 6 and Figure 7, the non-uniform distribution of aluminum and titanium in the weld metal compared to the base metal is clear. This non-uniformity results from the low welding heat and the high cooling rate of the molten pool. Furthermore, the high cooling rate transformed the dual alpha-beta structure into an alpha structure containing martensitic and Widmanstätten phases, and these brittle structures reduce the tensile properties of the weld metals[18, 19].

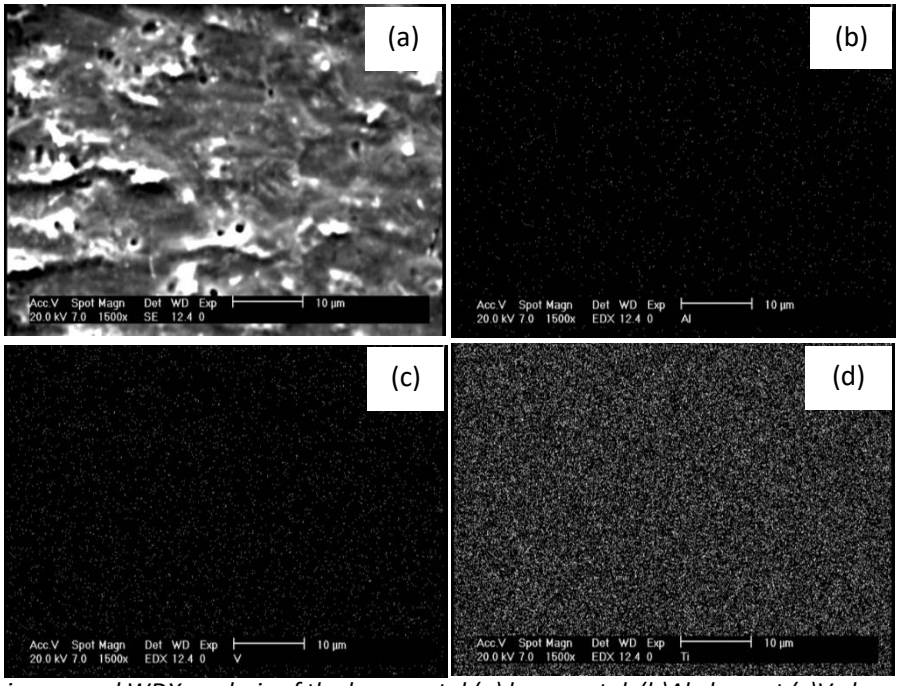

Figure 6. SEM image and WDX analysis of the base metal (a) base metal (b)Al element (c)V element (d) Ti element

In addition to the discontinuities and the formation of brittle structures, cracks and voids were observed in the weld metal with an 80-ampere current. Figure 8 shows the crack resulting from welding with an 80-ampere current. These cracks occur during the final stage of solidification due to thermal shrinkage. Since the base metal also undergoes shrinkage but remains at a lower average temperature due to the absence of melting, its contraction is comparatively less. Therefore, the shrinkage of the weld metal is stopped by the base metal, and as a result, the thermal stresses created lead to crack formation. Weld cracks in titanium alloys significantly reduce fatigue resistance[20].

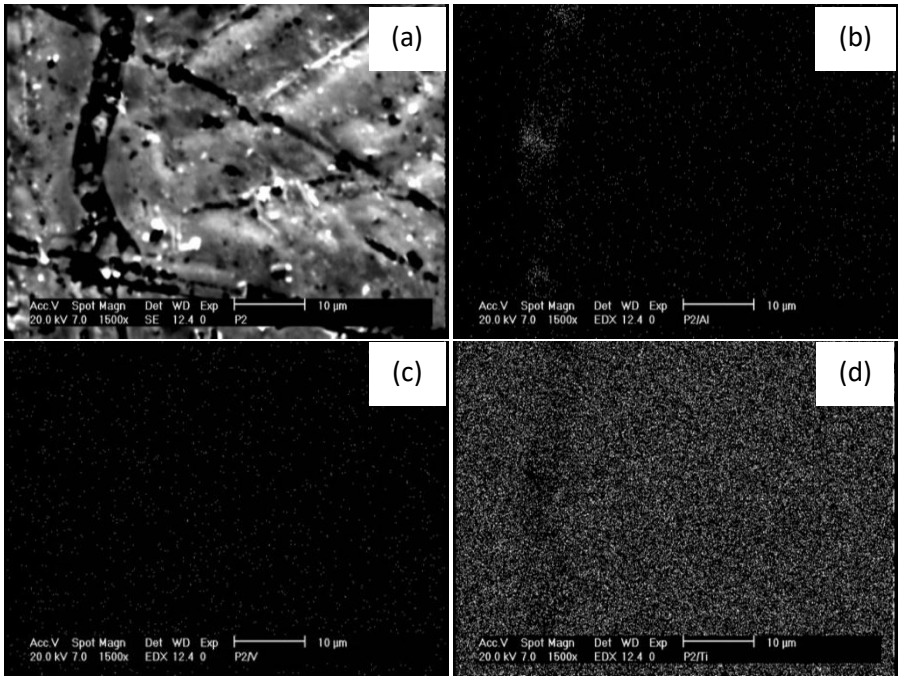

Figure 7. SEM image and WDX analysis of the weld metal at 80 A current (a)weld metal (b)Al element (c)V element (d)Ti element

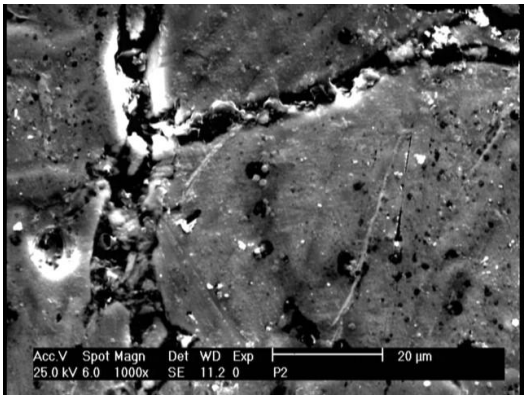

Figure 8. SEM Image of cracks and pores in the weld metal at 80 A current

Figure 9 presents the microstructure of titanium weld metal produced using a 120-ampere current. The image indicates that higher welding currents result in a more uniform microstructure compared to welds made with an 80-ampere current. Additionally, no porosity was present in this weld metal; however, martensitic brittle structures were still observed.

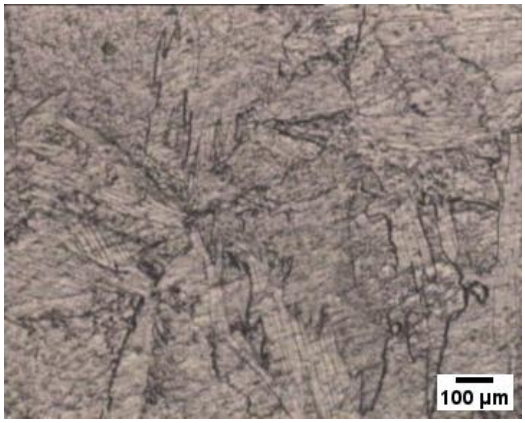

Figure 9. Optical microstructure of the weld metal welded with a current of 120 A

Figure 10 shows that using a 120-ampere current, in addition to eliminating cracks and reducing voids, improved the mixing of the main elements of the alloy compared to that achieved with an 80-ampere current. Figure 11 illustrates the solidification behavior of the Ti-6Al-4V alloy. The diagram indicates that, irrespective of the welding heat input, the high cooling rates inherent to the process lead to the transformation of α and β phases into martensitic structures. Thus, heat treatment was used to enhance the microstructure of the weld metals.

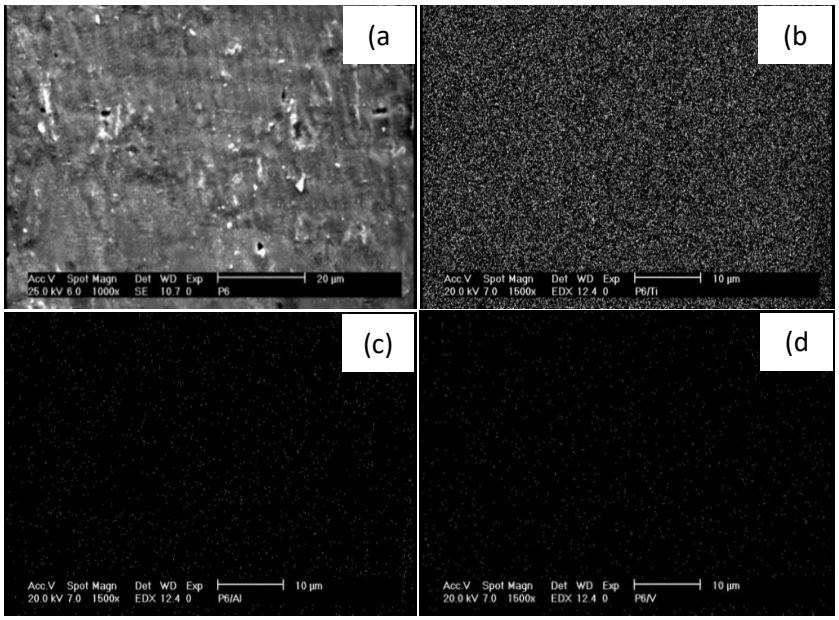

Figure 10. SEM image and WDX analysis of the weld metal at 120 A current (a)weld metal (b)Ti element (c)Al element (d)V element

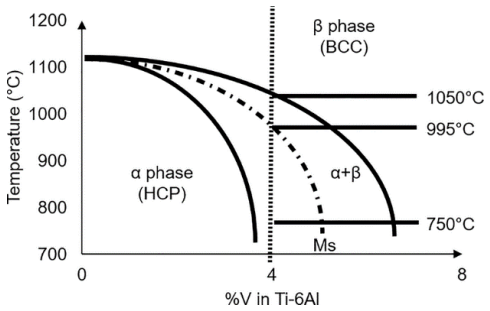

Figure 11. Phase diagram of Ti6AlV alloy

3.2.1. Effect of Heat Treatment on Microstructure

Based on the obtained results, a 120-ampere current was selected as the optimal current, and in the next stage, the effect of heat treatment at 1000°C was investigated. As shown in Figure 12, Since cooling was performed in the furnace, alternating layers of alpha and beta phases were formed next to each other. These layered structures improve mechanical properties, including enhanced fatigue and tensile strength, improved corrosion resistance, and reduced residual stresses in the weld metals[17, 21-24].

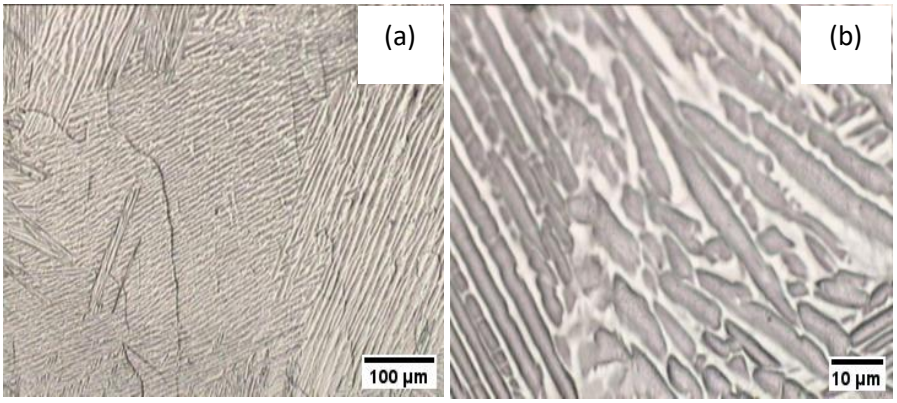

Figure 12. Optical microstructure of the weld metal welded at 120 A and heat treated at 1000 °C (a) Magnification: 100× (b) Magnification: 1000×

Additionally, WDX analysis showed that the continuity of elements was improved after heat treatment (Figure 13). Uniform distribution of elements leads to uniform physical and mechanical properties.

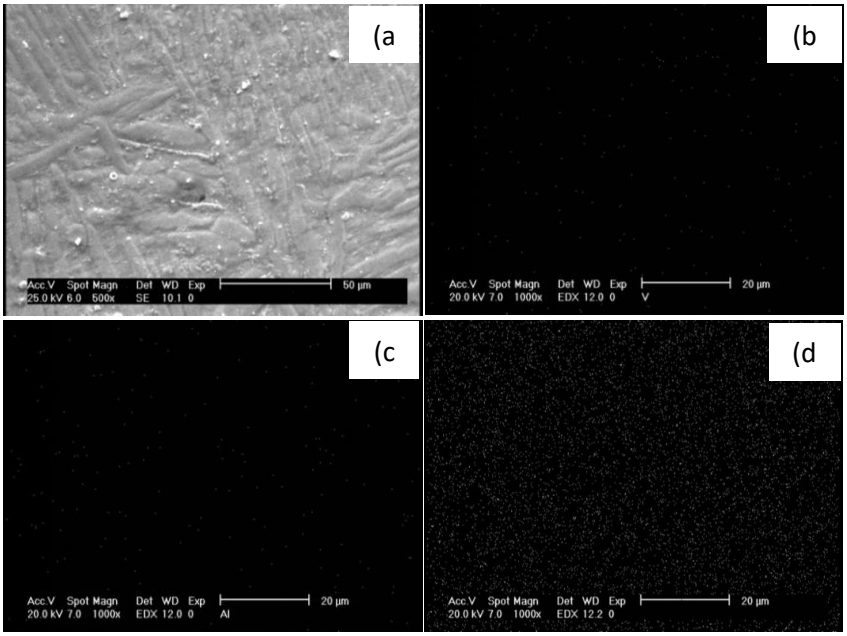

Figure 13. SEM image and WDX analysis of the weld metal welded at 120 A and heat treated at 1000 °C (a)weld metal (b)V element (c)Al element (d)Ti element

4. Conclusions

The results of the heat treatment at 1000 °C on the weld metals produced by TIG welding of the Ti-6Al-4V alloy are summarized as follows:

1) Macroscopic examinations of the welded metals showed that heat treatment at 1000 °C resulted in a more uniform macrostructure in the weld and HAZ regions.
2) Increasing the welding current from 80 to 120 A led to a reduction in cracks and porosity.
3) SEM-WDX analysis results showed that using a 120 A welding current improved the uniformity of aluminum, titanium, and vanadium distribution in the fusion zone compared to the 80 A current.
4) Heat treatment at 1000 °C improved the microstructure by promoting the formation of layered structures instead of undesirable martensitic and Widmanstätten structures.
5) SEM-WDX analysis showed that the distribution of titanium, aluminum, and vanadium was more uniform in the heat-treated samples than in those welded at 120 A.

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Electrochemical-Blackening of Electroless Ni-P Coatings on AISI 4130 Steel: Mechanism and Corrosion Properties

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ABSTRACT

The formation of a uniform, efficient, corrosion-resistant, and low-cost black surface is one of the primary goals in various applications, such as military equipment, optical components, and solar absorbers, to conceal military assets from enemy detection, produce modern instruments, and enhance solar cell efficiency, respectively. In this paper, electrochemical-blackening electroless Ni-P has been fabricated, and the effect of voltage and time has been investigated. The results indicate that the corrosion resistance of electroblacked electroless Ni-P coatings on steel substrates is significantly higher than that of traditional blackening treatment. The optimum electroblacked coating was achieved by carrying out electrochemical-blackening treatment at 5 V, in 2.5 M phosphoric acid solution at 45 °C for 135 seconds and the results of corrosion tests revealed that applying electroless Ni-P coatings on steel surfaces, followed by electrochemical-blackening decreased corrosion current density from 4.6×10-5 to 3.8×10-6 µA/cm2 in 3.5 wt% NaCl solution.

Keywords : Electrochemical-Blackening, Electroless Ni-P, Corrosion, Solar absorber .

1. Introduction

Formation electroless coating is an autocatalytic process, meaning that the chemical reduction is accelerated by the deposited coating itself. This technique was first introduced by Wurtz in 1844 for nickel deposition. Although nowadays, nowadays electroless method has been used for depositing metals such as nickel, copper, cobalt, palladium, and silver, electroless nickel-phosphorus coatings have particularly attracted the attention of researchers and industrial practitioners (Sha et al., 2011). Among the key applications of electroless Ni–P coatings are improved corrosion and wear resistance, lubrication, solderability, and the restoration of over-machined parts. Moreover, in comparison with electroplating (electrodeposition), electroless coating provides several advantages such as the Ability to coat non-conductive surfaces, unique chemical and physical properties, lower porosity, and saving a noticeable amount of electricity (Sahoo & Das, 2011)

In the traditional chemical blackening process, the black colour is achieved by immersing the uncoated sample in an acidic solution for a specific period, leading to the controlled corrosion of the surface. Although this process changes the colour of the surface to black, it significantly reduces its corrosion resistance due to the formation of numerous surface pores. In contrast, the modern blackening technique involves a two-step process: first, an electroless nickel–phosphorus (Ni–P) coating is applied to

the surface of the sample, and then the coated sample undergoes a blackening treatment. This method was first introduced by Kumar et al. in 1980 and has attracted attention for its effectiveness in enhancing surface properties (Kumar et al., 1980; Krishnan et al., 2006). Both chemical and electrochemical blackening techniques can be used to produce a black surface; however, previous studies have shown that the electrochemical blackening method (electroblackening) provides more reproducibility and surface uniformity compared to chemical blackening (Xing et al., 2013)

Formation According to SEM observations, the surface of the blacked electroless Ni-P coating contains numerous conical pores, ranging in size from one and two nanometres to several hundred micrometres. The size of porosity has an influence on coating properties like corrosion behaviour that was examined in this study. The morphology of these pores can resemble either a volcanic crater or a stalagmite-like structure. It is worth mentioning that volcanic crater morphology exhibits higher light absorption compared to stalagmite morphology. The results derived from electrochemical tests like polarisation indicated that applying electroless Ni-P can increase the corrosion and wear resistance because the electroless coating plays a key role in separating the corrosive solution and substrate like a barrier layer. Although following treatment such as chemical and electrochemical blackening can change the morphology and thickness of primary electroless coating, the corrosion resistance of blacked electroless Ni-P coating is much more than the uncoated substrate (Dominguez et al., 2015)

The formation of a corrosion-resistant black coating was the ultimate goal of this study, driven by the formation of two-layer coatings that provide our desirable properties. To achieve the mentioned goals, a two-step surface modification process was employed. Initially, a uniform and corrosion-resistant electroless Ni–P coating was applied onto the surface of the steel substrate. This layer acts as a barrier, significantly enhancing the surface's resistance to corrosive environments. However, due to the metallic brightness and reflective appearance of the as-deposited electroless Ni–P coating, an additional surface treatment was required to achieve the desired black appearance. Therefore, an electrochemical-blackening process was carried out to change the colour of Ni–P coating into a black, which is more suitable for applications such as military equipment, optical components, and solar absorbers where low reflectivity is critical (Dominguez et al., 2017).

2. Materials and Methods

In this study, AISI 4130 steel (din 1.7218) sheets with a thickness of 3 mm were utilized and their chemical composition is provided in Table 1. Before undergoing the electroless Ni-P coating and electroblackening process, some preparation steps were carried out on the surface. Firstly, they were cut to size and abraded using silicon carbide (SiC) papers with different grit sizes from #120 to #2000 to achieve a smooth surface. Next, the samples were degreased in acetone to remove any residual contaminants and rinsed with deionized water and thoroughly dried.

Table 1. Chemical composition of AISI 4130 (din 1.7218)

Alloy	**Composition (wt. %)**					
	C	*Mn*	*Cr*	*Ni*	*Si*	*Fe*
AISI 4130 (din 1.7218)	*0.39*	*0.78*	*0.68*	*1.31*	*0.021*	*Bal.*

For Ni-P electroless coating, an appropriate electrolyte was prepared by dissolving 24 g/L nickel sulphate, 24 g/L hypophosphite sodium, 12 g/L sodium acetate and 10mL acetic acid in deionized water, and the electrolyte solution was continuously stirred using a magnetic stirrer for half an hour to ensure that all components were completely dissolved. For the electroblackening process, 2.5 M phosphoric acid solution was prepared. The Ni-P electroless coating was applied on the substrate surface at a constant

temperature (75 ℃) on various time (60 min, 120 min, 180 min, 240 min, and, 300min) for optimising the duration of process. Then, the electroblackening treatment, in accordance with Fig. 1, was carried out using unipolar direct current (DC) for 135 seconds (45 sec at the cathode/90 sec at the anode), as outlined in Table 2, under varying voltages and temperatures. It is worth mentioning that the applied voltage was continuously monitored throughout the electroblackening process.

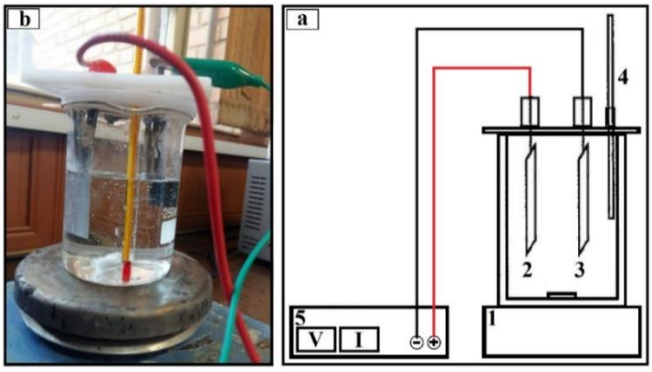

Figure 1. a) Schematic diagram of electrochemical-blackening process (1: stirrer, 2,3: working and counter electrode, 3: 4: thermometer, 5: power supply) b) Macroscopic image of electrochemical-blackening process

Table 2. operational parameters investigated in this study

Parameters			
Temperature (℃)	35	45	55
Voltage (V)	5	7.5	10

To evaluate the corrosion behaviour of the coated samples, a three-electrode electrochemical cell was used that a saturated calomel electrode (SCE) served as the reference electrode, stainless steel as the counter electrode, and the coated sample as the working electrode. To ensure accurate measurements, only a specific area of the working electrode was exposed corrosive environment (3.5% NaCl), while the remaining surface was masked with beeswax to prevent unwanted reactions. Moreover, the thickness of the electroless Ni–P coating was initially assessed using non-destructive techniques, followed by a destructive method involving cross-sectional analysis after cutting the sample. The morphology of the electroblacked coating was then characterized by optical and scanning electron microscope (SEM).

3. Results and Discussion

3.1. Characterization of Electroless Ni–P Coating Prior to Electroblackening Treatment

To optimize the duration of the electroless Ni-P process, the primary samples were coated for various times. Subsequently, the coating thicknesses were measured using non-destructive testing methods and

the results are listed in Table 3. To verify the accuracy of the thickness values obtained by non-destructive techniques, a cross-sectional microscopic image was taken from a coated sample for two hours. The average thickness measured from the cross-section was then compared with the value obtained from non-destructive methods. The results confirmed that non-destructive techniques can accurately estimate coating thickness with acceptable error. Based on these findings, a coating duration of four hours was chosen as the optimum time for applying electroless Ni-P coating. Accordingly, the electroless Ni-P coating had been formed on all the samples under optimal parameters before the electrochemical-blackening process was carried out.

Table 3. *Thickness of electroless Ni-P coating at different electroless process times*

Duration of Electroless Process (Hour)	**Thickness of Coating (µm)**
1	*10*
2	*22*
3	*31*
4	*38*
5	*40*

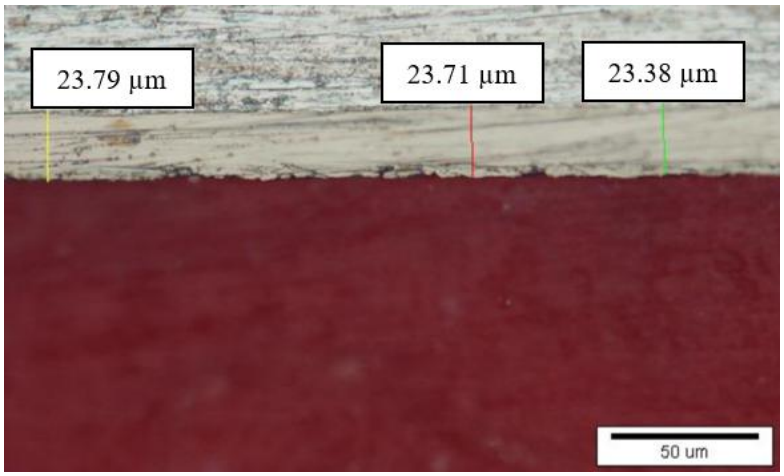

Figure 2. The cross-sectional OM image of electroless Ni-P coating

Moreover, it is worth noting that the hardness test results revealed an increase in hardness from 160 HV in the uncoated sample to 316 HV in the electroless Ni-P coated sample. The electroless Ni-P coating not only improves corrosion and wear resistance, but also partially retains its structure after the electrochemical-blackening process. Consequently, it contributes to improved corrosion performance compared to samples undergoing direct chemical blackening in NaOH solution without the electroless Ni-P coating.

3.2. Characterization of electroblacked electroless Ni-p coating

Identifying the optimal operating parameters that assist to the formation of a coating with desirable properties is the primary goal of this study. Therefore, the investigation was initially focused on the role

of voltage in the electrochemical blackening process of the electroless Ni–P coating on a steel substrate. For this purpose, the electroblackening process was carried out at different voltages 5 V, 7.5 V, and 10 V, on constant temperature (45 ℃) for 135 seconds (45 sec at the cathode-90 secat the anode). Figure 3 shows the macroscopic images of the steel samples electroblacked at different voltages. Sample (a), coated at 5 V, exhibits a completely uniform and black coating in comparison to samples (b) and (c), which were coated at 7.5 V and 10 V, respectively. Excessive corrosion is observed in the central region of sample (b) and across nearly the entire surface of sample (c), resulting in a shift in colour toward white and a noticeable destruction on corrosion behaviour of coating and colour uniformity.

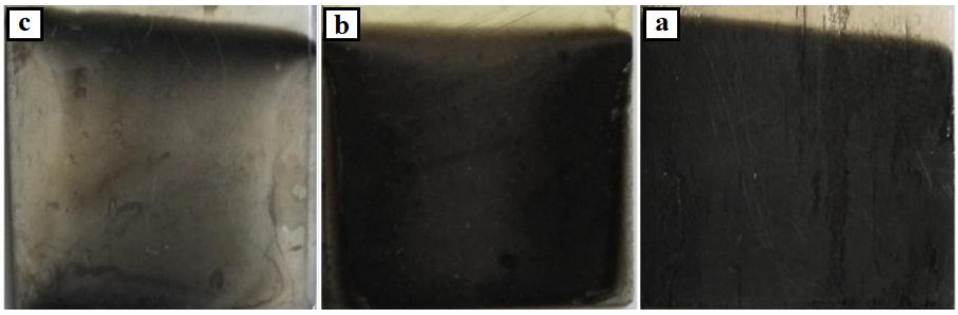

Figure 3. Characterization of electroblacked electroless Ni-P coatings applied under different voltages on constant temperature (45 ℃) for 135 seconds (45 sec at the cathode/90 sec at the anode)
a) 5V b) 7.5V c) 10 V

Following the identification of the optimal voltage, the study focused on investigating the optimal temperature for the electrochemical blackening process of the electroless Ni–P coating on a steel substrate. Accordingly, the process is carried out at various temperatures 35 ℃, 45 ℃, and 55 ℃, on constant voltage (5V) for 135 seconds (45 sec at the cathode/90 sec at the anode). Figure 4 indicates the macroscopic images of the steel samples electroblacked at different temperatures. Sample (b), coated at 45 V, exhibits a completely uniform and black coating in comparison to samples (a) and (c), which were coated at 35 ℃ and 55 ℃, respectively. Excessive corrosion is observed in the central region of sample (c) and ununiform corrosion almost the entire surface of sample (a); as a result, the coating exhibits a shift in colour toward white, along with a degradation in both corrosion resistance and black colour uniformity.

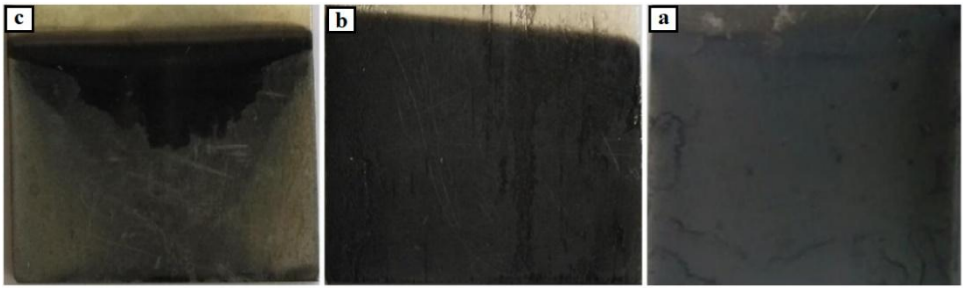

Figure 4. Characterization of electroblacked electroless Ni-P coatings applied under different temperatures on constant voltage (5V) for 135 seconds (45 sec at the cathode/90 sec at the anode)
a) 35℃ b) 45℃ c) 55℃

The optical microscopy (OM) and scanning electron microscopy (SEM) images illustrating the surface morphology of the electroless Ni-P coated and electroblacked electroless Ni-P coated samples are indicated in Figures 5 and 6. As observed in the mentioned figures, the electroblackening treatment results in the formation of numerous conical pores distributed across the surface. These surface features exhibit both advantages and drawbacks. On one hand, the pores create a path that facilitate the penetration of corrosive solution, and allowing them to reach the substrate. This can lead to a reduction in the overall corrosion resistance of the coating. On the other hand, these microstructural features enhance and improve the light-absorbing capacity of the surface, contributing to the development of a

darker, blackened appearance (Wang et al., 2088). Increasing surface roughness and presence of light-trapping pores play a critical role in the optical transformation induced by the electroblackening process (Cui et al., 2006)

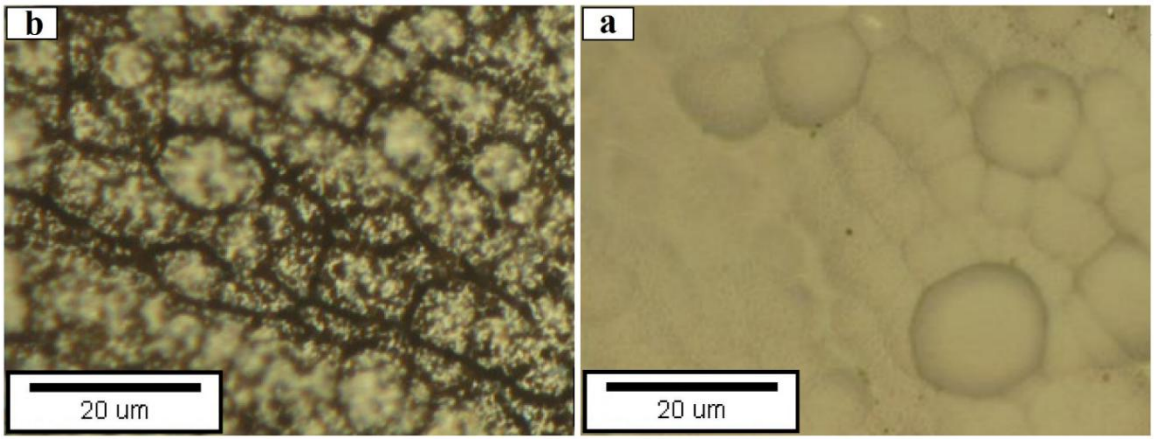

Figure 5. OM images of morphology of coatings
a) Electroless Ni-P coating b) Electroblacked electroless Ni-P coating

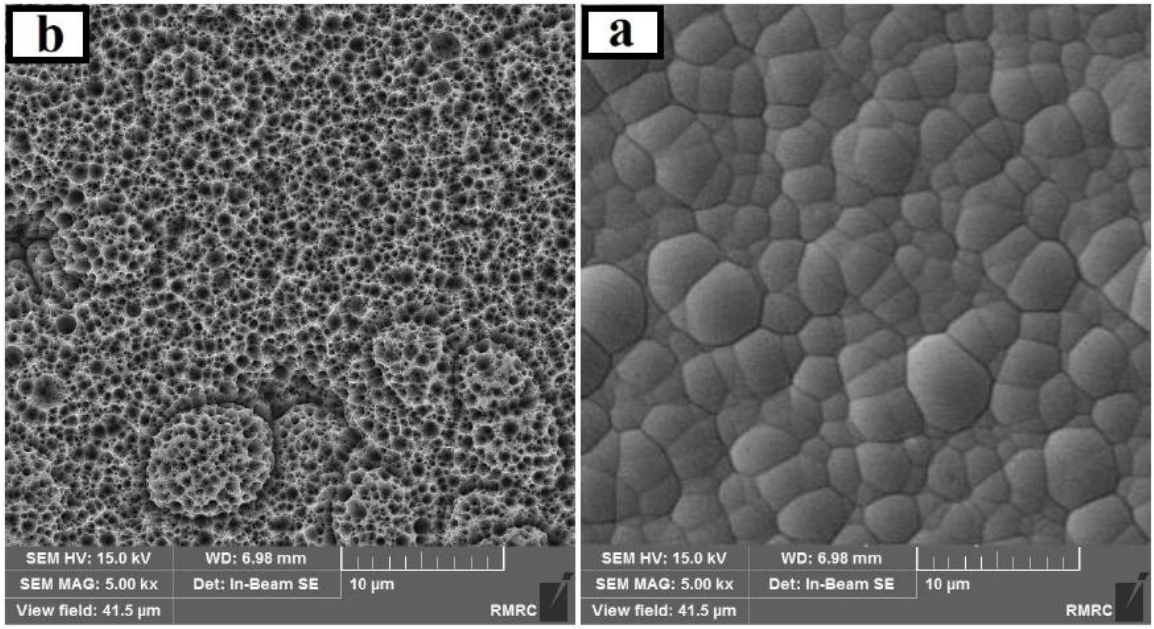

Figure 6. SEM images of morphology of coatings
a) Electroless Ni-P coating b) Electroblacked electroless Ni-P coating

3.3. Corrosion behaviour of electroblacked electroless Ni-p coating

Figure 7 illustrates the polarization curves of the uncoated sample, the electroless Ni-P coating, and the electroblacked electroless Ni-P coating. Table 2 represents the electrochemical data derived from these curves, including corrosion current density, corrosion potential, and electrical polarization resistance for all samples. As shown in Figure 7 and Table 2, the corrosion current density was significantly lower in the presence of both types of electroless Ni-P coatings (simple and electroblacked). During the electroless coating process, a protective layer forms on the surface, effectively isolating the substrate

from the corrosive environment and thereby substantially enhancing corrosion resistance. As a result, both anodic and cathodic reactions are postponed, leading to a reduction in the corrosion rate. Furthermore, the corrosion potential of the coated surfaces shifts towards more noble values, indicating a decreased tendency toward corrosion. However, it should be noted that the electroblackening treatment creates a lot of conical pores on the surface. These pores can serve as pathways for corrosive agents to reach the substrate (Saxena et al., 2010). Consequently, the corrosion resistance of the electroblacked electroless Ni-P coating is lower than that of the simple electroless Ni-P coating.

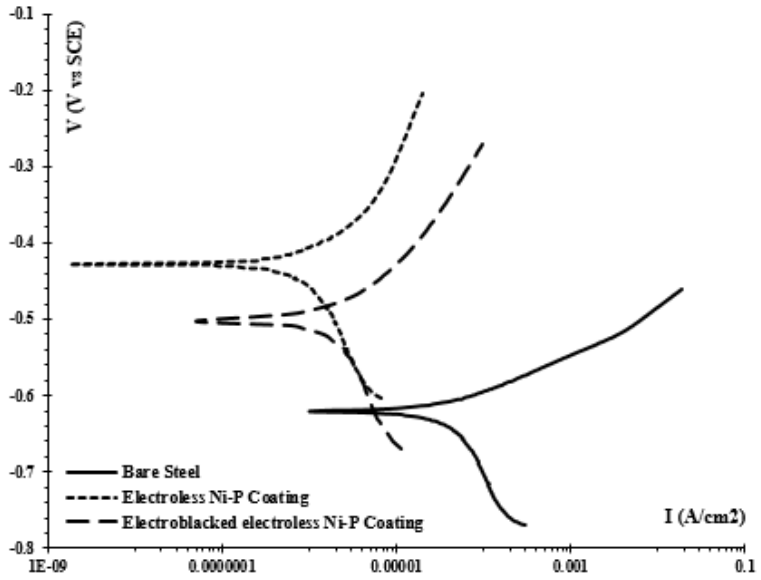

Figure 7. The polarization curves of uncoated sample, electroless Ni-P coated sample, and electroblacked electroless Ni-P coated sample in 3.5 wt% NaCl solution

Table 4. Corrosion parameters derived from the polarization curves in Figure 7

Samples	R_p ($\Omega.cm^2$)	E_{corr} (V)	i_{corr} (A/cm^2)
Uncoated sample	403.2	-0.62	4.6×10^{-5}
Electroless Ni-P Coating	18789	-0.43	1.1×10^{-6}
Electroblacked Electroless Ni-P coating	11403	-0.50	3.8×10^{-6}

4. Conclusions

This study investigates the characteristics of electroless Ni-P coatings and electroblacked electroless Ni-P coating on AISI 4130 and study about their corrosion behaviour and surface morphology that the key findings are listed below:

An excellent electroless Ni-P coating with a thickness of 38 µm can be achieved by performing the process in an optimised electrolyte at 75 ℃ for 4 hours.

Traditional blackening methods used to blacken steel surfaces, are not effective for blackening electroless Ni-P coatings. To achieve a blacken surface on electroless Ni-P coating, the electrochemical-blackening treatment must be employed under the optimal parameters.

The electrochemical-blackening process, performed in a suitable solution at the constant voltage (5V) and temperature (45 ℃) for 135 seconds (45 sec at the cathode/90 sec at the anode), results in the preferential corrosion of approximately one-third of the total thickness of the electroless Ni-P coating. The entire process (applying electroless Ni-P coating and electrochemical-blackening treatment) provided both desired properties, such as corrosion resistance and a blackened surface.

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Corrosion Behaviour of ZrO2 Nanoparticle-Modified Plasma Electrolytic Oxidation Coatings on AA5052 Aluminium Alloys

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ABSTRACT

In the third millennium, aluminium is the second most widely used engineering alloy, utilized across various industries. Although aluminium and its alloys are generally considered chemically passive due to the formation of a protective film on their surface, enhancing their corrosion resistance through surface modification processes such as anodizing and plasma electrolytic oxidation (PEO) is crucial. The PEO process creates a thick, porous, and protective coating that enhances corrosion resistance, moreover, the addition of nanoparticles like ZrO_2 into the electrolyte assist to reduce coating porosity and improve its protective properties. This study examines the effects of PEO coatings with and without ZrO2 nanoparticle on corrosion behaviour of AA5052 Aluminium alloys, incorporation. Electrochemical corrosion tests demonstrated that the PEO coating reduced the corrosion current density by 15.5 times, while the zirconia-modified PEO coating achieved a 40.1 times reduction compared to the uncoated sample.

Keywords : AA5052, Corrosion Behaviour, Plasma Electrolytic Oxidation, ZrO2 Nanoparticles.

1. Introduction

The continuous growth of production harmful emissions from fossil fuel consumption has an influence on the different aspects of human life. Therefore, in recent decades, reducing dependence on fossil fuels has become a priority, with one promising approach being the development of lightweight vehicles. The transportation industry has achieved notable progress through the use of advanced materials that simultaneously decrease vehicle weight and improve performance (Friedrich & Schumann, 2001). Aluminium and magnesium along with their alloys have gained widespread interest because of their excellent electrical and thermal conductivity combined with high strength-to-weight ratio and low density. However, their corrosion behaviour remains a major restriction, necessitating the surface modification techniques to enhance corrosion and wear resistance (Davis, 1997).

Various surface treatment methods have been explored to improve the properties of aluminium alloys, including electro/electroless deposition, thermal spraying, chemical/physical vapor deposition, and conversion coating (Gupta et al,. 2007). Plasma Electrolytic Oxidation (PEO) stands out among surface treatment techniques for producing a protective oxide layer that effectively minimizes corrosion destruction. PEO is considered as a plasma chemical and electrochemical surface modification technique,

which is alternatively referred to as micro-arc oxidation and plasma electrolytic anode treatment (Hussein et al., 2013). The substrate undergoes connection to a high-voltage power supply and immersion in an electrolyte during the PEO process. The interface between the metal surface and the electrolyte generates multiple micro-plasma discharges when applied voltage surpasses a critical breakdown (V_{br}), which results in the creation of a thick oxide ceramic coating (Yerokhin et al, 1999).

In recent years, there has been a growing interest among researchers in enhancing PEO coatings by using nanoparticles to fill the pores of PEO coating and by sealing the porosities in the pores via immersion in a specific solution. In other words, the addition of different types of nanoparticles can have a significant influence on the PEO coating (Ghasemi et al., 2009). In particular, incorporating a secondary oxide phase (ZrO_2) within the oxide conversion coating has been identified as an effective way to enhance the properties of PEO coating. Addition of zirconia (ZrO_2) nanoparticles into PEO oxide films on aluminium alloys was highly recommended because of the improvement of properties of coating like corrosion and wear resistance (Nadimi et al., 2021). It is worth noting that the presence of ZrO_2 nanoparticles at high temperatures during the plasma process led to the formation of corrosion-resistant phases, further strengthening the protective properties of the coating (Barati et al., 2021).

This study examined the modifications and improvements of AA5052 surface characteristics by applying PEO coatings under varying conditions and investigated the corrosion behaviour of PEO coatings with and without ZrO_2 nanoparticles through electrochemical measurements.

2. Materials and Methods

In this study, AA aluminium alloy sheets with a thickness of 2.5 mm were utilized that their chemical composition is provided in Table 1. Before undergoing the plasma electrolytic oxidation (PEO) process, some preparation steps were carried out on the surface. Firstly, they were cut to size and abraded using silicon carbide (SiC) papers with grit sizes ranging from #120 to #2000 to achieve a smooth surface. Next, the samples were degreased in acetone to remove any residual contaminants and rinsed with deionized water and thoroughly dried. To control the area of surface during PEO process, the samples were covered with a heat-shrink shield before the PEO process (Fig. 1-a).

For the PEO coating, a silicate-based electrolyte was prepared by dissolving 10 g/L sodium silicate, 1 g/L sodium fluoride, and 1.5 g/L potassium hydroxide in deionized water. Additionally, ZrO_2 nanoparticles (2 g/L) were incorporated to enhance the coating properties. This electrolyte solution was continuously stirred using a magnetic stirrer for 2 hours to ensure the uniform dispersion of all components. Then, the PEO treatment was conducted under bipolar pulsed direct current (DC) for 510 seconds, with constant operational parameters including a current density of 450 mA/cm², a 50% duty cycle, and a 50 Hz frequency. Throughout the PEO process, the applied voltage was continuously monitored, and to prevent overheating, the electrolyte temperature was maintained below 25°C using a water double-walled beaker and water circulation (Fig. 1-b).

For the PEO coating, a silicate-based electrolyte was prepared by dissolving 10 g/L sodium silicate, 1 g/L sodium fluoride, and 1.5 g/L potassium hydroxide in deionized water. Additionally, ZrO_2 nanoparticles (2 g/L) were incorporated to enhance the coating properties. This electrolyte solution was continuously stirred using a magnetic stirrer for 2 hours to ensure uniform dispersion of all components. Then, the PEO treatment was conducted under bipolar pulsed direct current (DC) for 510 seconds, with constant operational parameters including a current density of 450 mA/cm², a 50% duty cycle, and a 50 Hz frequency. Throughout the PEO process, the applied voltage was continuously monitored, and to prevent overheating, the electrolyte temperature was maintained below 25°C using a water double-walled beaker and water circulation (Fig. 1-b).

To evaluate the corrosion behaviour of the coated samples, a three-electrode electrochemical cell was used (Fig. 1-c). In this setup, a saturated calomel electrode (SCE) served as the reference electrode, stainless steel as the counter electrode, and the coated sample as the working electrode. To ensure accurate measurements, only a specific area of the working electrode was exposed corrosive environment (3.5% NaCl), while the remaining surface was masked with beeswax to prevent unwanted reactions (Safari et al., 2024)

Table 1. Chemical composition of AA5052 alloy

Alloy	Composition (wt. %)					
	Mg	*Zn*	*Fe*	*Mn*	*Si*	*Al*
AA5052	*2.27*	*0.01*	*0.34*	*0.01*	*0.08*	*Bal.*

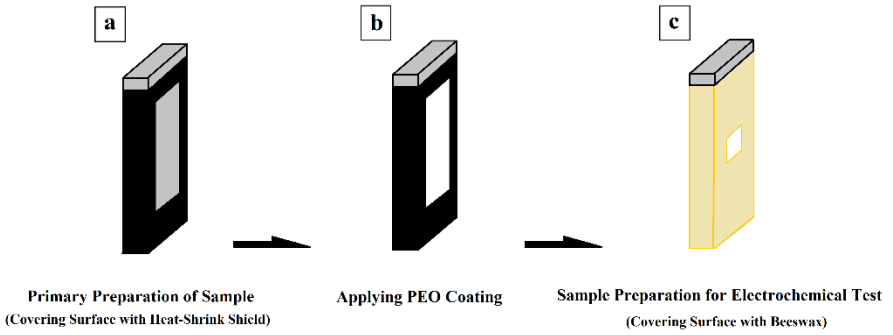

Figure 1. Schematic diagram of sample preparation

3. Results and Discussion

3.1. Coating growth mechanism, thickness, and morphology

The PEO process consists of four main stages, during which the coating growth takes place. These stages include anodic oxidation (Stage I, up to the breakdown voltage), PEO (Stage II, from the breakdown voltage to the critical voltage), and PEO stable (Stage III, from the critical voltage to the final voltage). It is important to note that entering the fourth stage and its associated occurrence can negatively impact the structure and overall quality of the coating. Therefore, in this study, the PEO process was limited to 510 seconds to prevent the development of this stage in all samples.

In Stage I, a thin barrier layer forms on the surface without the occurrence of sparks. Simultaneously, a large volume of gas is released due to the oxidation of water and hydroxyl ions, which is subsequently absorbed on the anode surface. In other words, the anode becomes covered by a thin passive film and enveloped in a continuous gas layer (Fig. 2-I).

In Stage II, the process reaches the breakdown voltage, large amounts of small white sparks appear on the sample surface and rapidly sweep across the anode. The sparks generated at this stage differ in shape, size, and colour compared to other stages (Fig. 2-II).

In Stage III, the voltage stabilizes at a constant value, referred to as the critical voltage. At this point, steady-state sparking develops on the anode surface, and the cell voltage remains relatively stable. The colour and size of spark gradually change to orange and increase in size (Fig. 2-II).

It is worth noting that according to previous research, Stage IV of the PEO process is known by the occurrence of relatively large discharges at specific locations on the surface, which can decrease the quality of the coating. To avoid this issue, the coating process was stopped before reaching this stage (Qiu et al., 2015).

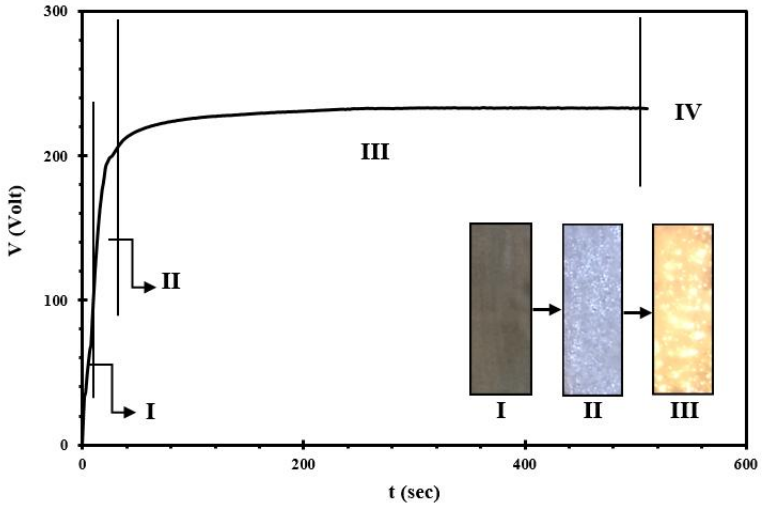

Figure 2. V-t curve of the PEO process along with the macroscopic image of sample surface at different stage of the PEO process in silicate electrolyte,
I) gas released II) very small white sparks created III) sparks colour change to orange

During the Plasma Electrolytic Oxidation (PEO) process, electrical discharges are initiated when the applied voltage exceeds the dielectric breakdown potential of the barrier layer. The visible aspect of discharges is the appearance of sparks on the substrate surface, which contributes to the formation of a thick, porous, and protective oxide coating and porosities are formed as a result of electrical discharges occurring during the PEO process. Moreover, it should be noted that the Molten oxide material is ejected through these channels and immediately comes into contact with the electrolyte “that is typically maintained below 25 °C” where it rapidly solidifies. The surface morphology of the resulting PEO coating, including microchannel structures at various magnifications, is illustrated in Fig. 3. The thickness of PEO coating is 13.5 µm, measured using a non-destructive method. It is worth mentioning that non-destructive techniques are considered reliable for thickness measurements of PEO coatings up to 40 µm (Aliasghari et al., 2014).

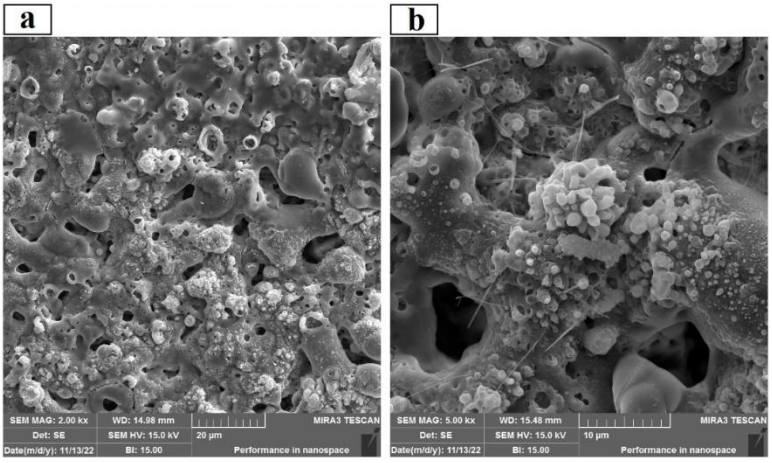

Figure 3. a) SEM image of surface morphology of PEO coating b) SEM images of microchannels discharge

3.2. Detection of ZrO_2 nanoparticles in PEO coating

According to electrochemical principles, the incorporation of ZrO_2 nanoparticles into the Al_2O_3 layer follows the proposed mechanism. The dispersed nanoparticles within the electrolyte carry a negative charge. As a result, their negatively charged surfaces drive them to migrate toward the aluminium alloy substrate, which serves as the positively charged anode (Fig. 4). After the beginning of oxidation process, an initial thin protective layer rapidly forms on the substrate in the alkaline solution, capturing the nanoparticles within it. As the process continues, the initiation of sparking and dielectric breakdown allows nanoparticles to be further adsorbed into the oxide film. Additionally, fluctuations of the molten oxide during sparking lead to the partial incorporation of nanoparticles from the surrounding solution near the electrical discharge site. The rapid solidification of the molten oxide upon contact with the solution, result in incorporation nanoparticles in the oxide films. (Seify et al., 2021).

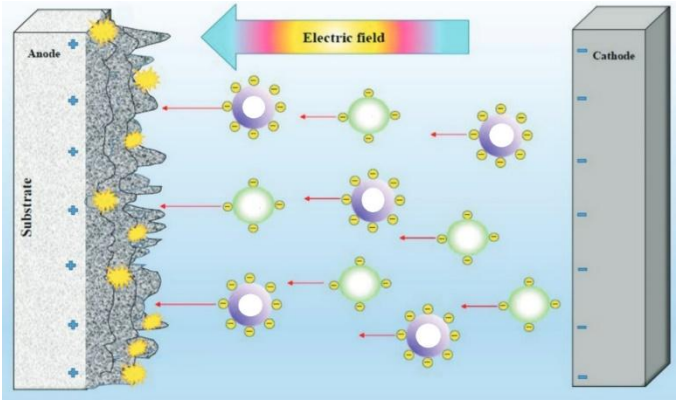

Figure 4. Schematic representation of the coating growth mechanism (seify et al., 2021)

To acquire a high-quality coating, nanoparticles should be uniformly distributed on the PEO coating. However, ensuring uniform nanoparticle distribution remains one of the most significant challenges in the PEO process for applying nanoparticle-modified coating. Figure 5 illustrates the surface morphology of the modified PEO coating along with the elemental distribution map. The elemental maps confirm that the nanoparticles are uniformly distributed throughout the coating. This uniformity improves the coating properties such as corrosion and wear resistance. Achieving uniform distribution requires complete dispersion of the nanoparticles in the electrolyte. To ensure proper dispersion, the electrolyte containing

ZrO_2 nanoparticles was stirred for 90 minutes at a speed of 125 rpm before the PEO process was carried out.

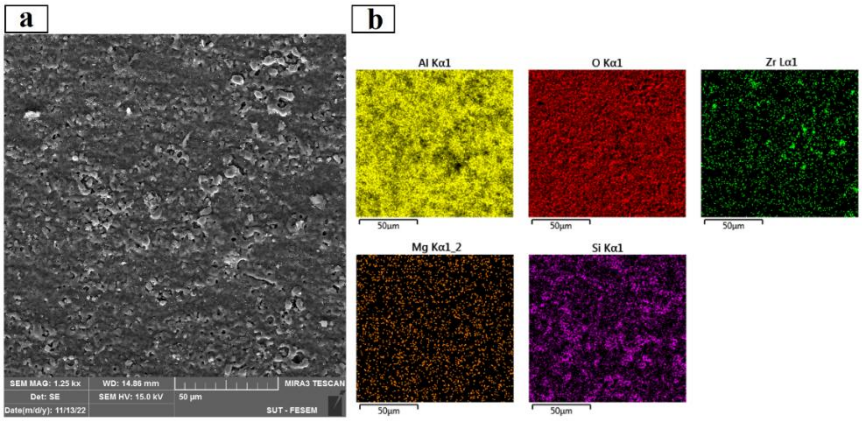

Figure 5. a) SEM image of surface morphology of modified PEO coting b) Elemental distribution maps from the part a

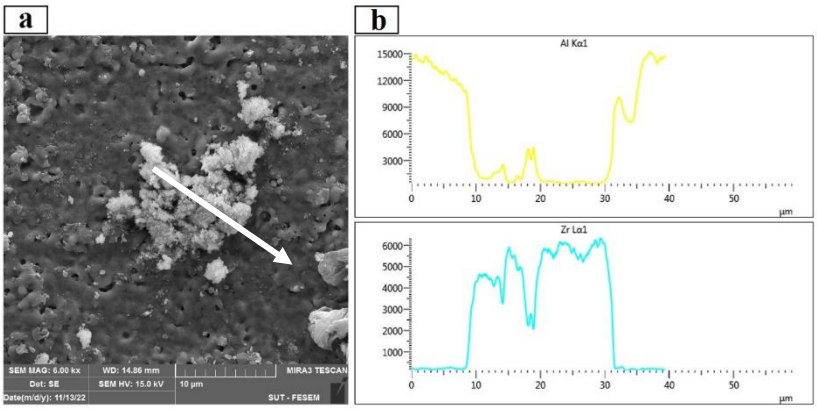

Figure 6. a) SEM image of ZrO_2 nanoparticles in modified PEO coating b) EDS elemental linescan across specified arrow in part a

3.3. Corrosion behaviour of PEO coating

Fig. 7 illustrates the polarization curves of uncoated sample, PEO coating and modified PEO coating. Table 2 also includes electrochemical data acquired from these curves, including as corrosion rate, corrosion potential, and electrical resistance for all samples. As presented in Fig. 7 and Table 2, the corrosion current density (i_{corr}) is considerably lower in presence of PEO coating (unmodified and modified). During PEO coating process, a thick oxide layer is formed on the surface, considerably increasing the surface's corrosion resistance. Because, this oxide layer almost disconnects the corrosive environment from the sample surface. Therefore, anodic and cathodic reactions are delayed and the corrosion rate is minimized. It is also found that the corrosion potential of surfaces with protective coating tends to more noble potentials, which also reflects a decrease in the surface tendency to corrosion. However, it should be noted that the PEO coating is porous and contains tiny fissures, such that corrosive solutions can penetrate throughout the coating and reach the substrate surface, causing anodic and cathodic reactions and corroded substrate. However, using the ZrO_2 nanoparticles lead to fill the porosity in PEO coating and decrease the penetration of corrosive solution. Therefore, the corrosion current density of modified PEO coating with nanoparticle is 2.52 time less than unmodified PEO coating.

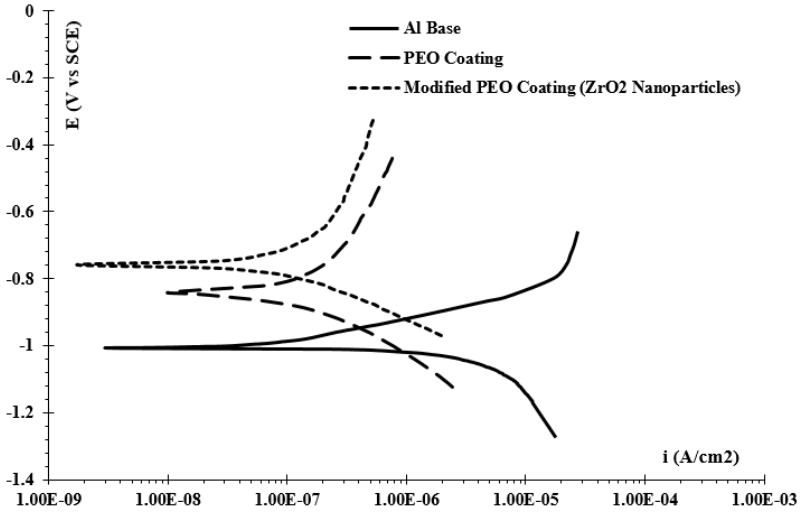

Figure 7. The polarization curves of uncoated sample, PEO coating, and modified PEO coating in 3.5 wt% NaCl solution

Table 2. Corrosion parameters derived from the polarization curves in Figure 7

Samples	R_p ($\Omega.cm^2$)	E_{corr} (V)	i_{corr} (A/cm^2)
Uncoated sample	*4298.4*	*-1.01*	*7.15×10^{-6}*
PEO Coating	*37586*	*-0.84*	*4.53×10^{-7}*
PEO Coating Modified with ZrO_2 Nanoparticles	*66178*	*-0.75*	*1.78×10^{-7}*

4. Conclusions

This study investigates the characteristics of zirconia-modified PEO coatings on AA5052 substrates in silicate electrolytes and compares their corrosion behavior with simple PEO coatings. The key findings are summarized as follows:

SEM images reveal an almost uniform distribution of ZrO_2 within the PEO coating, indicating that the chemical composition sodium silicate (10 g/L), sodium fluoride (1 g/L), potassium hydroxide (1.5 g/L), and ZrO_2 nanoparticles (2 g/L) in deionized water, along with the operational parameters (current density of 450 mA/cm², 50% duty cycle, and 50 Hz frequency) and preparation method, are optimal.

Morphological analysis indicates that the pore diameter in the PEO coating is larger than in the zirconia-modified PEO coating, as the incorporation of ZrO_2 nanoparticles effectively fills the pores.

The corrosion rates of the simple PEO coating and the zirconia-modified PEO coating are 4.53×10^{-7} A/cm² and 1.78×10^{-7} A/cm², respectively, demonstrating reductions of 15.5 and 40.1 times compared to the uncoated sample.

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The role of machine learning methods in the NISQ era: A prospective study and challenges

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ABSTRACT

Today, the development of advanced technologies plays a key role in the growth of humanity, and in this regard, the use of quantum science, machine learning, and the use of quantum processors is one of the fundamental solutions for the growth of science. Noisy Intermediate-Scale Quantum (NISQ) algorithms are designed to operate on quantum computers that are too small and noisy to implement fault-tolerant quantum error correction. These algorithms leverage the capabilities of current quantum hardware, which typically includes tens to hundreds of qubits, to perform computations that can potentially outperform classical systems for specific tasks. NISQ devices face challenges such as decoherence and gate errors, but they hold promise for advancements in fields like optimization, simulation of quantum systems, and machine learning, paving the way for future developments in quantum computing technology. In this study, we attempted to demonstrate the importance of this issue and raise challenges so that future researchers can pursue appropriate research areas.

Keywords : Quantum Computing, Machin Learning, Noisy Intermediate-Scale Quantum (NISQ), Quantum Science.

1. Introduction

Over the last 35 years, there has been a lots of research being done in order to quantum computers. All the research and surveys show its potential for solving complicated and incredibly tough problems that are unfeasible on any classic computers and processors [1]. At the beginning of the research in 1982, the idea of using quantum systems for computational sciences was a theorical concept to improve the simulation of physical systems [2, 3].

Quantum computing (QC) is growing field which has received a significant support caused by its importance in industry and academia. Quantum Machine Learning makes some advantages over classical models like: speedup in training, training time, ability to directly model quantum mechanical system. We can name NISQ era as a result of development of quantum computing [4].

Noisy Intermediate-Scale Quantum (NISQ) refers to the current generation of quantum processors with 50–500 imperfect qubits that suffer from high error rates and limited coherence times, preventing full error correction. These devices enable near-term quantum experiments and hybrid quantum-classical algorithms but require advanced error mitigation techniques, such as machine learning, to produce useful results. Now they are growing fast but problems of noisy calculations of quantum computers still exist [5].

Machine Learning (ML), a subset of Artificial Intelligence (AI), is a discipline that learns patterns from data to build predictive or decision-making models, enabling automated problem-solving and process optimization [6].

Machine learning (ML) significantly enhances NISQ (Noisy Intermediate-Scale Quantum) devices by mitigating errors and optimizing performance through data-driven approaches. ML techniques, such as neural networks (NNs) and autoencoders, can model complex noise patterns (e.g., gate errors, crosstalk, and decoherence) and predict error rates, enabling tailored error-mitigation strategies without requiring additional physical qubits [1, 2]. Reinforcement learning (RL) further optimizes quantum circuits in real-time by adapting to noise fluctuations, while Gaussian processes track time-varying noise to improve calibration [3, 4]. These methods complement hybrid quantum-classical algorithms (e.g., VQE and QAOA), where classical ML components optimize parameterized circuits and suppress noise-induced errors [5, 6]. By integrating ML across the NISQ stack—from low-level error correction to high-level algorithm design—researchers achieve more reliable quantum computations despite hardware limitations [7, 8].

2. Machine Learning for the NISQ era

Error Mitigation & Noise Characterization in NISQ hardware

Machine learning techniques are increasingly being leveraged to address two critical challenges in Noisy Intermediate-Scale Quantum (NISQ) devices: error mitigation and noise Characterization. ML algorithms help reduce the impact of quantum noise without requiring additional physical qubits for error correction, and ML models learn and predict noise patterns to enable more effective error mitigation strategies. These approaches are particularly valuable in the NISQ era where full quantum error correction is impractical due to limited qubit counts and high error rates. You can see machine learning proposed approaches in table 1 [7-9].

Table 1. Machine Learning Proposed Approaches

ML Method	Application	Advantages	Limitations
Neural Networks	Noise modeling, error prediction	High accuracy for complex noise patterns	Requires large training datasets
Autoencoders	State purification, error filtering	Effective for coherent errors	Limited to specific error types
Gaussian Processes	Time-varying noise tracking	Adapts to drifting noise	Computationally expensive
Reinforcement Learning	Adaptive mitigation strategies	Real-time optimization	Requires careful reward engineering

Neural Networks for Noise Modeling and Prediction in NISQ hardware

Neural networks (NNs) are machine learning models that learn complex patterns in quantum noise by training on calibration data. They can model noise processes (e.g., gate errors, crosstalk, decoherence), Predict error rates for specific circuit configurations and in the end suggest mitigation strategies tailored to observed noise patterns. This approach is data-driven and particularly valuable for NISQ hardware where noise characteristics are device-specific, time-varying and too complex for analytical modeling [10, 11]. It is worth noting that researchers are advised to focus more on related research, given the applications of this field.

Quantum Machine Learning (QML) on NISQ Devices

Quantum Machine Learning (QML) refers to the integration of quantum algorithms with classical machine learning techniques, implemented on Noisy Intermediate-Scale Quantum (NISQ) processors. These hybrid approaches aim to:

1. Enhance classical ML by leveraging quantum parallelism for specific tasks (e.g., kernel methods, optimization).
2. Develop quantum-native models (e.g., Quantum Neural Networks) that exploit quantum states for computational advantage.
3. Address NISQ constraints (noise, limited qubits) through error-resilient algorithms and classical co-processing [12-14] .

Quantum Circuit Optimization in the NISQ Era

Quantum circuit optimization involves modifying quantum circuits to minimize resource usage (qubits, gates, depth) while maintaining functionality, critical for NISQ hardware with limited coherence times and high error rates. This type is aiming to reduce gate counts, improving qubit mapping to match hardware connectivity, and Mitigating noise effects through circuit restructuring [15].

Hybrid Quantum-Classical Algorithms in the NISQ Era

Hybrid algorithms combine quantum and classical processors to leverage their respective strengths:

1. Quantum: Handles exponential-state-space tasks (e.g., sampling, optimization).
2. Classical: Manages optimization, error correction, and post-processing. Designed to tolerate NISQ noise while providing practical advantages.

In hybrid quantum-classical algorithms researchers commonly use: Variational Quantum Eigen solver (VQE), Quantum Approximate Optimization Algorithm (QAOA) and Classical ML-Enhanced Optimization [16-18].

2. Methods summary

Machine learning (ML) is playing a transformative role in addressing the critical challenges of Noisy Intermediate-Scale Quantum (NISQ) devices, including high error rates, limited coherence times, and scalability constraints. ML techniques such as neural networks (NNs), autoencoders, Gaussian processes, and reinforcement learning (RL) are being leveraged for error mitigation and noise characterization, enabling accurate noise modeling and adaptive correction strategies without requiring additional physical qubits [7-11]. These approaches are complemented by quantum circuit optimization methods, where graph neural networks (GNNs) and RL optimize qubit mapping and gate sequences to minimize resource usage and mitigate noise effects [15]. Furthermore, hybrid quantum-classical algorithms, such as the Variational Quantum Eigen solver (VQE) and Quantum Approximate Optimization Algorithm (QAOA), integrate classical ML for parameter optimization, enhancing their robustness against NISQ-era noise [16-18].

The synergy between ML and NISQ hardware extends to Quantum Machine Learning (QML), where quantum-enhanced models like Quantum Neural Networks (QNNs) and quantum kernels are developed to exploit quantum parallelism while tolerating hardware imperfections [12-14]. Together, these ML-driven advancements are bridging the gap between theoretical quantum advantage and practical realizability in the NISQ era, paving the way for near-term applications in optimization, chemistry, and material science. However, challenges such as data efficiency, generalization across devices, and real-time processing remain active areas of research [10, 11, 15].

We are facing some limits in NISQ era which can be solved by advanced tools such as machine-Learning. In table 2 you can find overview of NISQ limits and its machine-learning proposed approach. These limitations may be good areas for future studies by researchers to address.

Table 2. NISQ Limitations and ML Solutions overview [8, 9, 19-21]

NISQ Limitation	ML Approach
High gate errors	Neural networks for noise modeling
Shallow circuit depth	RL for gate sequencing
Barren plateaus in VQE	Gradient-based ML optimizers
Qubit connectivity	GNNs for qubit mapping
Noisy QNN training	Classical data preprocessing

Modern machine learning has provided us with generative modeling techniques that are perfectly suited for the emerging landscape of NISQ hardware. However, many fundamental questions still must be answered if such machine-learning techniques are to become fully integrated with NISQ hardware. As these devices continue to grow, they will develop in lockstep with powerful classical algorithms to aid in all stages of state preparation, measurement, verification, error correction, and more. With the dawn of artificial intelligence as the most powerful classical computing paradigm of a generation, it stands to reason that machine learning of quantum many-body states will play a critical role in the NISQ era and beyond [7].

Prospective Challenges

In general, the use of quantum processors and also NISQ technology & hardware has many challenges, as it is a new field in advanced science. We can identify the following two challenges that researchers should consider as research areas in the future.

1. Real-Time Processing: Many ML-based error mitigation techniques require computational overhead that exceeds NISQ coherence times, limiting real-time applicability.
2. Integration with Fault Tolerance: As quantum hardware progresses beyond NISQ, ML techniques must adapt to work alongside quantum error correction (QEC) rather than just mitigation.

Relevant Research Suggestions

Finally, considering the identified challenges, the following areas are suggested for future research:

1. Development of quantum-aware neural architectures that intrinsically account for device physics
2. Quantum-Aware Neural Architectures: Designing ML models (e.g., quantum graph networks) that inherently account for quantum hardware constraints in their structure.
3. creation of hybrid quantum-classical compilers that automatically select optimal ML techniques based on circuit characteristics

3. Conclusion

The integration of machine learning (ML) with Noisy Intermediate-Scale Quantum (NISQ) devices has emerged as a transformative strategy to overcome critical limitations such as high error rates, limited coherence times, and scalability constraints. Through techniques like neural networks for noise modeling, reinforcement learning for circuit optimization, and hybrid quantum-classical algorithms enhanced by classical ML, researchers have demonstrated significant improvements in error mitigation, resource

efficiency, and computational reliability. Quantum Machine Learning (QML) further extends these capabilities by leveraging quantum parallelism while tolerating hardware imperfections. However, the NISQ era remains a transitional phase, and the synergy between ML and quantum computing is still evolving. While current ML-driven approaches show promise, fundamental challenges must be addressed to fully realize practical quantum advantage.

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Nano sensors application in Petroleum industries, A general review

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ABSTRACT

Maintaining strict oversight of ambient gas levels, especially those that pose toxicological risks, is essential for preventing environmental damage. This urgent need emphasizes the importance of highly accurate and reliable gas-sensing technologies, which current systems still struggle to fully provide. Fifth-generation nano-enabled gas sensors have the transformative ability to fill this gap, offering numerous advantages such as functioning at room temperature, flexibility, high selectivity, low cost, self-powering, humidity resistance, and small size. These qualities are crucial for smoothly integrating gas sensors into the expanding Internet of Things (IoT) ecosystem. This perspective highlights the recent trends and advances (2020–2023) in designing and creating tailored nanomaterials for next-generation gas sensors, optimized for high performance in various challenging environments like point-of-care testing and on-site environmental monitoring. Additionally, it discusses the challenges tied to these advanced materials and showcases ongoing scientific efforts to overcome these limitations.

Keywords : Nano gas sensors, Volatile Organic Compounds (VOCs), Point-of-Care Diagnostics, Remote Environmental Monitoring, Selective Gas Detection

1. Introduction

The timely and accurate monitoring of diverse gaseous species within our environment is of paramount importance. A significant portion of environmental gaseous pollutants comprises volatile organic compounds (VOCs), alongside critical inorganic gases such as CO2, CO, NOx, SOx, Cl2, O3, H2S, and SF6 [1-3]. The primary sources of these emissions are anthropogenic activities, including industrial processes, biomass combustion, waste incineration, vehicular exhaust, the unfortunate consequences of warfare, and leaks from mining operations. Exposure to these gaseous pollutants can lead to a spectrum of health issues, ranging from minor discomfort to severe and long-term complications, thereby underscoring the critical need for continuous and effective surveillance of their atmospheric concentrations.

Beyond the detection of hazardous substances, the monitoring of other atmospheric constituents such as O2, H2, and N2 is equally vital for various applications, including industrial safety and process control. The emergence of artificial intelligence (AI) has ushered in a transformative era for sensing technologies, particularly by enabling sophisticated remote-sensing applications capable of real-time data acquisition and analysis [4]. Furthermore, the recent proliferation of the Internet of Things (IoT) has instigated a paradigm shift in the field of gas sensors, facilitating the development of low-cost air-quality (LCAQ) sensors. The potential deployment of numerous such units promises to significantly enhance the capabilities of existing air-quality monitoring networks [5]. The advent of 5G technology has further streamlined the connectivity and integration of IoT devices [6]. Consequently, the concept of Artificial Intelligence of Things (AIoT) has materialized, enabling LCAQ sensors to collect environmental sensory information and transmit it wirelessly to cloud-based platforms for comprehensive analysis and informed decision-making [7].

Over the preceding years, a variety of commercial air-monitoring equipment and systems have been developed and are currently employed to provide real-time assessments of hazardous gaseous pollutant levels. However, the accuracy of these LCAQ sensors when deployed in diverse ambient environments can exhibit considerable variability [5]. These uncertainties can stem from the influence of fluctuating environmental conditions, such as the presence of interfering chemical species, humidity variations, and temperature fluctuations, all of which are subject to geographical location [5]. Recognizing these limitations, ongoing and significant progress is being made towards the development of advanced, high-performance gas sensors. Current research endeavors are increasingly focused on the design and fabrication of intelligent gas sensors which can showcase advanced features and overcome past challenges associated with environmental gas sensors [8]. Significantly important work is being performed to achieve the development of improved, light-active, portable, room-temperature/low-temperature, wearable, humidity-resistant, IoT-enabled, multiple gas-selective, and dog-nose-mimicking gas sensors.

2. Nanomaterials For Smart Gas-Sensing Systems

The advancement of smart gas-sensing systems relies heavily on the tailored properties of nanomaterials. These materials, with their unique physicochemical characteristics, offer unprecedented opportunities for enhancing sensor performance in terms of sensitivity, selectivity, response time, and operational conditions.

A. MXene-Based Gas Sensors

In recent years, two-dimensional (2D) MXenes have garnered significant attention as promising building blocks for the next generation of advanced gas sensors. These materials exhibit a compelling array of advantageous features, including a high signal-to-noise ratio, the capability for room-temperature operation, excellent electrical conductivity, and versatile surface chemistry [32]. Consequently, MXenes have demonstrated considerable potential in diverse applications such as quantum sensing, highly sensitive pressure sensors, and flexible electronic devices integrated into fabrics [33-35].

However, a primary impediment to the widespread practical implementation of MXenes lies in their inherent low chemical stability, particularly their susceptibility to oxidation and hydration when exposed to humid environments [36]. Recognizing this critical challenge, researchers are actively focused on developing and implementing various modification strategies to enhance their long-term stability and performance. For instance, one effective approach involves decorating the surface of MXene nanosheets with a protective layer of titanium dioxide (TiO2) to effectively inhibit oxidation-induced degradation [9]. Furthermore, the modification of MXenes with antioxidant molecules, such as L-ascorbic acid, has also proven to be a successful route in significantly improving the overall stability of these promising 2D materials [37].

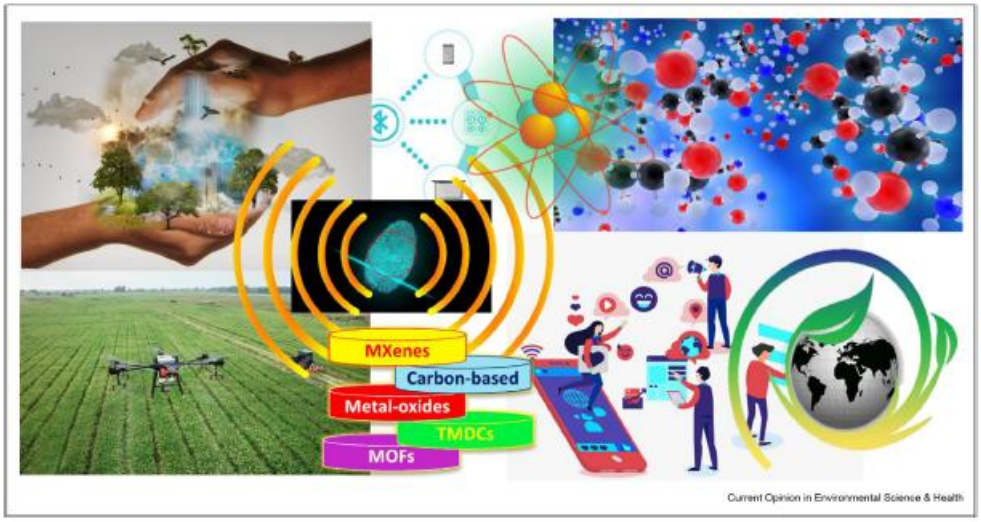

Figure 1- Advanced nanomaterials for the development of smart technology-driven environmental gas sensors.

B. Carbon-Nanomaterial-Based Gas Sensors

Carbon-based materials, particularly carbon nanotubes (CNTs), graphene, graphene oxide (GO), and reduced graphene oxide (rGO), possess extraordinary mechanical and electrical properties that have rendered them highly suitable for the development of compact, wearable, and room-temperature gas sensors [38, 39]. Graphene-based nanostructures, such as nanoscrolls, have even been employed to create gas sensors that mimic the intricate capillary structure of a dog's nose, highlighting the biomimetic potential of these materials [40-42] (Figure 2b).

Capman et al. [43] focused on enhancing the selectivity of electronic noses by leveraging the adaptable and selective binding properties of graphene. Graphene can be functionalized with a diverse array of chemical receptors, enabling the fabrication of machine-learning-integrated gas sensors. The researchers utilized graphene-based varactor arrays for the rapid and selective detection of varying concentrations of multiple VOCs. Each array comprised 108 individual sensors, functionalized with thirty-six distinct chemical receptors to achieve cross-selectivity. The sensor system offered rapid measurements, with multiplexed data acquisition from all 108 sensors occurring within tens of seconds. By integrating machine-learning-based signal analysis using a Bagging Random Forest algorithm, the device demonstrated the ability to distinguish between octane, methyl ethyl ketone, toluene, hexanal, and ethanol with an impressive accuracy of 98%. Even with the addition of 1-octene, a compound structurally similar to octane, the system maintained a high accuracy of 89%.

While traditional machine learning approaches rely on human expertise for feature selection, deep learning (DL) automates this crucial process [44], mimicking the human brain's learning mechanism through artificial neural networks (ANNs). Recently, Hwang et al. [45] presented a DL-enabled technology for the in situ, early-stage determination of mixed chemical vapor composition (without requiring target dilution or condensation of the original vapor) using AI-integrated arrayed nanoelectrodes based on multiplexed DNA-functionalized graphene. Seven graphene-based single-stranded DNA (ssDNA) sensor arrays were fabricated on a single chip and used to detect individual gases (H2S, NH3, NO, and NO2) as well as mixtures of these gases. Feature selection for gas classification was performed using the Boruta algorithm. The sensor exhibited high sensitivity and excellent selectivity. The feature selection analysis enabled the achievement of recognition rates of 99% and above for mixed gases under low humidity conditions, and 98% and above in humid environments. The researchers utilized PyTorch 1.10.0 and Python 3.7 frameworks to construct a one-dimensional (1D) convolutional neural network (CNN) architecture. This DL technique was employed for the classification of gases from chemical vapor mixtures through convolution-based feature extraction during the data scanning process for 1D vector-type data. The 1D CNN demonstrated nearly perfect discrimination of the chemical vapor's compositional state

under both high- and low-humidity conditions, suggesting promising applications for this sensor in areas such as breath analysis.

CNTs are also considered promising candidates for electronic noses due to their nanoscale dimensions, high surface-area-to-volume ratio, and the sensitivity of their electrical resistance to changes in the local chemical potential. In contrast to metal oxides, CNTs can operate at lower temperatures and consume less power, inspiring researchers to explore their use in smart gas-sensing devices. The sensitivity and selectivity of CNT-based sensors are often enhanced by functionalizing them with polymers, noble metal nanoparticles (NPs), and metal oxides [46]. While these materials have recently found applications in commercial electronic noses, their practical long-term performance has yet to be fully evaluated. Peters et al. [47] assessed the efficiency of a commercially available CNT-based hand-held electronic nose device (Smell Inspector by Smart Nanotubes Technologies). This device comprises four chips, each containing 16 independent gas sensors, along with integrated temperature and humidity sensors. The researchers conducted experiments exposing the instrument to ppm-level concentrations of four VOCs with varying polarities and scent profiles. Connected to a PC via a USB port, the device utilized Smell Annotator software for odor detection, annotation, and digitization. The device exhibited a response range of 0.5-8.0 ppm and a detection limit of 0.1-0.5 ppm, identifying VOCs based on their scent patterns. However, the study revealed limitations in achieving sufficient reproducibility with the sensor, and the sensor response diminished over several months, potentially due to sensor poisoning. Despite these limitations, this work indicates that such commercially available sensors can offer low-level room-temperature detection and hold potential for applications in security services, the food industry, healthcare, and environmental monitoring. The identified limitations, however, underscore the necessity for future improvements in this sensor technology.

Carbon-based materials are also considered highly suitable for the development of flexible gas sensors. In this context, Zhu et al. [7] presented the development of a machine-learning-enabled, three-dimensional, foldable, and flexible H2 sensor. They achieved rapid patterning of rGO on various flexible substrates using an inkjet printing technique. Sensitivity towards H2 was induced by coating the rGO with a thin (2 nm) layer of palladium nanoparticles (Pd NPs) using e-beam evaporation. Principal component analysis (PCA) was employed for the statistical analysis of the sensor's response patterns. Notably, the IoT functionality (Bluetooth wireless network) was powered by a triboelectric textile that simultaneously monitored ambient humidity and temperature, calibrating the graphene gas sensor and establishing its initial resistance [7] (Figure 2c). The synergistic combination of carbon-based and metal-oxide-based materials has also been reported to yield enhanced selectivity, sensitivity, and room-temperature efficiency in converting methane [74]. Furthermore, researchers are increasingly focusing on incorporating metal-organic frameworks (MOFs) embedded with other nanostructures to address challenges related to the surface adsorption of multiple analytes. Several such approaches have been discussed in a recent review by Bhaliya et al. [69], who concluded that current research efforts are still focused on overcoming the complexities of designing tiny electronic devices based on MOFs and array-integrated sensors utilizing multiple MOFs [69]. The integration of MOFs with other nanomaterials holds promise for surpassing the performance limitations of individual components in gas-sensing applications.

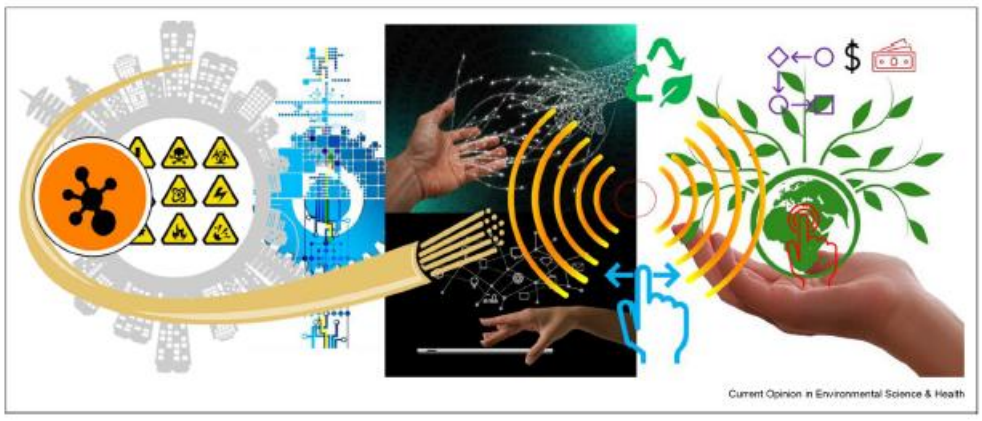

Figure 2- Diagrammatic representation of conclusion, challenges, and viewpoint presented in this review.

3. CONCLUSION, CHALLENGES, AND PERSPECTIVES

The current research landscape clearly indicates that nanomaterials, including MXenes, carbon-based materials, metal oxides, transition metal dichalcogenides (TMDCs), and metal-organic frameworks (MOFs), are at the forefront of innovation for developing high-performance smart gas-sensing systems. However, a critical observation from recent studies is that relying on a single material type often falls short of delivering the comprehensive advantages required for optimal sensing performance. Each material class inherently possesses its own set of strengths and weaknesses. Consequently, a significant focus within the scientific community lies in the strategic modification of these materials to maximize their beneficial attributes while mitigating their inherent limitations.

Numerous advanced sensing systems have been successfully engineered through the synergistic integration of two or more of these distinct material types. Researchers have effectively demonstrated the potential of these integrated nanomaterials in creating smart gas sensors that are compatible with contemporary technological frameworks. Nevertheless, further practical efforts and rigorous experimental validations are essential to ensure the reliable applicability of these systems in long-term, real-world scenarios.

Several key challenges still impede the widespread utilization of these nanomaterials for practically viable modern gas sensors. These challenges include the development of low-cost, user-friendly smart systems, thorough evaluation of their long-term and real-life efficiency and reliability, and the successful scaling-up of the fabrication processes for these nano-enabled gas sensors. It is also important to acknowledge the continuous advancements in commercial gas sensor technologies, which are incorporating significant modifications such as the transition from analog to digital interfaces. The performance of these commercial sensors has reportedly been enhanced through optimized model training, randomized calibration techniques, and the implementation of more sophisticated operational modes like temperature-cycled operation (TCO), with ongoing research actively pursuing further improvements in these areas. The seamless integration of smart gas sensors with IoT devices via wireless communication technologies, such as LoRA, Zigbee, Wi-Fi, and Bluetooth, unlocks the potential to generate valuable data streams for end-users and decision-makers [75].

Another critical concern that warrants careful consideration is the generation of electronic waste (e-waste), chemical waste, and solid waste throughout the lifecycle of these gas sensor systems, encompassing their development, operation, and eventual disposal. For the large-scale and sustainable utility of such systems, it is imperative to address this issue proactively to prevent environmental contamination [76]. Recognizing this pressing challenge, the scientific community has begun to prioritize environmentally conscious approaches, adopting strategies such as the use of greener solvents and precursors during the fabrication processes and the development of bio-inspired, bio-derived, and bio-mimetic sensing systems [76-80]. For instance, a recent...

AI statement

In writing this article, artificial intelligence was used to collect references. Artificial intelligence was also used to improve writing and grammatical points, and the cases were limited to two mentioned.

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Optimization of Friction Stir Welding Parameters for Dissimilar Joining 5xxx and 6xxx Series Aluminum Alloys

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ABSTRACT

This study investigates the effect of friction stir welding (FSW) parameters on the microstructure and mechanical performance of dissimilar joints between AA5052-H38 and AA6061-T6 aluminum alloys. A total of eight welding conditions were explored, varying rotational speed, traverse speed, and material placement on the advancing/retreating sides. Microstructural analysis revealed distinct changes in grain morphology across the weld zones, with dynamic recrystallization observed predominantly on the advancing side. Tunnel and kissing bond defects were correlated with increased traverse speed and insufficient heat input. Tensile testing showed that optimal mechanical properties were achieved when AA5052 was placed on the advancing side at moderate rotational speeds, with a maximum ultimate tensile strength of 197 MPa. These results highlight the critical role of parameter optimization and alloy positioning in tailoring FSW joint performance for dissimilar aluminum alloys

Keywords : Friction Stir Welding (FSW), Dissimilar Aluminum Alloys, Welding Parameters, Microstructure Evolution, Ultimate Tensile Strength (UTS)

1. Introduction

The use of aluminum alloys for weight reduction in aircraft, marine, and land vehicles is rapidly increasing due to their low density, excellent corrosion resistance, good forming properties, and upgradeable mechanical properties [1]. Among various joining techniques, friction stir welding (FSW), a relatively new solid-state process developed in 1991 by The Welding Institute (TWI), has emerged as a promising method for joining dissimilar aluminum alloys [2]. FSW is particularly suitable for joining aluminum alloys that are prone to defects, such as solidification cracks, porosity, and distortion, when welded using conventional fusion welding techniques [3]. Since FSW is a solid-state process with low heat input, it avoids melting and solidification of the base metal, thereby eliminating these defects while significantly improving joint strength [4]. These advantages are especially critical for high-strength aluminum alloys from the 2XXX and 7XXX series, which typically exhibit poor weldability in fusion welding processes [5]. Verma et al. [6] investigated the friction stir welding of AA1100 and AA6061 aluminum alloys, which are commonly used in aerospace applications. In their study, they joined 5 mm-thick plates of these materials using a cylindrical pin tool. Tensile testing revealed that the weld strength was lower than that of the base AA6061 alloy but comparable to the AA1100 alloy sheet. Rajkumar et al. [7] investigated dissimilar friction stir welding of AA6061 and AA5052 aluminum alloys at a rotational speed of 710 rpm and transfer speeds of 20 and 28 mm/min. Their results demonstrated that better material mixing occurs in the turbulent zone at the lower transfer speed (20 mm/min). Additionally, tensile tests revealed that welds produced at slower transfer speeds exhibited higher strength compared to those made at higher speeds. Jamshidi Aval et al. [8] investigated residual stress and microstructure evolution in dissimilar friction stir welds between AA7075-T6 and AA6082-T6 aluminum alloys. Their analysis revealed atomic diffusion occurring both within the stir zone and at the alloy interface, demonstrating effective material mixing. The study established important relationships between process parameters and residual stresses: increasing heat

input was found to simultaneously reduce maximum residual stresses while expanding the heat affected zone's size. Additionally, the researchers observed that natural aging of the weld zone provided a secondary stress relief mechanism, reducing residual stresses by 15-20 MPa. These findings collectively demonstrate how thermal management and post-weld aging can be leveraged to control residual stresses in high-strength aluminum alloy joints. Bofa et al. [9] examined the friction stir welding of AZ31 magnesium and AA6061-T6 aluminum alloys, identifying intermetallic compound formation as the primary factor compromising joint integrity. Their work demonstrated that workpiece configuration critically influences weld quality, with optimal results achieved exclusively when positioning the magnesium alloy on the advancing side of the weld, a finding that underscores the importance of material placement in mitigating detrimental phase formation during dissimilar alloy joining. Khanna et al. [10] investigated the joining of AA6061-T6 and AA8011-H14 aluminum alloys, specifically examining the effects of alloy positioning relative to the weld centerline and tool offset under constant welding parameters. Using radiographic testing to verify weld and subsurface quality, their thermal analysis revealed an asymmetric temperature distribution when applying a 1 mm offset toward the softer metal (AA8011-H14), with slightly higher temperatures recorded on the advancing side. Microstructural characterization further demonstrated that optimal weld quality was achieved when the softer alloy was positioned on the advancing side with this controlled tool offset, highlighting the importance of strategic material placement in dissimilar aluminum joining processes. Zamankhan et al. [11] conducted a comprehensive microstructural analysis of both similar and dissimilar friction stir welds between AA2219 and AA7475 aluminum alloys. Their investigation revealed a consistent pattern across all welding conditions, with the thermomechanically affected zone (TMAZ) exhibiting the lowest hardness values, particularly on the retreating side of the weld. This finding highlights the critical influence of material flow dynamics and thermal gradients on localized softening behavior in aluminum alloy joints. Infante et al. [12] investigated the fatigue behavior of friction stir welded joints between dissimilar AA6082 and AA5754 aluminum alloys, comparing them with similar alloy joints. Their fatigue testing revealed a significant finding: both similar and dissimilar joints exhibited superior fatigue resistance compared to the base metals themselves. This unexpected result suggests that the friction stir welding process may induce microstructural changes that enhance fatigue performance in aluminum alloy joints. Abolusoro et al. [13] investigated how tool rotation speed affects weld characteristics in dissimilar AA6101-T6 and AA7075-T651 aluminum alloys while maintaining constant feed rate. Their comprehensive analysis revealed three key findings: (1) thermal monitoring showed progressive temperature increase over time, with advancing side temperatures consistently exceeding those on the retreating side; (2) tensile testing demonstrated an inverse relationship between process temperature and ultimate strength; and (3) microstructural examination identified material discontinuity in the turbulent zone, while optimal material mixing - evidenced by maximum penetration and grain entanglement - occurred at intermediate rotation speeds. These results collectively demonstrate the critical balance required between thermal input and mechanical mixing in dissimilar aluminum welding. Ilangovan et al. [14] conducted a comparative study of similar and dissimilar friction stir welds between AA5083 and AA6061 aluminum alloys, analyzing both microstructural characteristics and mechanical properties. Using optical and scanning electron microscopy, they systematically examined various weld zones, revealing that dissimilar joints achieved a peak hardness of 115 Vickers with 56% joint efficiency. Their microstructural analysis correlated these mechanical properties with two key factors: the absence of defects in the weld zone and the presence of refined grain structure, demonstrating how microstructural features directly influence joint performance in aluminum alloy welding. Giraud et al. [15] conducted a systematic investigation of dissimilar friction stir welds between AA7020-T651 and AA6060-T6 aluminum alloys across a range of process parameters (1100-300 mm/min travel speed and 1000-2000 rpm rotational speed). Their thermal analysis revealed no significant temperature differential between the advancing and retreating sides, despite using highly sensitive measurement equipment. Mechanical testing demonstrated consistent failure behavior, with tensile fractures consistently occurring in the lower hardness region regardless of the alloys' relative positioning. This finding highlights the dominant role of localized mechanical properties over material configuration in determining joint failure characteristics. Sundaram et al. [16] systematically investigated the influence of key process parameters, including pin geometry, rotational speed, and axial force, on the mechanical properties of friction stir welded AA2024 and AA5083 aluminum alloys. Their comparative analysis revealed significant performance variations based on tool design: hexagonal pin tools produced welds with both the highest tensile strength and greatest elongation, while cylindrical tools yielded the lowest

values for these mechanical properties. These findings demonstrate the critical role of tool geometry in determining weld quality for similar aluminum alloy joints. Kumar et al. [17] investigated material flow behavior in dissimilar friction stir welding, establishing a direct correlation between process parameters and joint quality. Their research demonstrated that increased rotational speeds enhance material mixing, leading to superior mechanical properties. Specifically, the study revealed that optimal shear tensile strength (achieved at 1400 rpm with a travel speed of 60 mm/min) directly corresponded to the degree of material homogenization in the stir zone. These findings highlight the critical relationship between rotational velocity, material flow characteristics, and ultimate joint performance in dissimilar welding applications. Torzhevsky et al. [18] systematically investigated how tool rotation and travel speeds influence the macrostructure, microhardness, and mechanical properties of dissimilar friction stir welds between 7020-T651 and 5083-H111 aluminum alloys. Their comprehensive analysis revealed that optimal strength properties were achieved using specific processing parameters of 800 rpm rotation speed combined with 200 mm/min travel speed. This parameter combination produced superior joint characteristics compared to other tested conditions, demonstrating the critical importance of parameter optimization in dissimilar aluminum alloy welding. Laska et al. [19] investigated the mechanical properties of dissimilar friction stir welds between AA5083 and AA6060 aluminum alloys, focusing on the effect of tool speed variations. Their results demonstrated a direct correlation between increased tool speed and enhanced hardness in the weld zone. This strengthening effect was attributed to two key factors: (1) greater heat input promoting more complete material plasticization, and (2) more effective dynamic recrystallization leading to grain refinement. The findings highlight how process parameters can be optimized to control microstructural evolution and improve joint performance in dissimilar aluminum welding applications. Wang et al. [20] conducted a comprehensive investigation of material flow mechanisms in dissimilar friction stir welding of three high-strength aluminum alloys (AA2024-T351, AA6061-T651, and AA7075-T735). Their study revealed two key process-property relationships: (1) reduced tool rotation speeds enhanced overall weld quality by improving material mixing homogeneity, while (2) increased travel speeds produced joints with superior tensile strength. These opposing parameter effects demonstrate the complex optimization required when joining dissimilar wrought aluminum alloys, where balancing rotation and travel speeds is critical for achieving both sound weld integrity and desirable mechanical properties. As shown in the studies conducted, the joining of dissimilar aluminum alloys is one of the most widely used industrial and interesting topics in research fields, for this reason, the aim of this project is to investigate the effect of variables such as transfer speed, rotational speed, and the location of the alloys in the progressive and retrograde directions on the microstructural morphology and mechanical properties of the joint. For this purpose, in this study, the desired welds were made in eight different states and mechanical and microstructural studies were performed on them.

2. Experimental procedure

This study employed 5 mm-thick AA5052-H38 and AA6061-T6 aluminum alloy sheets (200 × 120 mm), with chemical compositions detailed in Table 1 as measured by optical emission spectroscopy. Surface preparation involved degreasing with acetone and oxide removal using a wire brush before butt-welding in a fixture-clamped configuration. Welding was performed using an H13 hot-work steel tool with a 15 mm shoulder and 5 mm diameter threaded cylindrical pin (4.8 mm length), maintaining constant parameters of 0.1 mm penetration depth, 3° tilt angle, and counterclockwise rotation matching the pin's right-handed threads. The experimental matrix systematically investigated the effects of traverse speed, rotation speed, and alloy positioning (advancing/retreating sides) on joint characteristics. The welding parameters (rotational and traverse speeds) for each experimental condition are detailed in Table 2. Tensile testing was performed using an Instron M200 universal testing machine (20 N maximum force, 0.5 mm/min rate, ±0.1 N accuracy) with loading applied perpendicular to the weld direction. Following ASTM E8M-11 standards [21] (Figure 1), two specimens were wire-cut from each weld sample, yielding a total of 16 test specimens for evaluation.

Table 1. Chemical composition of the base materials used in this research.

Alloy	Mg	Mn	Cu	Cr	Si	Fe	Zn	Ti
AA5052	2.5	0.1	0.1	0.25	0.25	0.4	0.1	-
AA6061	1	-	0.25	0.19	0.6	0.7	0.25	0.15

Table 2. Codes employed for the notation of samples and their welding conditions.

Sample No.	Retreating side	Advancing side	traverse speed (mm/min)	Rotational speed (rpm)
1	AA5052	AA6061	60	600
2	AA5052	AA6061	90	600
3	AA5052	AA6061	120	600
4	AA5052	AA6061	180	600
5	AA5052	AA6061	90	800
6	AA5052	AA6061	90	1000
7	AA6061	AA5052	90	600
8	AA6061	AA5052	90	1000

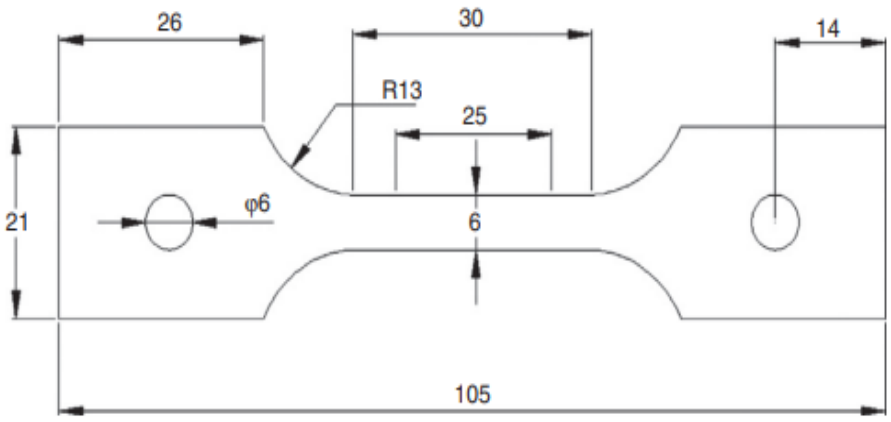


Figure 9. The specimen of the tensile test according to ASTM E8M-11[20].

Weld quality evaluation involved cross-sectional analysis and metallographic examination of the joints. Following ASTM E3 guidelines, samples were sectioned perpendicular to the weld direction and progressively polished using 120 to 5000 grit sandpaper. The prepared surfaces were then etched with specific solutions (Table 3), with etching durations determined according to standard protocols [22]. Macro- and microstructural characterization was performed using an Olympus BH2 optical microscope, with particular focus on examining distinct regions including the thermo-mechanically affected zone (TMAZ), heat-affected zone (HAZ), and weld nugget.

Table 3. Composition of etchant solutions [22].

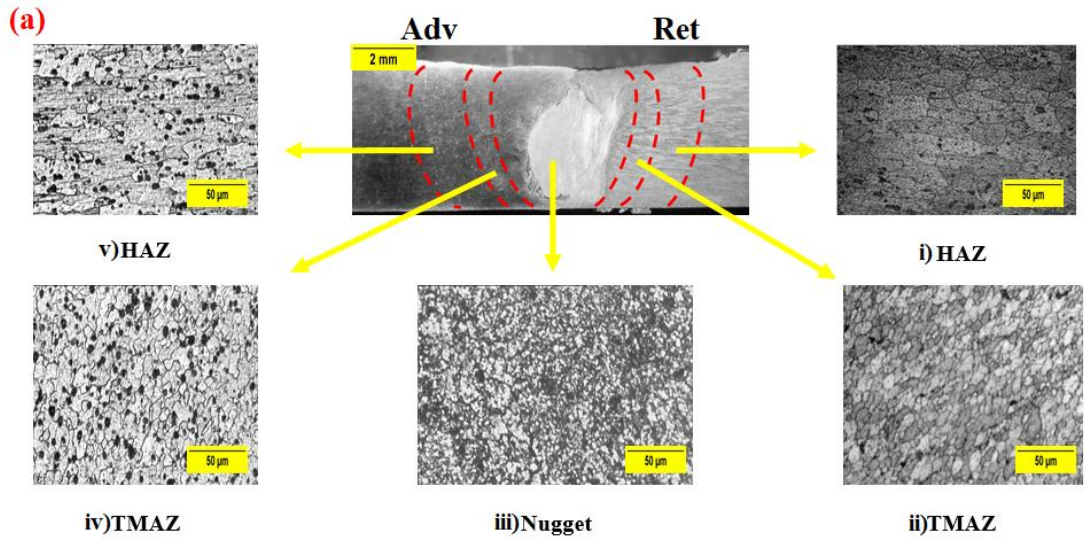
Etchant	composition
Poulton reagent Coarse structure	12ml hydrochloric acid + 6 ml nitric acid + 1 ml hydrofluoric acid + 1 ml distilled water
Modified Poulton	50ml of Pluton solution + 25 ml of nitric acid + 40 ml of chromic solution 3 g of chromic acid in 10 ml of distilled water

3. Results and discussions

3.1. Microscopic examinations

The microstructural and macrostructural characteristics of the samples 1 through 4 are presented in Figure 2. Macrostructural examination of the cross-sections reveals three distinct regions: (1) weld nugget, (2) heat-affected zone (HAZ), and (3) thermo-mechanically affected zone (TMAZ). In samples 1, 2, 3 and 4, the aim is to investigate the effect of traverse speed at a constant rotational speed (600 rpm). As can be seen in the macroscopic images of Figures 2a to 2d, at advancing rates of 60 and 90 mm/min, the weld cross-section is free of voids and tunnel defects, but at the same time, a kissing bond (KB) defect can be observed in their cross-section. According to Attallah [23], this defect is caused by the oxide layer being pulled in from the surface and being located in the middle of the material at the joint line. Also, it is very difficult to detect this defect with microstructure and for definitive characterization, complementary EDS analysis should be used to characterize the oxide particles [24]. Zhou et al. [25] studied the effect of KB on the fatigue strength of AA5083 joints and concluded that the presence of this oxide layer can decrease the fatigue life of the joints by 0.05 to 0.025 times that of the defect-free state. Cross-sectional analysis of Samples 3 and 4 revealed tunnel defects that formed due to suboptimal welding parameters. These defects typically originate from improper selection of critical process variables, including: (1) rotational speed, (2) traverse speed, (3) tool vertical force, (4) tool offset, and (5) tool geometry. The observed cavities suggest insufficient material flow and incomplete consolidation during the welding process [26]. The absence of tunnel defects in Samples 1 and 2, in contrast to their presence in Samples 3 and 4, suggests a direct correlation between traverse velocity and defect formation. Specifically, the increased transfer velocity reduces heat input, leading to insufficient material flow and localized plasticization. This thermal-mechanical imbalance results in incomplete material combination, ultimately confirming as the observed tunnel defects [27]. Therefore, it can be said that Samples 1 and 2 received higher heat input compared to Samples 3 and 4. The critical threshold for tunnel defect formation at 600 rpm was identified at transfer velocities exceeding 90 mm/min. Microscopic examination revealed these defects formed on the retreating side within the AA5052 alloy side, suggesting material-dependent flow behavior under reduced heat input conditions [28]. As previously stated, the AA5052 alloy was in the H38 temper condition while the AA6061 alloy was in the T6 temper condition. Typical hardness values for these

materials are approximately 77 Brinell for AA5052 and 95 Brinell for AA6061 [29]. Khan et al. [26] characterized defect formation mechanisms in dissimilar friction stir welds between AA5083-H116 and AA6061-T6 aluminum alloys. Their results demonstrated that tunneling defects nucleate preferentially under zero tool offset conditions, with defect propagation localized to the advancing side adjacent to the higher-strength AA6061-T6 base material. This phenomenon correlates with asymmetric material flow induced by the strength differential between the joined alloys. This is in contradiction with Khan's observations. The reason for this can be related to welding parameters such as traverse speed and rotation speed as well as the amount of energy stored through cold working. As observed in the microstructural images presented in Figure 4, a comparison between the HAZ and TMAZ on both the advancing and retreating sides reveals distinct differences in grain morphology and orientation. On the advancing side, the grain structure within the TMAZ exhibits a significant deviation from that in the HAZ, indicating substantial grain reorientation. Specifically, in the HAZ, grains appear elongated along the rolling direction, while in the TMAZ, the formation of new, more equiaxed grains suggests the occurrence of dynamic recrystallization. This microstructural transformation is associated with a localized reduction in mechanical strength on the advancing side. Conversely, on the retreating side, the grains within the TMAZ largely retain their elongated morphology characteristic of the rolling process. This suggests that dynamic recrystallization in this region has either not initiated or has not reached completion. Additionally, across all microstructural figures (figures i to v), dark, nearly circular particles are visible along the grain boundaries. These features are most likely Mg_2Si precipitates, which are characteristic of the AA6061 aluminum alloy [30].



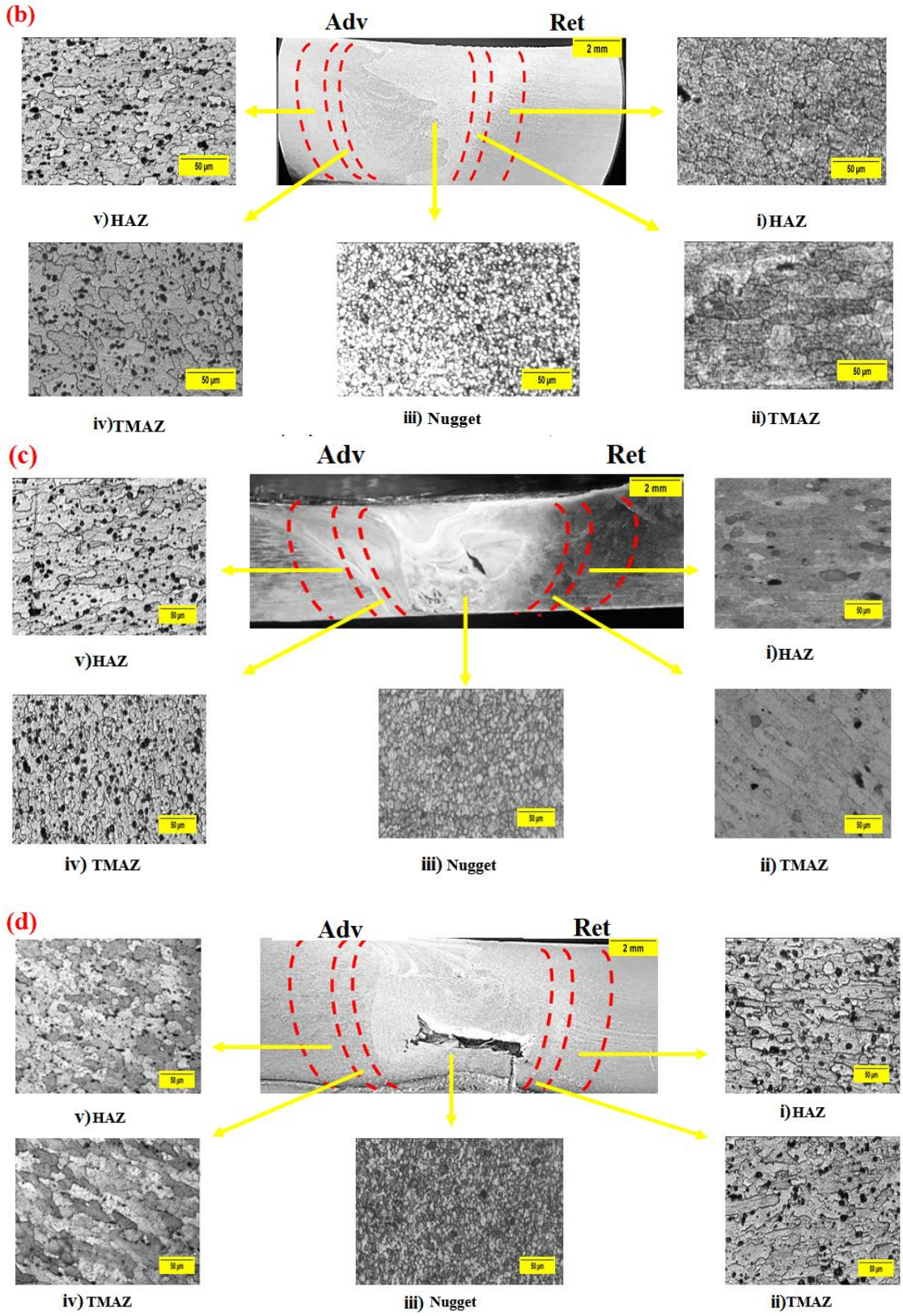


Figure 10. Cross-sectional view of Samples 1 through 4 welded at a rotational speed of 600 rpm and a traverse speed of a) 60, b) 90, c) 120, and d) 180 mm/min along with corresponding micrographs from selected regions: i) HAZ on the retreating side, ii) TMAZ on the retreating side, iii) weld nugget, iv) TMAZ on the advancing side, v) HAZ on the advancing side.

Following the investigation of traverse speed, the effect of rotational speed was examined using Samples 5 and 6. At a constant traverse speed of 90 mm/min, increasing the tool's rotational speed resulted in enhanced grain growth within the weld nugget due to the higher heat input associated with increased frictional energy [31]. Furthermore, the material flow behavior was noticeably altered; as the rotational speed increased from 600 to 1000 rpm, the flow pattern transitioned into a more distinct layered structure. This resulted in the formation of alternating layers of AA6061 and AA5052 alloys within the stir zone, indicating material segregation under intensified stirring conditions [32]. Additionally, in both Samples 5 and 6 (Figure 3), the characteristic onion-ring flow pattern is clearly visible at the center of the weld, further confirming the presence of distinct material flow features.

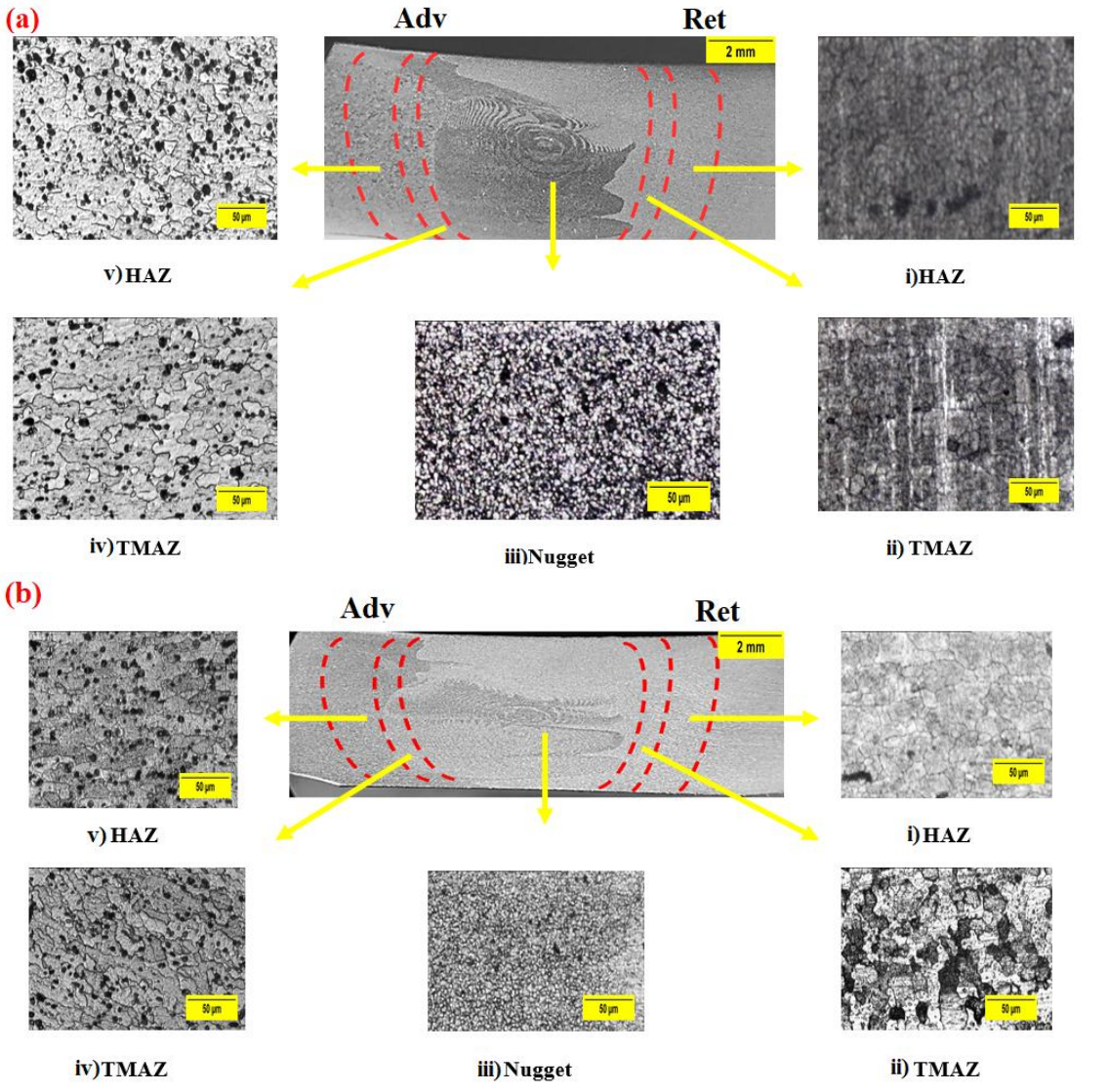


Figure 11. Cross-sectional view of Samples 5 and 6 welded at a traverse speed of 90 mm/min and a rotational speed of a) 800, and b) 1000 rpm, along with corresponding micrographs from selected regions: i) HAZ on the retreating side, ii) TMAZ on the retreating side, iii) weld nugget, iv) TMAZ on the advancing side, v) HAZ on the advancing side.

In Samples 2, 6, 7, and 8, the influence of the material positioning on the advancing and retreating sides was studied under constant traverse speed and varying rotational speeds. As shown in Figures 2b, 3b, 4a, and 4b, the material flow patterns at identical rotational speeds are largely comparable across these samples. Notably, the spacing between onion-ring flow structure becomes closer together with increasing rotational speed, consistent with enhanced stirring action and higher thermal input [33]. Furthermore, in Samples 6 and 8, elevated rotational speeds result in increased heat generation, which in turn promotes grain growth across various weld zones [34]. A particularly significant observation is the influence of rotational speed on the extent of recrystallization, as illustrated in Figures 4a and 4b. In Sample 7 (Figure 4a), grains in the TMAZ on the retreating side (where the AA6061 alloy is located), partially retain their elongated morphology inherited from the rolling process. In fact, dynamic recovery, which involves the rearrangement of dislocations, may be the dominant mechanism on the retreating side, leading to a mixed grain structure with potential for partial recrystallization [35]. In contrast, on the advancing side, where the shear strain is stronger, dynamic recrystallization is more extensive, leading to the formation of grains with new orientations. Additionally, in Sample 8 (Figure 4a), increasing the rotational speed from 600 to 1000 rpm results in noticeable changes in grain morphology on both the advancing and retreating sides, with more fully recrystallized grains emerging because of the higher heat input and enhanced plastic deformation [35].

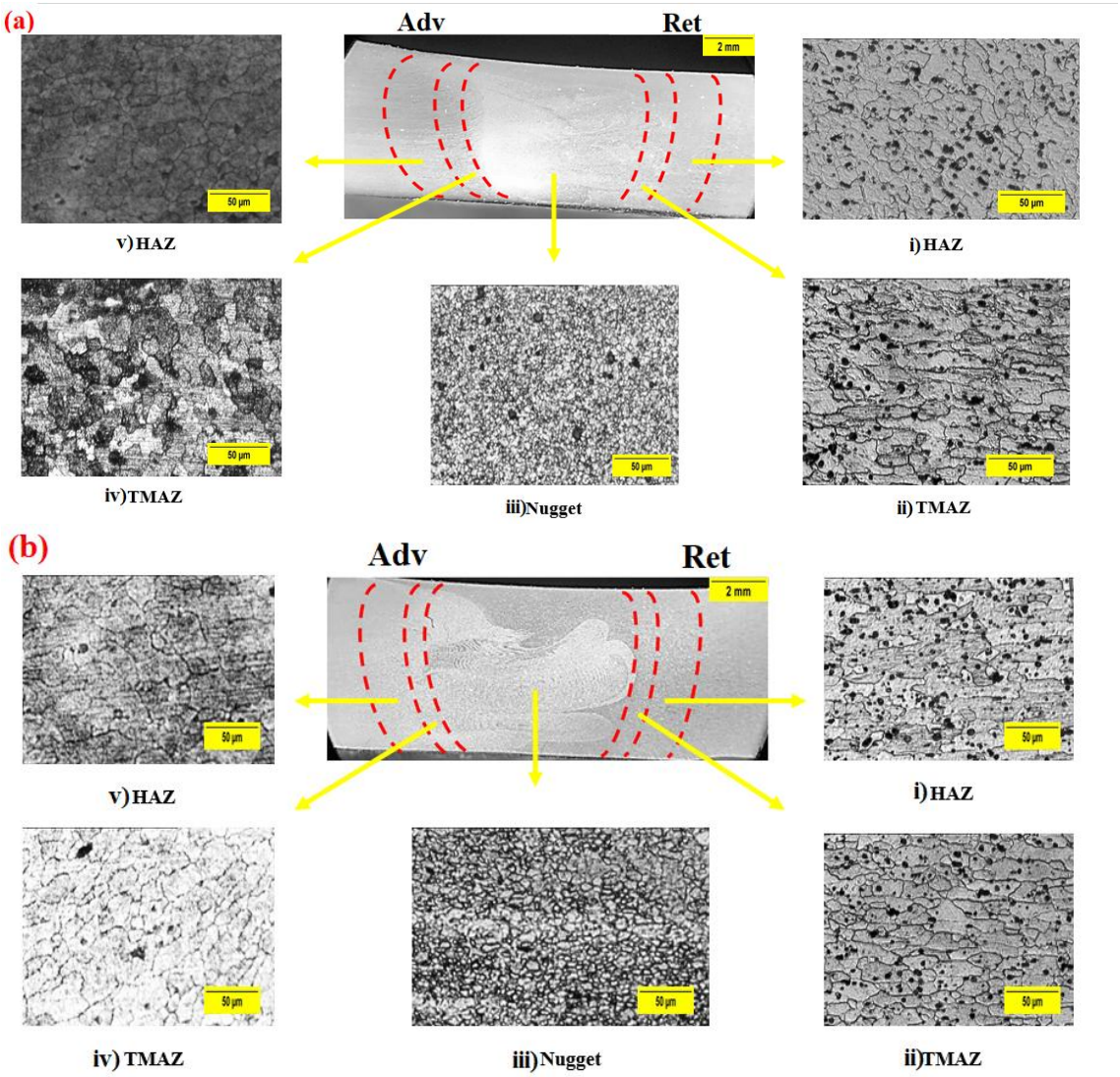


Figure 12. Cross-sectional view of Sample 7 and 8 welded at a traverse speed of 90 mm/min and a rotational speed of a) 600, and b) 1000 rpm, which AA5052 is located on the advancing side, along with

corresponding micrographs from selected regions: i) HAZ on the retreating side, ii) TMAZ on the retreating side, iii) weld nugget, iv) TMAZ on the advancing side, v) HAZ on the advancing side.

Based on the microstructural analyses and corresponding metallographic images, it can be concluded that the grain structure of the aluminum alloy undergoes significant modification as a result of friction stir welding. In nearly all samples, the grain size within the weld nugget is notably smaller than that observed in the base metal, HAZ, and TMAZ, indicating dynamic recrystallization during the process. Additionally, in all examined samples, the grain size in the HAZ appears to be larger than that in the TMAZ, the weld zone, and even the base metal. Consequently, the HAZ consistently exhibits the coarsest grain structure among all weld regions, which is anticipated to negatively affect the local mechanical strength in this zone [36], [37].

3.2. Mechanical properties testing

To evaluate the mechanical performance and fracture behavior of the welded joints, uniaxial tensile testing was conducted. The tensile test results are summarized in Table 4 and illustrated in Figures 5 through 8. Among all samples, Sample 7 (welded at a rotational speed of 600 rpm and a traverse speed of 90 mm/min, with the AA5052 alloy positioned on the advancing side) exhibited the highest ultimate tensile strength (UTS), followed by Samples 6 and 5, which were produced at higher rotational speeds. This enhanced mechanical performance can be correlated with the microstructural and macrostructural features discussed in section 3-1, and shown in Figure 4. As previously discussed, dynamic recrystallization occurs predominantly on the advancing side, where the AA5052 alloy is located. The formation of new, equiaxed grains in this region contributes to improved ductility. Conversely, on the retreating side, where the AA6061-T6 alloy (a precipitation-hardened material) is situated, thermal exposure during welding leads to precipitate coarsening. This phenomenon reduces the alloy's strength due to the lower interfacial energy barrier between the coarsened precipitates and the matrix, making it easier for cracks to initiate and propagate. As a result, fracture consistently initiates from this region [38], [39].

Table 4. Tensile test results

Sample No.	Average ultimate tensile strength (Mpa)	Location of failure
1	179	Weld Nugget
2	165	Weld Nugget
3	90	Weld Nugget
4	60	Weld Nugget
55	187	AA 6061
6	195	AA6061
7	197	AA6061
8	119	Weld Nugget

The graph presented in Figure 6 corresponds to the stress-strain of Samples 1 through 4. As shown in Figure 2, Samples 3 and 4, recorded significantly lower UTS values of approximately 90 and 60 MPa, respectively. This reduction in strength is consistent with the tunnel defects described in Section 3.1, which were attributed to insufficient heat input at higher traverse speeds [40]. In contrast, Sample 1 achieved the highest UTS of approximately 179 MPa, followed by Sample 2 at around 165 MPa. As discussed in earlier sections, increasing the traverse speed reduces the thermal input in the stir zone, leading to incomplete material mixing and potential defect formation. However, in the case of Sample 1, the process parameters appear to have generated sufficient heat for effective plastic flow and defect-free welding, resulting in improved strength and ductility, as indicated by the larger area under its stress-strain curve. Between Samples 3 and 4, further increasing the traverse speed from 120 to 180 mm/min led to a

noticeable decline in UTS from 90 to 60 MPa. Additionally, in Figure 6 Sample 4 exhibited reduced ductility, fracturing at a strain of 0.9%, compared to 1.1% for Sample 3.

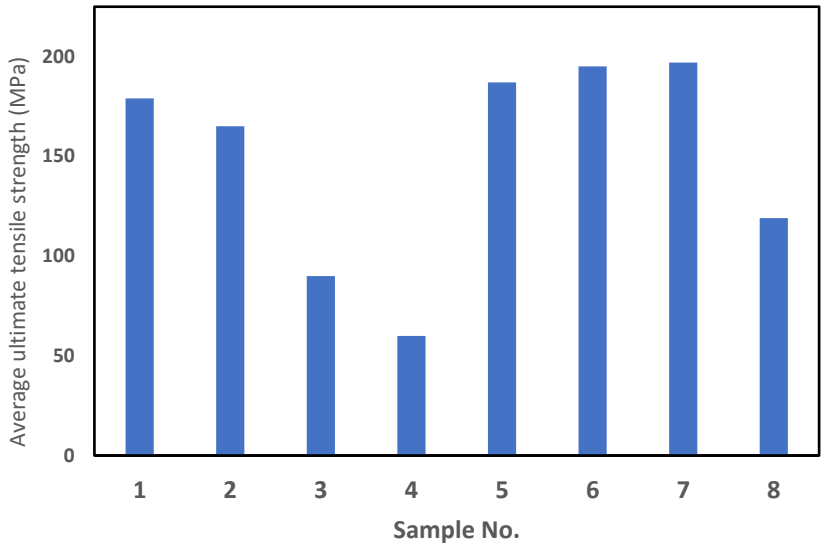


Figure 13. Tensile test results of samples.

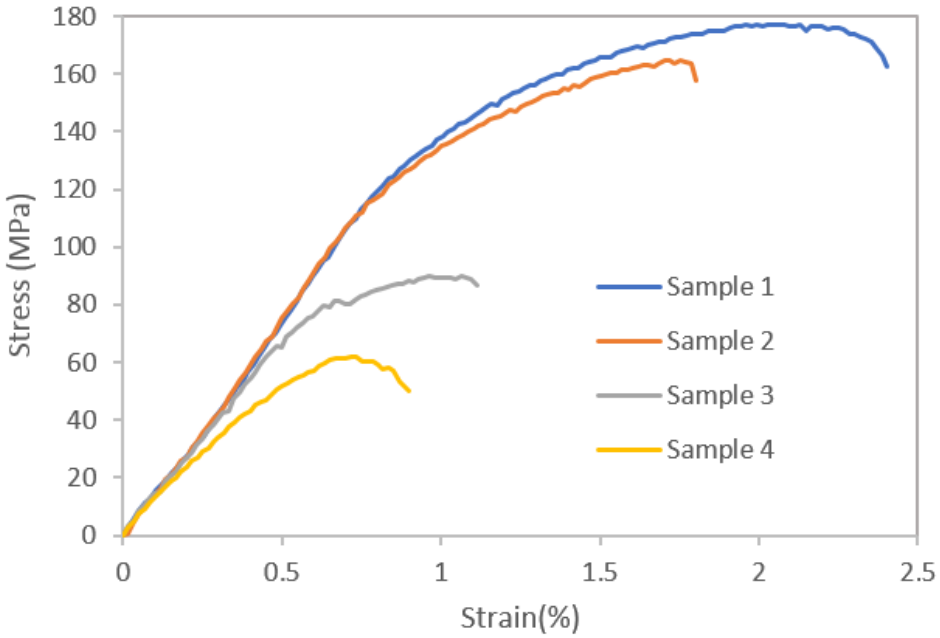


Figure 14. Comparison of stress-strain diagrams in samples 1, 2, 3 and 4.

Figure 7 presents the stress-strain diagrams for Samples 2, 5, and 6, which were fabricated at varying rotational speeds while maintaining a constant traverse speed of 90 mm/min. As shown in this figure, the UTS of Samples 2, 5, and 6 were measured at 165, 187, and 195 MPa, respectively. These results clearly demonstrate that, under constant traverse speed, increasing the rotational speed leads to an improvement in UTS [31]. In terms of ductility, Sample 5 exhibited the highest fracture strain, while Sample 2 showed the lowest. Consequently, the toughness, represented by the area under the stress-strain curve, was greatest in Sample 5, followed by Sample 6, and lowest in Sample 2. This trend suggests

that although Sample 6 had the highest UTS, its slightly reduced toughness compared to Sample 5 may be attributed to microstructural changes associated with excessive heat input, particularly grain coarsening [41]. It is worth noting that microstructural and macrostructural observations between Samples 5 and 6 did not reveal significant differences in the examined sections. Therefore, the marginal reduction in toughness in Sample 6 is likely due to localized microstructural variations outside the region analyzed by standard metallographic methods.

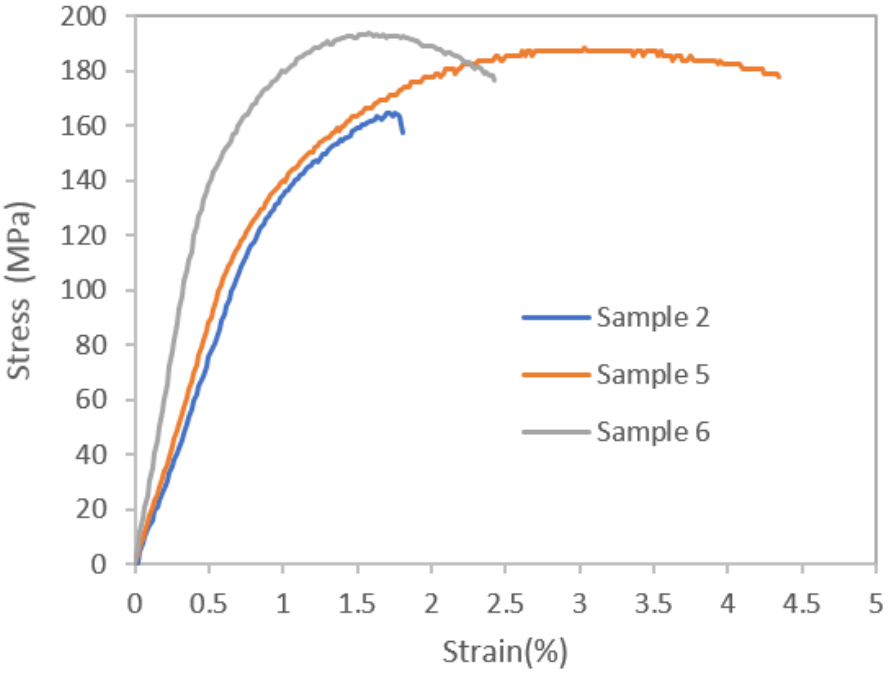


Figure 15. Comparison of tensile tests in samples 2, 5 and 6.

Based on the stress-strain data presented in Figure 7, a comparison between Samples 2 and 7, both welded under identical rotational speed (600 rpm), and traverse speed (90 mm/min), but with reversed alloy positioning on the advancing and retreating sides, reveals a significant influence of material placement on joint performance. When AA5052 alloy is positioned on the advancing side (Sample 7), the joint exhibits a notable increase in mechanical properties. Specifically, the UTS rises from approximately 165 MPa in Sample 2 to around 197 MPa in Sample 7. In addition, the toughness, represented by the area under the stress-strain curve, is considerably higher in Sample 7 than in Sample 2. This improvement can be attributed to the different thermal and mechanical responses of the two alloys in the HAZ area. During welding, the temperature in the HAZ on the advancing side can approach the solidus temperature, estimated at approximately 550 °C [27]. Under these conditions, AA5052 (a strain-hardened alloy) primarily undergoes dynamic recrystallization, which helps refine the microstructure and preserve ductility. In contrast, AA6061 (a precipitation-hardened alloy) experiences partial recrystallization in the TMAZ, but in the HAZ, elevated temperatures promote precipitate coarsening rather than strengthening, leading to a greater loss in mechanical properties. Furthermore, the advancing side experiences higher shear deformation and more intense mechanical stirring. When AA5052 is on this side, the material exhibits greater potential for recrystallization and grain refinement under these conditions, which further contributes to the improved ductility and strength [42].

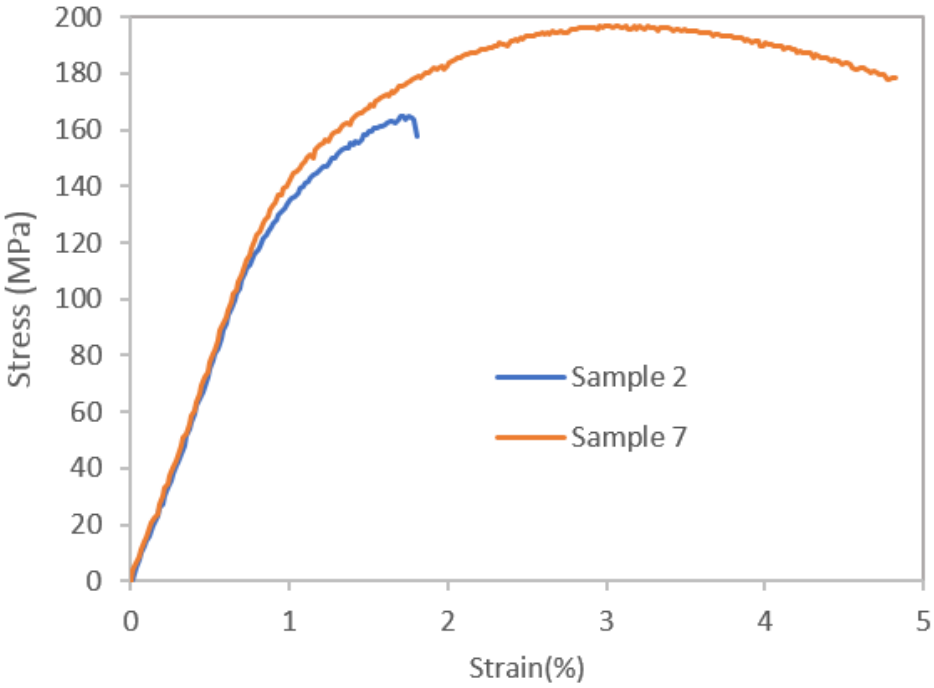


Figure 16. Comparison of tensile test in samples 2 and 7.

4. Conclusions

The present study demonstrates that the mechanical and microstructural characteristics of AA5052-AA6061 dissimilar FSW joints are highly sensitive to process parameters and alloy positioning. Increasing the traverse speed beyond 90 mm/min at a constant rotational speed of 600 rpm resulted in tunnel defects and reduced tensile strength due to insufficient heat input. Conversely, increasing the rotational speed improved material flow and promoted dynamic recrystallization, enhancing both strength and ductility. Among the tested configurations, the highest joint efficiency was achieved when AA5052 was placed on the advancing side, confirming the beneficial influence of alloy placement on plastic deformation behavior. These findings emphasize the importance of optimizing both thermal and mechanical conditions to ensure defect-free welds and superior joint performance in dissimilar aluminum alloy applications.

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Nanotechnology-Based Modifications of Anodes in MFCs: Toward Efficient Wastewater Treatment and Bioelectricity Production: A Comprehensive Review

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ABSTRACT

Water scarcity and the persistent energy crisis represent critical global challenges necessitating the development of environmentally benign and sustainable energy solutions. The accelerating depletion of fossil fuel reserves underscores the urgent need for alternative energy sources that mitigate carbon emissions while preserving ecological integrity. Microbial fuel cells (MFCs) present a promising bioelectrochemical technology, enabling electricity generation through the microbial oxidation of organic and biodegradable substrates present in wastewater. This dual functionality, encompassing both wastewater treatment and energy recovery, has garnered significant scientific interest. This review provides a comprehensive analysis of recent progress in MFC technology, with a particular emphasis on the pivotal role of anode materials in enhancing device performance. Furthermore, the investigation of diverse anode materials and their nanoscale modifications for improved MFC efficiency is explored. This current review also examines the impact of surface modifications and varied anode compositions on power output and system stability. The electrochemical mechanisms underpinning these enhancements are elucidated, offering insights into the economic viability of MFCs. By simultaneously addressing wastewater remediation and energy production, MFCs offer a sustainable pathway toward mitigating pressing energy and environmental concerns.

Keywords : Water scarcity, Energy crisis, wastewater treatment, Energy recovery, Electrochemical mechanisms

1. Introduction

Energy and water stand as two fundamental pillars underpinning both human comfort and societal progress [1]. The widespread utilization of fossil fuels throughout the preceding century has played a pivotal role in facilitating industrial and commercial expansion [2]. However, the confluence of environmental pollution, escalating population figures, the depletion of natural resource reserves, and the phenomenon of global warming has precipitated a dual energy and water scarcity crisis for humanity [3]. Notably, contaminated water harbors a substantial reservoir of organic carbon molecules alongside thermal and chemical energy, resources potentially exploitable for the synthesis of value-added products [4]. In contrast to resource recovery, conventional wastewater treatment systems primarily focus on purification [5]. While activated sludge represents the most prevalent biological treatment modality, membrane bioreactors and sequential batch reactors also serve as viable alternatives [6]. Nevertheless, traditional wastewater treatment and resource recovery paradigms are characterized by elevated operational and maintenance costs, rendering them energy-intensive and economically demanding [7]. Consequently, significant research interest has been directed toward the advancement of environmentally sound methodologies for concurrent wastewater treatment and energy generation,

aiming to address both resource limitations and environmental protection imperatives [8]. Beyond its role in sanitation, energy is indispensable for the sustenance of civilization. Moreover, the increasing sophistication of society amplifies our demand for a reliable and consistent power supply. Alarmingly, energy consumption accounts for approximately 60% of total greenhouse gas emissions [9]. Although energy is generally considered a conserved quantity, its conversion between different forms and across various systems is a fundamental principle [10]. The severity of the energy crisis is further compounded by factors such as the high costs associated with maintaining energy generation infrastructure, the limited availability of clean energy sources, the rising frequency of climate change-induced accidents and natural disasters, geopolitical conflicts, and inadequacies in energy storage technologies [11]. To mitigate these inefficiencies, microbial fuel cells (MFCs) offer a potentially more cost-effective and ecologically benign approach to wastewater treatment [12]. The foundational concept of employing bacteria to oxidize organic compounds for electricity generation was initially proposed in 1911 by the British botanist Potter [13]. Since then, MFCs have attracted considerable attention from the scientific community as a promising avenue for sustainable energy production. By harnessing the organic pollutants present in wastewater, MFCs not only generate electricity but also contribute to water purification [14]. This concept has witnessed a surge of academic interest over the past decade [15, 16]. A critical breakthrough occurred in 1999 with the confirmation that bacteria possess the capability to externally transfer electrons to electrodes, thereby validating Potter's early hypothesis [13]. The subsequent development of this technology has positioned it as a potentially transformative solution for both power generation and wastewater treatment [17]. The performance of MFCs is influenced by several key components, including the microbial inoculum, the electrode material, the chemical substrate serving as fuel, and the proton exchange membrane (PEM). Among these, the electrode material exerts a substantial influence on MFC performance and, consequently, its commercial viability [18]. Numerous investigations have indicated that the anode material, which facilitates the attachment and electron transfer of exoelectrogenic microorganisms, often constitutes a primary bottleneck limiting the power output of MFCs [19]. Ideal anode materials should exhibit a suite of desirable characteristics, including excellent mechanical strength and toughness, robust chemical stability and corrosion resistance, biocompatibility to support microbial communities, a large specific surface area to enhance microbial attachment and electron transfer, high electrical conductivity to minimize internal resistance, and relatively low cost for practical implementation [20].

A Concise History of Bioelectrochemical Systems (BESs)

The genesis of bioelectrochemistry can be traced back to Luigi Galvani, who observed that an electrical spark induced muscle contraction in a deceased frog, a phenomenon he termed "animal electricity" [21, 22]. However, the seminal observation directly relevant to microbial electricity generation was made by Potter in 1911. He demonstrated that microorganisms, specifically yeast and Escherichia coli suspended in a liquid medium with a platinum electrode, could produce electricity [13, 23]. This finding was later corroborated by Cohen in 1931, who achieved a voltage of 35 V at a current of 0.2 mA utilizing a stacked bacterial fuel cell system [13, 24].

Despite these foundational studies, MFC technology did not garner substantial attention until 1963. An initial surge of interest was sparked by NASA's proposal to employ MFCs for converting human waste into energy during space missions [25]. Nevertheless, this initial momentum waned as subsequent proposed applications, such as powering biosensors or self-sustaining robots, lacked well-defined objectives [26]. It was only later that a renewed and significant wave of research emerged, driven by the discovery of more cost-effective materials and a deeper understanding of the fundamental bioelectrochemical mechanisms underlying the technology [27]. Recent research has predominantly focused on the anode side of MFCs, with the cathode side primarily considered in the context of the oxygen reduction reaction [28]. As research into MFCs progressed, exploring diverse microbial interactions, potential electrochemical reactions, and the production of high-value products, the concept expanded, giving rise to the broader field of Microbial Electrochemical Systems (MESs) or Bioelectrochemical Systems (BESs) [29].

Classification of BESs Based on Catalyst Type

Bioelectrochemical Systems (BESs) encompass a range of biotechnology-driven devices designed for the production of valuable compounds and electricity. A primary classification of these technologies is based on the type of catalyst employed, broadly dividing them into two categories:

1. Enzyme-catalyzed BESs: These systems utilize enzymes as biocatalysts to facilitate electrochemical reactions.
2. Microorganism-catalyzed BESs: These systems harness the metabolic activity of microorganisms to drive electrochemical processes [30].

Within the realm of microorganism-catalyzed BESs, a significant category known as Microbial Electrochemical Systems (MESs) exists. Figure 1 also shows a general summary of the methods.

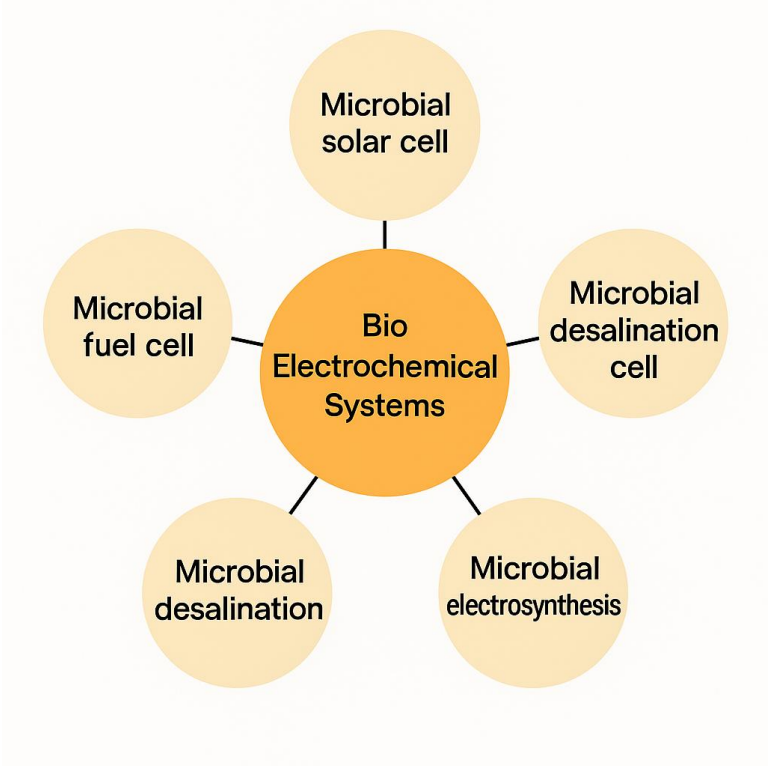

Figure 1- An overview of various types of BESs.

Microbial Electrochemical Systems (MESs)

MESs can be further categorized into three main types:

- Microbial Fuel Cells (MFCs): In MFCs, the oxidation of a substrate in the anode compartment leads to the transfer of electrons to the cathode [31] (Fig. 1). Notably, many MFCs can generate bioelectricity by utilizing diverse carbon-rich wastewater streams as substrates, simultaneously achieving pollution reduction and energy generation due to the rapid biodegradability of these substrates [32].
- Microbial Electrolysis Cells (MECs)
- Microbial Desalination Cells (MDCs)

Beyond these primary categories, other variations of MESs exist, including:

- Microbial Solar Cells (MSCs) [33]
- Plant Microbial Fuel Cells (PMFCs) [34]

Enzymatic Electrochemical Systems (EESs)

In Enzymatic Electrochemical Systems (EESs), enzyme electrodes serve as the interface for external electron donation or acceptance. These systems are characterized by relying solely on enzymatic reactions with a defined electron transfer kinetic potential. 1 Consequently, EESs are frequently employed in in vitro investigations aimed at elucidating electron transfer mechanisms [35]. Utilizing electrochemical techniques to study biological electron and ion transfer offers exceptional control and precision, making EESs a potentially cost-effective and readily accessible approach for evaluating enzyme reaction kinetics [36]. For instance, when NADH was immobilized on an electrode as the sole electron acceptor, in vivo electron and proton transfer processes could be observed [30]. However, it's important to note that the methodologies for efficient electron transmission and overall product generation within EESs are still in the early stages of development.

This statement highlights the innovative and versatile nature of microbial fuel cells (MFCs), a technology recognized for its cost-effectiveness, sustainability, and environmental benefits [38]. As a form of sustainable energy production, MFCs uniquely integrate bioelectricity generation with wastewater treatment by harnessing the microbial oxidation of organic compounds [24].

A typical MFC comprises one or two chambers separated by a membrane. The anode and cathode electrodes reside in distinct compartments filled with an aqueous solution, and the membrane prevents electrolyte diffusion between these compartments [35] The anode chamber houses the anode (positive electrode), while the cathode chamber contains the cathode (negative electrode). The solutions within these chambers are termed the anolyte and catholyte, respectively. An external circuit connects the cathode and anode, enabling electron flow and, consequently, electric current production [33]. Protons migrate through the proton exchange membrane (PEM) to the cathode, while electrons travel from the anode to the cathode via the external circuit. The difference in redox potential between the anodic and cathodic chambers drives this electron flow. Within the anode chamber, bacteria oxidize chemical or organic waste, generating protons and electrons, which are crucial to the breakdown of organic compounds [25]. The anodic reaction is represented by Equation (1):

$$n, CH2O + n, H2O \longrightarrow n, CO2 + 4n, e - +4n, H + \quad (1)$$

Oxidative conditions are established in the cathode chamber by the introduction of oxygen. Electrons and protons are consumed in the cathode compartment. The continuous flow of electrons ultimately produces electricity. In MFCs, oxygen is commonly referred to as the electron acceptor in cathodic reactions, as shown in Equations (2) and (3):

$$n, O2 + 4n, e - +4n, H+ \longrightarrow 2n, H2O \quad (2)$$

$$n, O2 + 2n, H+ \longrightarrow n, H2O2 \quad (3)$$

The overall reaction in an MFC is described by Equation (4):

$$n, CH2O + n, O2 \longrightarrow n, CO2 + n, H2O + biomass + bioelectricity \quad (4)$$

The anode and cathode are critical components, and their material composition, electrical conductivity, biocompatibility, surface area, and non-toxicity to bacteria significantly influence MFC performance. the MFC's overall performance [25]. These elements play a vital role in electron transfer as well as in the efficiency of oxidation and reduction processes of organic matter, ultimately influencing the generation of electric power [25]. The PEM is crucial for the optimal operation of the MFC. The choice of membrane material and pore size is critical, as these factors directly influence proton transfer and reduce oxygen transport to the cathode [25].

MFCs are bio-electrochemical systems with an anaerobic anode chamber and an aerobic cathode chamber, separated by a PEM or salt bridge. Microorganisms in the MFC oxidize a substrate, producing electrons. These electrons are captured by the anode electrode and move to the cathode via an external wire. Protons diffuse across the PEM, and at the cathode, they combine with electrons and oxygen to produce water [26].

Microbes that can exchange electrons with BES electrodes have specific biological characteristics or produce metabolites in response to environmental factors and their genetic makeup [27]. Geobacter and

Shewanella sp. have been thoroughly investigated for their EET, which occurs through two main routes: direct and indirect [26].

Direct Electron Transfer (DET)

In DET, microbes transfer electrons directly to the electrode surface without a mediator. This is possible for bacterial species that respire near the electrode surface and have exposed c-type cytochromes in their outer cell membrane [50]. Examples of bacteria with this mechanism include Enterococcus gallinarum, Shewanella putrefaciens, Geobacter sulfurreducens, and Geobacter metallireducens [26]. Approximately 111 genes in Geobacter and 42 genes in Shewanella are related to c-type cytochromes [10].

Indirect Electron Transfer (IET)

As biofilm forms at the anode surface, EAB spread away from the electrode surface, making electron transfer more difficult. IET is accomplished by creating a mediator or shuttle. Redox mediators can be supplied externally or secreted by microbes. Artificial mediators such as thionine, phenothiazines, neutral red, phenoxazines, and benzyl viologen have been added to systems to overcome this limitation [15]. Some bacteria secrete mediators like quinone and flavin, which function as electron shuttles [20]. Mediators work well when the electroactive microbe is at the outermost layer of the EAB or farthest from the electrode in a planktonic culture. Nanowires, cytochromes, and mediators maintain the conductive nature of EAB [18].

Formation of EABF

When microbes adhere to biotic or abiotic surfaces, they create a microbial aggregation membrane, or biofilm. This biofilm acts as "protective clothing," allowing bacteria to tolerate harsh conditions such as ultraviolet radiation, extreme pH, extreme temperature, high salinity, high pressure, starvation, and antibiotics. Biofilm is a self-defense mechanism for microbial growth [22], and its three-dimensional structure provides bacteria with a built-in barrier and protective layer [25].

The production of a three-dimensional biofilm structure involves multiple phases: (1) reversible attachment, (2) irreversible adhesion, (3) initial biofilm structure development through the generation of tiny colonies, (4) biofilm maturation, and (5) dispersion, as shown in Fig. 2 [30]. Using organic molecules (such as proteins, lipids, polysaccharides, and fatty acids) or inorganic substances (like water and inorganic salts), bacteria start the process of producing a biofilm by forming a suitable surface layer [30]. A mixed structure of extracellular polymers, either in single or combination populations, then embeds this biofilm [27]. Once bacteria have attached to a biotic or abiotic substance, they communicate with one another through an extracellular signaling mechanism based on quorum sensing (QS).

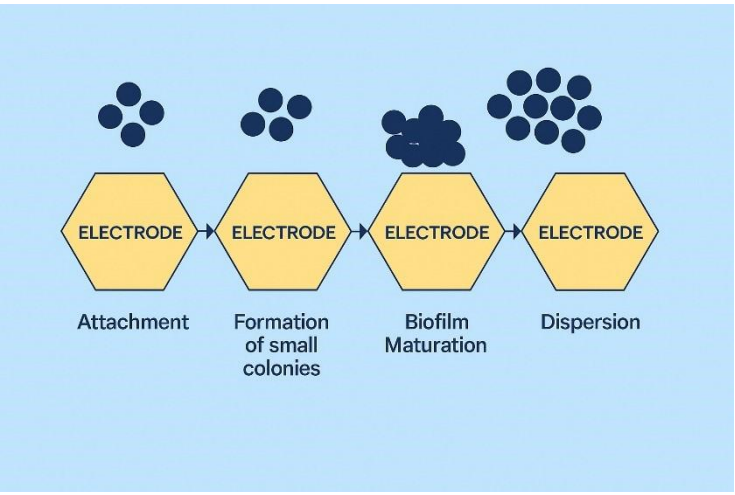

Figure 2.The five fundamental steps that result in the creation and growth of biofilm.

Electrochemical Impedance Spectroscopy (EIS)

EIS is an efficient and non-destructive way to study the bio-electrochemical processes of MFC [15]. Electrochemical impedance spectroscopy examines different electrochemical processes at different frequencies. By placing a small, variable-frequency sinusoidal alternating (AC) potential on top of a direct current (DC) potential, the amount of current flowing through the cell may be determined. A pseudolinear trend of the impedance is obtained for the generally non-linear electrochemical systems by adding a small AC potential, usually between 1 and 10 mV [10]. Essentially, this technique uses two electrodes to identify variations in the solution resistance caused by byproducts of microbial metabolism [10]. However, EIS can change as a result of microbial metabolism and microbial cells adhering to the working electron (WE) [9].**Recent advancements in nanotechnology applied in the modification of MFCs anodes**

Decorating the interface between anodes and exoelectrogens is necessary; carbon-based nanomaterials are commonly utilized. They not only possess the advantages of conventional carbon materials but also display a high surface area, which is beneficial for bacteria attachment and increase the number of contacting active sites for EET [18].

Carbon nanofibers (CNFs) and Carbon Nanospheres (CNs)

Organic waste and glucose are two examples of natural and recyclable materials that are frequently used in the manufacturing of high-performance CNFs and CNs [19]. By carbonizing and activating organic matter at high temperatures, a solid phase is created that produces nano-spheres with consistent diameters, improved appearance, and a larger surface area. In addition, in long-term operation, the produced nanosphere shows good electrical conductivity and biocompatibility [32]. CNs improved bacterial adhesion active sites resulted in higher electron transfer rates and a notable boost in energy density, indicating that their inexpensive cost may make them useful in real-world applications [32].

Nanofiber technology, which has a number of benefits over conventional electrode materials, is being used to advance the development of MFCs. Composites, polymers, metals, and ceramics are some of the materials that can be used to create nanofibers, which are extremely thin fibers with diameters between 1 and 100 nm [32]. Nanofibers can be used as electrode materials in MFCs because of their porosity, small diameter, and high surface area-to-volume ratio. Because there are more microbes adhering to the electrode, performance improves . Nanofiber’s small diameter makes it easier for microorganisms to reach the electrode surface, which enhances their metabolic activity and increases energy production. The growth and metabolism of microorganisms depend on the transport of nutrients and oxygen, which is made easier by the high porosity of nanofiber [32]. Furthermore, some nanofiber materials—such as graphene (Gr) and CNTs—have high electrical conductivity, which makes it easier for electrons to move between the microbes and the electrode and improves energy production .When conductive nanocomposite was added to the anode of MFCs, the power density increased by 1.8 times in comparison to commercial graphite felt. Carbon nanofiber's influence on MFCs stems from both its adoption qualities and conductivity. The conductive carbon nanofiber can be used to improve extracellular electron transport and bacterial adhesion at the same time. It is worth noting that it is suggested that quantum dots be used more in purifying water sources, as Ashkani et al. have pointed out in their research [36].

Carbon nanotubes (CNTs)

Researchers and industry professionals have widely employed CNTs in a variety of cutting-edge applications because of their remarkable mechanical, thermal, and electrical characteristics, whether in their standalone or reinforced composite forms. CNTs’ surface activity can be increased through physical, chemical, or photochemical modification to improve their qualities for certain uses. This surface activity enhancement of surface-modified carbon nanotubes (SM-CNTs) has been used by the researchers to meet a number of their research objectives [19]. Photocatalysts, electrocatalysts, and biocatalysts on CNTs can be stabilized for photochemical and electrochemical applications through surface modification, as evidenced by their dispersion stability in reaction media. SM-CNTs are more compatible with electrolytic membranes and coatings than unmodified CNTs. The performance of electrolyte membranes and electrodes can be improved by using SM-CNTs, which is a promising study field for the development of energy devices. A variety of fuel cells, including microbial, enzymatic, and high-temperature fuel cells, use

SM-CNTs to provide clean energy that potentially power the planet. By employing SM-CNTs to catalyze anodic and cathodic electrode processes and enhance conductivity, electrolyte membrane performance can be enhanced [32].

Graphene nanomaterials

Because of its good catalytic activity, high electron mobility, and acceptable biocompatibility, Gr, the building block of other graphite materials, is a suitable choice for an active anode-enhancing material [22]. This comprises Gr and its compounds, including reduced graphene oxide (rGO), graphene oxide (GO), single/multi-layered graphene, and hybrid nanocomposites .Different graphene-based nanocomposites have been applied in anode material in MFC applications.

The remarkable 2D-carbonaceous electrode nanomaterial such as Gr and CNTs have been used in many different applications because of their improved electrical conductivity, excellent electrochemical stability, and superior biocompatibility. In addition, CNTs made on Gr serve as reliable conducting channels between electrodes and the relevant components [33].

Metal based nanomaterials

Although metals are more conductive than carbon, their widespread use is limited by their corrosive properties. Within MFC, nanostructured metal materials are currently employed as anodes due to their superior conductivity, catalytic activity, and biocompatibility. Between the bacteria and the anode, to enhance the anode, nanoparticles act as a link for electron transport. There are active places for the anode's bacterial growth, which raises the rates at which energy is generated [17].

Manganese oxide (MnO2) nanoparticles

MnO_2 has garnered a lot of attention because of their excellent catalytic qualities in an electrochemical reaction system, high stability, low cost, and varied oxidation states. Alkaline and rechargeable batteries, sensors, supercapacitors, wastewater treatment, and catalysis have all made use of these fascinating composites [17]. As anode materials for energy conversion and storage device systems, they have also garnered a lot of interest. Since the sizes, phases, and characteristics of nanomaterials greatly affect their qualities and uses, a number of innovative and efficient methods have been developed to create MnO_2 nanoparticles with a variety of shapes and superior qualities [19].

Iron oxide (Fe_2O_3) nanomaterials

By enhancing electrical conductivity and promoting microbial activity, Fe2O3 raises MFC power production. Because of its ability to enhance the anode's surface structure and produce electrical energy in the MFC, Fe2O3 is a material that is appealing for anode electrode modification. According to studies, adding Fe2O3 to the anode electrode improves the adhesion of microbes by changing the surface from smooth to rough . In addition, because of the hydrogen link those forms between the oxygen atoms of Fe2O3 and the water molecule, covering the hydrophobic carbon surface with Fe2O3 can hydrophilize it . This material is a good choice because of its low cost, chemical stability, and accessibility.

In MFC configurations, it is commonly used as a modifier due to type C cytochromes (OmcA and MtrC) are strongly attracted to insoluble Fe2O , which affects the enhanced electron transport. According to studies, the percentage of electroactive bacteria on the anode, including Pseudomonas and Geobacter, increases when Fe(III) oxide is present [19].

Titanium oxide (TiO_2) nanomaterials

In comparison to traditional graphite and spongy materials, TiO2 nanoparticles and carbon-assembled core–shell nanoparticles from egg white protein were used to build the anode's capacitive layer, which produced more electricity [25]. Improved electrochemical activity and synergistic effects with carbon composite nanoparticles produced from egg white protein and TiO2 were responsible for the increased power output. These nanomaterials had a high specific surface area and were highly biocompatible. In Escherichia coli MFCs, Qiao et al. have demonstrated how to produce a special mesoporous TiO2-nanostructured polyaniline (PANI) hybrid and employ it as the anode [25].

Future scopes of MFCs

To reduce the losses brought on by activation, ohmic, and concentration overpotentials, low power densities in MFC operation must be explored . Optimizing the existing designs is one way to achieve this [9]. Targeting losses brought on by unnecessary chemical processes is also crucial. Examples of these include the direct oxidation of fuel by O2 passage into the anodic chamber or detrimental microbial metabolic activity [15]. The volumetric capacity of the system must be raised, nonetheless, without resulting in internal energy losses. Through electrode surface modification and the use of active catalyst coating, improved electron transport mechanisms between the electrode and the biocatalyst are being studied. Another crucial area that must be taken into account for the ongoing development of the MFC is mathematical modeling [33]. This helps to integrate our understanding of MFCs and their operations, pinpoint the variables influencing the generation of power, and provide guidance for scaling-up methods . The primary materials used in the electrodes and membranes of MFCs must be more affordable and have a longer lifespan for the technology to compete with other sustainable waste-to-energy options. Mass transfer to and from the electrodes can be increased by altering the electrodes with various nanocomposite materials.

Conclusion

Production of energy and treatment of wastewater are two of the most important worldwide issues that MFCs provide as a promising green technology. Through the utilization of electroactive microorganisms' metabolic processes, MFCs potentially offer a sustainable solution for converting organic waste into bioelectricity while simultaneously purifying wastewater. The performance of MFCs is greatly influenced by the anode material selection, and the incorporation of nanomaterials such metal oxides, graphene, and CNTs has demonstrated considerable promise in improving electron transport, microbial adhesion, and overall efficiency. This review highlights the advancements in anode modifications, emphasizing how these nanoscale improvements contribute to both increased power output and improved wastewater treatment efficiency. Moreover, MFCs' ability to reduce pollutants, such as COD and other organic contaminants, positions them as a viable alternative for sustainable energy production and environmental remediation. However, challenges remain in scaling up MFC technology for commercial applications, particularly in terms of cost, system stability, and long-term performance. Future research should focus on improving material sustainability, reducing system costs, and optimizing design configurations to enhance power generation and treatment efficiency on an industrial scale. With continued advancements in nanotechnology and bioelectrochemical systems, MFCs have the potential to play a key role in the global transition to cleaner energy and environmentally friendly wastewater treatment solutions. In addition, the creation of biofilms through genetic engineering and synthetic biology has recently drawn the interest of researchers who hope to increase the efficiency of MFCs by improving electron transfer, energy recovery, biofilm growth, and metabolic efficiency.

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Development of FMEA method for analyzing process risks in manufacturing parts using selective laser melting

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ABSTRACT

Selective laser melting is an additive manufacturing method that plays an effective role in the production of advanced parts in various industries. This method has risks that can be identified and analyzed by the FMEA method. The systematic FMEA method is one of the most popular methods in organizational, manufacturing, and logistics risk management. In the present study, focusing on three parts with different manufacturing complexities, manufacturing risks were identified, and risk priority scores were analyzed. The results showed that the range of risk priority scores is different and varies from a minimum of 8 to more than 120. The results also showed that a higher number of risks does not necessarily lead to a higher average risk priority number and that sensitivity in the manufacturing process may reduce risks. Also, greater dimensional complexity in parts can lead to an increase in the average risk priority number.

Keywords : FMEA Method, Risk Management, Risk Priority Number, manufacturing

1. Introduction

In general, failure mode and effect analysis (FMEA) is a systematic tool suitable for predicting failure modes and analyzing their effects [1]. Using this efficient tool, it is possible to identify and prioritize potential failure modes in a system, process, product and service, define and determine the necessary measures to eliminate or reduce the occurrence of potential failure modes, and finally, record the results of the analysis with the aim of providing a complete reference for solving future problems. In general, the analysis can be divided into two general types. These two types are potential failure modes and their analysis, and the second type is critical failure analysis [2]. According to the references, this system is divided into four general types. This division includes functional, design, process and logistics potential failure mode analysis [3]. It should be noted that logistics potential failure mode analysis has recently become popular in some organizations.

The Failure Mode and Effects Analysis (FMEA) method offers several significant advantages in quality management by systematically identifying potential failure modes in a process or product and assessing their impact on overall performance. One of its primary benefits is its proactive approach, allowing organizations to anticipate and mitigate risks before they result in defects or failures, thereby enhancing product reliability. FMEA fosters cross-functional collaboration, as it involves input from various teams, leading to a more comprehensive understanding of potential issues. Additionally, it prioritizes risks based on their severity, occurrence, and detection, enabling efficient allocation of resources to address the most critical concerns first. By implementing FMEA, organizations can improve customer satisfaction, reduce costs associated with recalls and warranty claims, and ultimately strengthen their commitment to continuous improvement in quality management [4, 5].

It is necessary to introduce the basic concepts of severity (S), occurrence (O), and detection (D) in the form of a general introduction. Severity is the amount of impact that will be imposed on the customer or organization during the design phase. In the references, various values have been determined for this number, one of the most appropriate values is between one and five. In the definition of occurrence, we

can state that the probability of an event occurring is called occurrence. Its value, similar to severity, can be different. Detection is also intended to be able to identify problems and failure modes, and its appropriate value is a number between 1 and 10 or 1 and 5 [6]. It is also necessary to state the concept of risk priority score. The risk priority number, or RPN can be calculated from the following equation.

$RPN = S \times O \times D$

If the risk priority number values are higher than the allowable limit, it is necessary to define a relevant corrective action in accordance with the standards of each organization or customer. Additionally, while defining the actions, the necessary follow-ups should be conducted for their implementation.

In this study, we chose to use the FMEA method to assess the risks associated with the selective laser melting process used in manufacturing engineering parts. As an additive manufacturing technique, selective laser melting plays a vital role in producing various components, including automotive parts [7], dental implants [8], and more[9-12]. By reviewing multiple sources, possible risks are identified, and then, through logical analysis, the importance of each risk in this process is determined. The study is considered interdisciplinary and highlights the significant connection between different fields.

2. Materials & Method

In the present study, in order to develop the FMEA method, several products manufactured by selective laser melting (SLM) method were examined. This examination included design, manufacturing process and post-manufacturing. Then, according to the criteria mentioned in Tables 1 to 3, various defects and their effects on the performance of the part and the customer were examined. Detailed charts and tables were used to analyze the information and data. Finally, for each part manufactured by SLM method, the average risk priority number was calculated to show which part is more sensitive in the design. The selected pieces were as follows:

1. Dental implants made using SLM,
2. Car ABS rings made using SLM,
3. Car engine connecting rods made using SLM.

Figure 1 (a-c) shows a picture of every part checked in this research.

Table 1- Impact Score Severity (S)

Effect	Effect on customer	Effect on Org.	Score
Very Severe	Design failure and severe loss to the organization	organization Irreversible costs	10
Severe	Creating problems in scheduling design work	implementation of many parts of the design	8
Moderate	Design changes and corrections	Weak design defects	6
Low Severity	Minor design changes and corrections	Very minor design defects	4
Very low Severity	No inconsistencies observed	No effect observed	2

Table 2- Proposed criteria for determining the occurrence number (O)

Failure probability	Failure rate	Score
Very High	80 – 100 %	10
High	60 – 80 %	8
Medium	40 – 60 %	6
Low	20 – 40 %	4
Very Low	0 – 20 %	2

Table 3- Suggested criteria for determining the detection number (D)

Detection possibility	methods	Recommended range of detection	Score
100 % Impossible	Undetectable	Cannot be detected or no control exists	5
Impossible	Controls probably do not detect	. Control is only possible through data acquisition	4
Low	Controls have a moderate chance	Control is possible through data acquisition and software	3
Possible	Controls probably detect	Fault detection from control methods	2
100% Possible	100% Detectable	Fault detection is completely possible	1

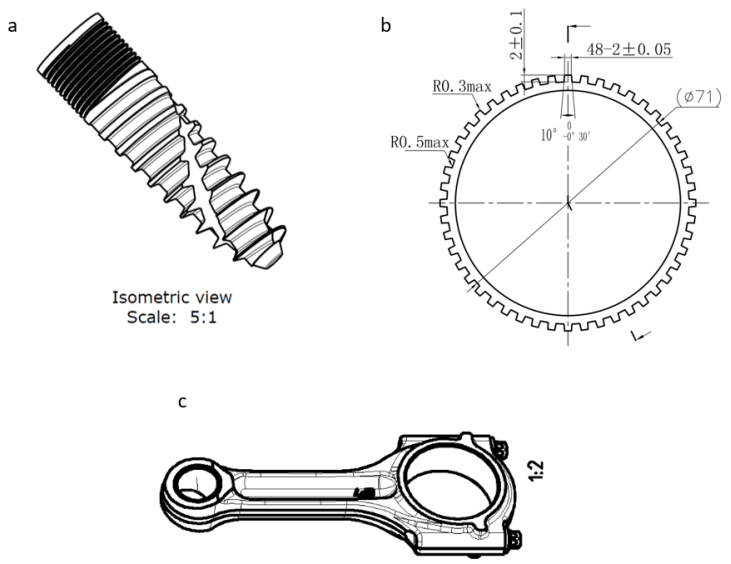

Figure 1- Parts manufactured using the selective laser melting method that were examined in the present study

3. Results and Discussion

Figure 2 shows the number of risks identified for each component. Table 1 also lists the risks identified. As is clear, dental implants have more risks during the manufacturing process, and their manufacturing process is more complex.

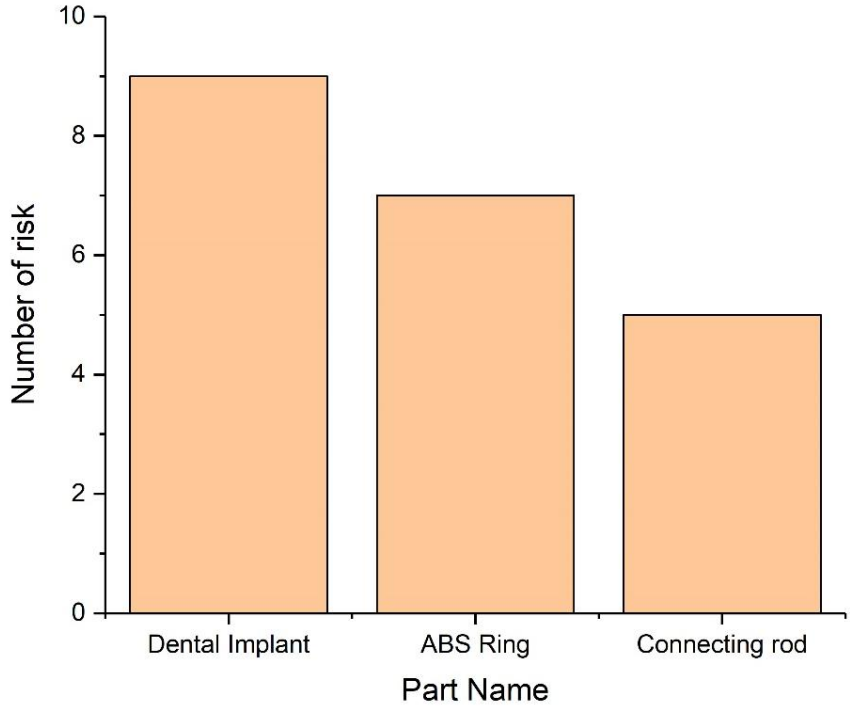

Figure 2- Risks identified in the manufacturing process of various parts.

Table 4- Various risks of components after reviewing the manufacturing process

Dental Implant	ABS Ring	Connecting Rod
Poor quality of the powder used	Poor quality of the powder used	Inappropriate large diameter of connecting rod
Uneven structure of the part	Not forming the ring teeth	Inappropriate small diameter of connecting rod
Failure to adjust the laser power	Not adjusting the laser power	Poor quality and uneven powder
Failure to adjust the laser distance	Not adjusting the laser distance	Non-melting and uneven structure
Power outage during the process	Breaking the ring teeth	Human error
Layer not melting	Sharpness of the ring teeth	---
Error in transporting the part	Human error	---
Inappropriate neutral gas used	---	---
Human error	---	---

Tables 5 to 7 show the analysis of various risks and the calculation of the risk priority score. As can be seen, although the number of risks of dental implants are higher, the average risk priority number for the ABS rim component has increased. This is important in two ways. First, the dental implant component and the ABS rim are from two different industries, medical and automotive, and according to our findings, the precision in the medical industry is higher and therefore the risk is lower. On the other hand, according to Figure 1, the presence of teeth on the rim is considered one of the manufacturing limitations in SLM technology and this has led to an increase in the average risk priority score. This shows that more precision should be used in the design of automotive parts in this manufacturing technology.

Table 5- R.P.N calculation for Dental implant manufactured by SLM Technology.

Dental Implant	S	O	D	R.P.N
Poor quality of the powder used	8	4	2	64
Uneven structure of the part	8	2	2	32
Failure to adjust the laser power	6	4	1	24
Failure to adjust the laser distance	4	4	2	32
Power outage during the process	4	2	2	16
Layer not melting	8	8	2	128
Error in transporting the part	4	2	1	8
Inappropriate neutral gas used	4	4	1	16

Human error	6	6	2	72
Average	---	---	---	43.5

Table 6- R.P.N calculation for ABS Ring manufactured by SLM Technology.

ABS Ring	S	O	D	R.P.N
Poor quality of the powder used	6	6	1	36
Not forming the ring teeth	10	6	2	120
Not adjusting the laser power	6	6	1	36
Not adjusting the laser distance	4	2	1	8
Breaking the ring teeth	10	2	3	60
Sharpness of the ring teeth	8	2	2	32
Human error	6	6	2	72
Average	---	---	---	52

Table 7- R.P.N calculation for connecting Rod manufactured by SLM Technology.

Dental Implant	S	O	D	R.P.N
Inappropriate large diameter of connecting rod	4	4	2	32
Inappropriate small diameter of connecting rod	4	2	2	16
Poor quality and uneven powder	4	6	2	48
Non-melting and uneven structure	4	2	1	8
Human error	4	2	1	8
Average	---	---	---	22.4

4. Conclusion

The potential FMEA method is considered a suitable method for identifying process risks and can play an effective role in increasing quality. In the present study, an attempt was made to show the relationship between different engineering processes and the results showed that this method can be effective in identifying risks. The results showed that advancedness and sensitivity in production processes can reduce

process risks and, on the other hand, greater complexity of manufacturing increases process risks. It is suggested that in the future, researchers should focus more on developing risk management and identification systems in advanced manufacturing processes.

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Investigating the effect of using an electric power steering system in a vehicle and its role in reducing fuel consumption

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ABSTRACT

The power steering system is one of the car's components responsible for steering the vehicle. The power steering system is a safety component that has been produced in various types over the past years and used on various cars. The latest generation of power steering is electric power steering (EPS), which has advantages over the previous generation, hydraulic power steering (HPS). One of the main advantages of EPS over previous generations is the elimination of the hydraulic pump assembly, resulting in reduced fuel consumption due to the lack of use of engine output power. It should be noted that other factors, such as the weight of components, are also effective in reducing fuel consumption. In the present study, an EPS system was designed and installed on a car in real sample. Then, under the same conditions, the distance traveled by the car and its fuel consumption were measured when two types of hydraulic and electric steering systems were installed on the car under the same conditions. The results showed that after traveling a distance of 100 kilometers, the vehicle's fuel consumption was reported to be 7.7 liters, which decreased to 6.7 liters after installing the EPS system and removing the hydraulic pump system, which indicates a 6.2 % reduction in fuel consumption and the positive effects of installing EPS in today's vehicles. The reason for this reduction in fuel consumption can also be attributed to weight reduction, removal of the hydraulic pump, and maintenance of engine power.

Keywords : Electronic Power Steering, Hydraulic Power Steering, Fuel consumption, Automotive Industry

1. Introduction

Electronic Power Steering (EPS) and Hydraulic Power Steering (HPS) are two common systems used in vehicles to assist drivers in steering, making it easier to turn the steering wheel. The EPS uses electric motors to provide steering assistance. The system relies on sensors that detect the driver's steering input and the vehicle's speed. Based on this information, the electric motor adjusts the amount of assistance required. Electronic Power Steering (EPS) is characterized by several key properties that enhance vehicle performance and driver comfort. Primarily, it utilizes electric motors to provide precise steering assistance based on real-time data from sensors that monitor the driver's inputs and vehicle dynamics, allowing for a highly responsive steering experience. One of its standout features is its ability to adjust the level of assistance based on vehicle speed; for instance, it offers more help at lower speeds for easier maneuvering and less assistance at higher speeds for improved stability. EPS systems are also lighter than traditional hydraulic systems, contributing to better fuel efficiency and reduced overall vehicle weight. Additionally, they require minimal maintenance as there are fewer components prone to wear and tear,

and they can be programmed for customizable driving preferences. This combination of efficiency, responsiveness, and adaptability makes EPS a popular choice in modern vehicles [1-6].

2. Materials & Method

In order to conduct the present study, a prototype of an EPS was first designed and manufactured. Figure 1 shows the final design of the prototype of the EPS. Then, a specific vehicle was selected. The vehicle conditions are listed in Table 1. In this vehicle, the hydraulic steering box system was first installed, and the necessary tests were performed. Then, by making the necessary changes to the ECU and electrical systems of the vehicle, the electric steering box was installed, and the same tests were repeated.

In order to investigate the changes, a distance of 100 kilometers was considered under the same conditions after installing both steering boxes. In both tests, a driver was used, and the vehicle speed was considered equal to 100 km/h using the cruise control system. The results were measured using the necessary equipment, and the fuel consumption was measured after installing both systems.

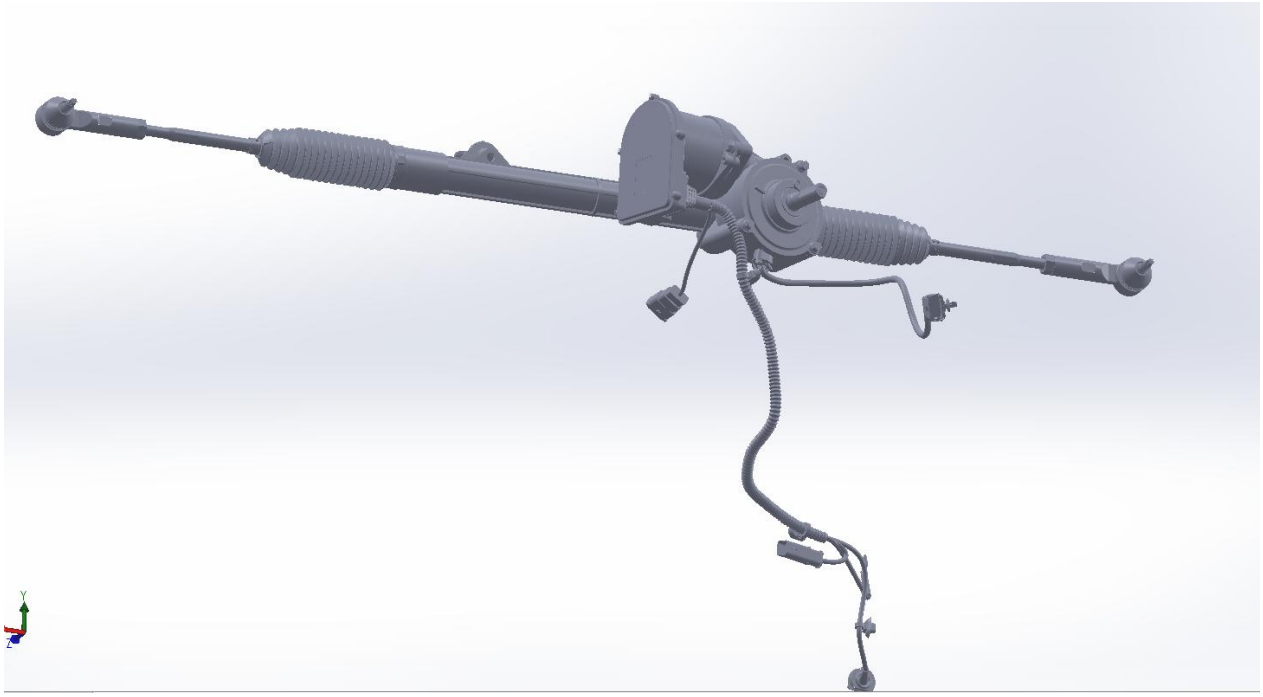

Figure 1- Schematic of Electronic Power Steering used in this research.

Figure 2- Installing the HPS in the cradle before installing it in the car

Table 1- Characteristics of the vehicle used in the research

Engine Power	115 horsepower
Weight of the vehicle with a full tank of fuel	1180 Kg
Engine Torque	135 N.m
Maximum vehicle speed in research	105 Km/h
Number of passengers	2
Vehicle length	4500 mm
Environment Temperature	28 degrees C
Wind speed	7 Km/h

3. Results and Discussion

The power required for the hydraulic pump is supplied by the vehicle's combustion engine. On average, according to various references [7], the power required for the hydraulic pump consumes about 5 horsepower of the combustion engine's power. Due to the free-center operation of the hydraulic pump, the pump is constantly active and this amount of engine power is constantly taken, which will lead to fuel consumption. Thermal energy is measured using the BTU unit, where one horsepower is equivalent to 4.42 BTU per minute. According to technical references [8, 9], to produce energy equivalent to 300 horsepower per hour, 24 gallons per hour or equivalent to 64 liters of fuel are required.

Considering what has been stated, based on the calculations mentioned in the continuation of the discussion, the combustion engine of the aforementioned vehicle with a power of 115 horsepower will require 24.5 liters of fuel per hour of operation (equivalent to 9.2 gallons). But if 5 horsepower is saved from the engine's power, it is equivalent to the engine operating at a power equivalent to 110 horsepower, in which case the vehicle's fuel consumption per hour will be reduced to 23.46 liters (or 8.8 gallons). In this case, the vehicle's consumption will be reduced by about 1 liter per hour, or 4.3 percent.

$$\text{If, HP= 115} \Rightarrow \frac{115}{x} = \frac{300}{64} \Rightarrow x = 24.5 \text{ Litr per Hour}$$

$$\text{If, HP= 110} \Rightarrow \frac{110}{x} = \frac{300}{64} \Rightarrow x = 23.46 \text{ Litr per Hour}$$

According to another type of calculation, the amount of fuel consumed is directly related to the thermal efficiency and the fuel injection rate. If, regardless of the type of hydraulic pump operation, the combustion engine is assumed to need to produce 5 horsepower, then its fuel consumption per hour will be calculated using the following equation, where HP is the engine power (horsepower), TE is the thermal efficiency and is equal to 0.3, FF is the amount of fuel consumed in pounds per hour, and 7.466 is a constant coefficient.

$HP = TE \times FF \times 7.466$

$\Rightarrow 5 = 0.3 \times FF \times 7.466$

$\Rightarrow FF = 2.23$ (Pound per Hour)

= 1.0035 (Lit. per Hour)

As seen in the calculations above, a 5 horsepower engine consumes one liter of fuel per hour, which was also stated in the previous section. Therefore, if the hydraulic pump assembly, which takes this amount of power from the combustion engine, is removed from the assembly, the fuel consumption per hour will decrease by 4.3 percent, which is achieved in the electric power steering assembly.

It should be noted that changes due to weight should not be ignored. In Table 2, the weight of the hydraulic power steering assembly, other accessories, and also a sample of the electric power steering assembly used in most cars in the world today are shown.

As can be seen, the electric power steering assembly is approximately 3350 grams lighter than the hydraulic power steering assembly, which uses kinetic energy to calculate the weight effect. Similar to the previous sections, a speed of 100 km/h or 27.7 m/s is assumed.

$$K=\frac{mV^2}{2} \Rightarrow k=\frac{1196.6\times(27.7)^2}{2} \Rightarrow K=459069/60\ J$$

$$K=\frac{mV^2}{2} \Rightarrow k=\frac{1200\times(27.7)^2}{2} \Rightarrow K=460374\ J$$

$$\Delta K=1304.4\ J$$

According to the above calculations, as can be seen, the difference in kinetic energy is 1304.4 joules per second, which is equivalent to 4695840 joules per hour or 1.74 horsepower per hour. Therefore, if electric power steering is used, due to weight reduction, 1.74 horsepower of engine power is saved, which is equivalent to a 1.52 percent reduction in fuel consumption. As mentioned, due to the elimination of the hydraulic pump, fuel consumption will also be reduced by 4.3 percent, so a total of 5.82 percent of fuel consumption is reduced when electric power steering is used instead of hydraulic steering.

Table 2- EPS and HPS total weight

Electronic power steering (part weights)		Hydraulic power steering (part weights)	
8450 g	Total weight of EPS	7400 g	Total weight of HPS
---	---	2350 g	Hydraulic pump
1000	Other equipment such as wires and ECU	2010 g	Other equipment such as hoses, clamps, etc.
---	---	1000 g	Hydraulic Oil
9400 g	Total	12760 g	Total

4. Conclusion

According to what was stated, by using electric steering instead of hydraulic steering, fuel consumption is reduced by 5.82%. It was also observed using a simulator and practical test that the amount of fuel consumption reduction was reported to be 6.2%. Therefore, the results are categorized as follows:

1. Due to the removal of the hydraulic pump from the vehicle assembly and the elimination of the problem of the pump's free center of operation, 5 horsepower is saved in engine power.

2. Using an EPS instead of a hydraulic steering box reduces fuel consumption in the vehicle by approximately 6% on average.

3. The weight of the vehicle will be approximately 3 kg less when an EPS is used instead of a HPS.

4. It is suggested that researchers conduct extensive research into the use of EPS in heavy vehicles.

5. Acknowledge

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Flexible Resistive Humidity Sensors Based on Graphene Oxide/Silicone Polymer

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ABSTRACT

Humidity detection plays a crucial role in monitoring ambient humidity to maintain comfortable domestic environments and optimize industrial atmospheres. Among the various sensor types, resistive gas sensors are widely used for detecting humidity due to their simple design, cost-effectiveness, and reliable electrical response. Despite their flexibility and lightweight nature, polymers are typically unsuitable for resistive sensors owing to their poor conductivity. To address this limitation, a silicone polymer was blended with graphene oxide (GO) nanosheets, leveraging the latter's oxygenated functional groups to enhance water molecule affinity. A homogeneous, highly porous structure was achieved by casting the polymer-GO suspension onto a sugar template, followed by room-temperature curing. When exposed to humidity levels ranging from 35% to 95%, the composite's electrical current increased linearly from 0.46 to 0.55 µA, demonstrating a robust sensitivity to ambient moisture. These results highlight a promising flexible humidity sensor fabricated via a straightforward and scalable method, making it suitable for wearable and portable applications.

Keywords : Humidity Sensor, GO, Silicone Polymer, Resistive, Flexible.

1. Introduction

Humidity sensing is a fundamental requirement for environmental monitoring, with significant implications for both domestic comfort and industrial process optimization [1]. Humidity sensors can be classified based on their detection mechanisms into capacitive, resistive, optical, piezoelectric, and surface acoustic wave sensors, among others [2]. Resistive humidity sensors are widely used for humidity detection, operating on the principle of resistivity variation in the presence of target gas molecules [3]. These molecules interact physically or chemically with the sensing material, leading to a change in resistivity depending on the nature of the interaction [4].

Since pure insulating polymers are unsuitable for use alone in resistive sensors, conductive additives are incorporated to generate measurable resistive signals [5]. Among various conductive materials, graphene oxide (GO) exhibits exceptional sensitivity to water molecules via physisorption [6]. The oxygen-containing functional groups on GO—such as hydroxyl, epoxy, and carboxyl—enhance its hydrophilicity, thereby improving the water vapor sensitivity of the polymeric composite [7]. This approach ensures optimal interaction between the sensing material and ambient moisture while preserving the structural integrity of the composite.

Porous polymer films are widely used in humidity sensors due to their high surface area, tunable pore structure, and ability to adsorb and desorb water molecules [8]. In such films, surface porosity provides a larger area for water absorption, enhancing humidity sensing sensitivity. Various methods can be employed to introduce porosity, including electrospinning [9], chemical foaming [10], 3D printing [11], and template-based [12] routes. Among these, the latter method has garnered significant attention in previous studies due to its low cost and ease of fabrication.

In this study, we developed a nanocomposite based on a silicone polymer and graphene oxide (GO) nanosheets, fabricated using a straightforward approach. To create a porous nanocomposite film, a sugar cube was used as a sacrificial template, resulting in micrometer-sized pores on the film's surface. When the relative humidity (RH) was increased from 35% to 95%, the current passing through the film rose uniformly from 0.46 to 0.55 µA. Additionally, the sensor exhibited response and recovery times of 1.53 s and 3.19 s, respectively. These outstanding results demonstrate the potential of this lightweight, fast-response humidity sensor for a wide range of applications.

2. Materials and Method

2.1. Preparation of PDMS Foams

To fabricate a porous composite of silicone polymer (RTV2) with GO nanosheets, the following procedure was employed. First, the polymer matrix was prepared by mixing the resin with 3-5 wt% hardener to achieve optimal stiffness and flexibility. Next, a GO suspension (synthesized via the modified Hummers' method as reported in our previous work [13]) was incorporated into the polymer mixture. The composite was then vigorously stirred for 5 minutes to ensure homogeneous dispersion of GO nanosheets.

The homogeneous mixture was cast onto cubic sugar templates in the form of disks with 4 cm in diameter and 5 mm in thickness. Following room-temperature curing of the polymer, the sugar template was removed by immersing the samples in deionized water for 24 hours, resulting in a well-defined porous structure (Figure 1). This facile templating approach yielded a composite material with a highly porous architecture, as confirmed by morphological characterization.

Figure 1. The preperation route of the flexible film.

2.2. Humidity Sensing Tests

To investigate the humidity sensing, a chamber containing an inlet for humidity was fabricated. A conventional humidifier was applied for raising the ambient humidity, while a hygrometer was measuring the RH values close to the silicone polymer-GO film. Figure 2 shows a shematic of the applied humidity sensing setup.

Figure 2. Schematic humidity sensing setup.

2.3. Instruments and Characterization

In order to verify the presensce of the functional groups, FTIR spectroscopy was performed via Thermo Nicolet Avatar. Moreover, Raman spectroscopy was carried out via the TakRam (N1-541, Teksan) under the wavelength of 532 nm. The electrical current passing through the fabrictaed film was measurred under the constant value of 5 V by means of an Autolab potensiostat (AUT71663-PGSTAT 30).

3. Results and Discussion

The existing bonds in the produced nanocomposite was investigated by FTIR analysis. As indicated the peaks on the diagram shown in Figure 3a, the whole peaks are relevant to the silicone polymer, while none of the GO characteristic peaks (Figure 3b) are observable due to its tiny amount. Moreover, the preparation of the GO nanosheets is confirmed by XRD and Raman tests as shown in Figure 3c and d, respectively. The main XRD peak at 11.7° corresponds to the (002) planes of GO nanosheets, while the small peak at 29.9° is relevant to graphite residue as the precursor of GO [14]. D-band and G-band of the prepared GO is also observed in Figure 3d at 1351 and 1593 cm^{-1}, respectively [15].

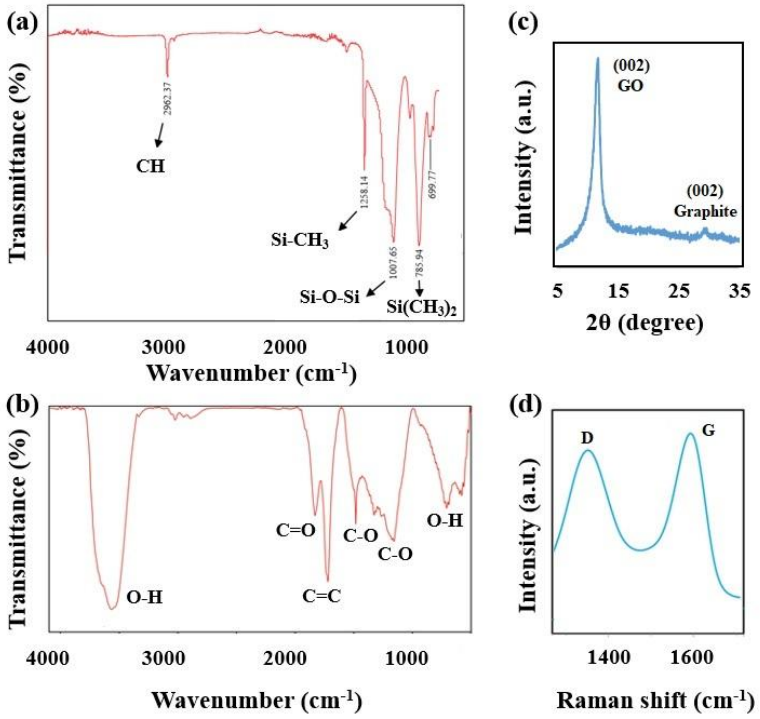

Figure 3. FTIR spectra of Si-GO nanocomposite (a) and GO (b), XRD pattern (c) and Raman spectrum (d) of GO.

To characterize the electrical response of the fabricated sensor to ambient relative humidity (RH) variations, current measurements were conducted under a constant applied voltage of 5 V while systematically increasing RH from 35% to 95%. As shown in Figure 4, the measured current exhibited a linear increase with rising RH values (R^2 = 0.96). Notably, water droplet accumulation on the sensor surface occasionally caused minor response non-uniformities and slight signal fluctuations, as evidenced by localized deviations in the curve [13]. By increasing humidity, a gradual but consistent decrease in resistance was observed. This phenomenon can be attributed to the adsorption of water molecules by the surface functional groups of graphene oxide, leading to increase in the mobility of surface charges [16].

The porous architecture of the composite film substantially enhanced the effective surface area for interaction with ambient water molecules. This structural characteristic facilitated both rapid moisture absorption and the formation of additional conductive pathways through the adsorbed water layers, thereby reducing the overall electrical resistance. Quantitative analysis revealed a linear current increase of 1.5 nA per 1% RH increment, corresponding to a resistance decrease of approximately 30 kΩ/%RH. The linear response suggests stable and reproducible humidity detection across the tested RH range.

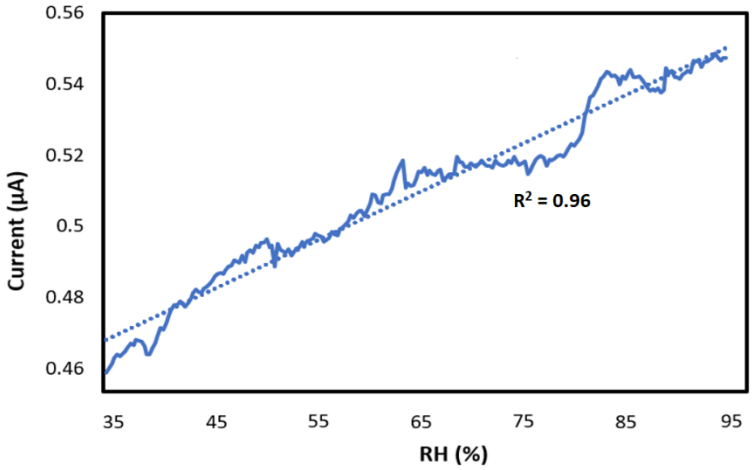

Figure 4. The current response diagram of the fabricated sensor upon RH variations.

The observed humidity response mechanism stems from water vapor interactions with the surface of the sensing material. At low humidity levels, water molecules initially form a chemisorbed monolayer on active sites [17]. As relative humidity increases, subsequent water layers develop through physisorption [18], both on the surface and within the porous network. This multilayer formation establishes proton conduction pathways via hydrogen bonding between water molecules and oxygen-containing functional groups (hydroxyl, epoxy, and carboxyl) on the graphene oxide nanosheets [19]. These interconnected pathways significantly enhance the ionic conductivity, accounting for the observed sensitivity to humidity variations.

To evaluate the sensitivity of the sensor, the current response is defined as $(I-I_0)/I_0 \times 100$, where I and I_0 are the current values at a specific point and the initial stage (RH = 35%), respectively. By converting the gathered data, the maximum response value at RH=95% was 20%. The slope of this diagram is defined as sensitivity which is calculated to be 8 (ΔI/I0%)/(ΔRH%). As the obtained sensitivity is a dimensionless value, it is comparable with other sensors functioning through a different sensing mechanism.

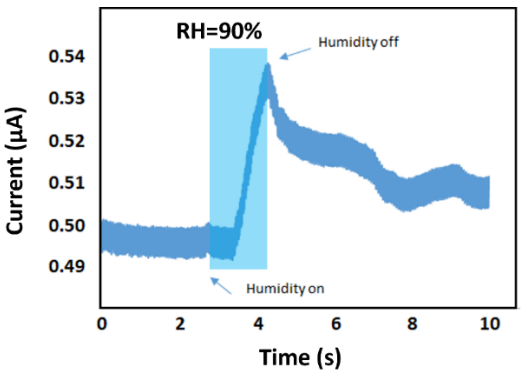

Figure 5. Response and recovery times of the fabricated humidity sensor.

Figure 5 presents the temporal response characteristics of the sensor when exposed to 90% RH and subsequent dry air. The device demonstrates rapid response (1.53 s) and recovery (3.19 s) times, attributable to three key factors: (1) the hydrophilic functional groups (-OH, -COOH) on GO nanosheets that enhance water molecule adsorption through strong electrostatic interactions, (2) the efficient proton conduction pathways established by hydrogen-bonded water networks, and (3) the interconnected

porous architecture that maximizes active surface area while minimizing diffusion path lengths for water molecules.

4. Conclusions

The fabricated sensor exhibited a linear current response, increasing from 0.46 to 0.55 μA across a humidity range of 35% to 95%, demonstrating robust and reproducible sensitivity. This performance, combined with the fast response (1.53 s) and recovery (3.19 s) times, establishes the composite as an outstanding candidate for next-generation flexible sensing applications. These results highlight the potential of the Si-GO as a high-performance, flexible humidity sensor suitable for wearable and portable applications. By leveraging cost-effective materials and an easily scalable fabrication process, this work provides a promising pathway for the development of next-generation humidity-sensing technologies.

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Effect of casting parameters on manufacturing a drive shaft's tripod, A simulation-based study

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ABSTRACT

Nowadays, the development of software simulation plays a key role in the manufacture of various parts, and automotive parts are of great interest. The part studied in the present study is the drive shaft used in the automotive, which plays an important role in the automotive system. In this study, casting simulation was performed to show that the ability to simulate is very important in production. The results showed that using simulation, shrinkage cavities and trapped air can be detected, and important analyses can be performed on the Niyama factor (coefficient), which is very key in the production process.

Keywords : simulation, Tripod, Drive shaft, Niyama factor, Casting.

1. Introduction

One of the oldest methods of metal forming, the casting process has been used to produce products such as arrowheads, shields, and other objects. Casting is widely used due to its flexibility in producing complex shapes and mass production. Various products such as pistons, cylinder heads, engine blocks, wheels, etc. are produced by the casting process. Metal casting is a versatile manufacturing process known to mankind. This process generally involves pouring molten metal into a refractory mold with a cavity of the desired shape and allowing it to solidify. After solidification, the desired metal object is removed from the refractory mold either by breaking the mold or by removing it. The solidified object is called the casting. Casting can produce products from a few grams to several hundred tons and from simple shapes such as watch cases to the most complex parts such as engine blocks. Almost any metal or alloy that can be easily melted can be cast. Casting has different types depending on the material, type of pattern, mold and casting technique, such as sand casting, gravity casting, precision casting, pressure casting, impact casting. To produce cast parts, knowledge is required in the field of mold and pattern preparation, melting and pouring molten metal, solidification and further cooling to room temperature, inspection and quality control. Due to the complex physics and the number of steps required to produce a cast part, the parameters that control the quality of a cast part are very large. The main sources of defects arise from improper part design, feeding system and gating [1]. To overcome these filling-related defects, a properly designed runner and runner system is crucial in producing good quality cast parts by providing uniform and homogeneous filling of the mold [2].

Casting and manufacturing methods used in the automotive industry have advanced significantly over time, improving the performance, durability, and cost-effectiveness of automotive components[3]. Manufacturers have also made every effort to reduce the net weight of their vehicles by using various materials with a high strength-to-weight ratio. Various car parts are being made much stronger than before to meet the high standards set by NCAP. Another casting process is centrifugal casting, which is mainly used for cylindrical parts. There are two basic types of centrifugal casting: horizontal and vertical. The horizontal and vertical types rotate around a horizontal and vertical axis, respectively. The horizontal

types are used to make pipes, tubes, casings, and simple tubular castings. The vertical types are used to make a wide variety of parts such as gear parts, wheels, yokes, brackets, and valve bodies. These types can even produce castings that are not cylindrical or symmetrical. The centrifugal casting process provides a high degree of metallurgical cleanliness and homogeneous microstructures.

Most casting processes solidify from both the inside and outside, so there is a risk of forming mid-wall shrinkage, whereas in centrifugal casting, it solidifies from the outside in, resulting in a part that is free of shrinkage and porosity. Due to centrifugal force, the high-density metal is pushed outwards while at the same time the lower-density components float inwards. Since these lower-density materials such as oxides, sulphides and gases float on the inside, there are no impurities in the casting. Another major advantage of this casting is that it reduces microporosity. One of the limitations of this casting is the limited length to diameter ratio of 2:1. Another challenge that can be faced is the irregular shape of the casting and the cost of making its mould. It is also difficult to cast very small inner diameters using this process [4].

Bhushan Shankar Kamble and Sandeep Madhukar Kadane have attempted is made to optimize the gating system by selecting the advanced ingate definition in die casting operation to overcome air entrapments, shrinkage porosity and smooth filling of mold cavity. The process parameters like component material, metal fill velocity and filling time are considered for optimizing the process. This could help in finding an optimal production method that could guarantee the required mechanical properties [5].

In recent years, with the development and advancement of modern science and technology[6], structural optimization tools and casting simulation have gained significant importance in the automotive industry. The industry is slowly transitioning to a CAE-based design process, as the adoption of CAE simulations has been demonstrated in providing new and inspiring lighter designs with shorter development cycles in recent years. On the other hand, casting simulation finds its application in the later part of the design process, especially by foundries to optimize the casting process by mold filling and solidification simulation [7].

This simulation method is a numerical method for calculating the quality of castings, taking into account mold filling, solidification and cooling, and provides numerical predictions of the mechanical properties of the casting, thermal stresses and distortion. Simulation accurately describes the quality of a casting before production begins. Casting equipment can be designed according to the required properties of the part. This has advantages beyond reducing pre-production sampling, as the accurate layout of the complete casting system also saves energy, materials and tools. The software supports the user in designing parts, determining the melting method and casting methods, up to pattern and mold construction, heat treatment and final finishing. This saves costs throughout the entire casting production path[8]. Casting simulation can be used to investigate the effects of various process conditions such as melt flow, heat transfer, solidification, and molten metal defect formation [9-11]. This technology can also predict the forming quality of castings, thereby reducing the cost of trial castings[12], as defects can be eliminated by visualizing mold filling, solidification, and cooling [13].

This has led to the casting companies starting to use CAE to simulate casting production before analysis. Simulation has helped to predict the location of defects and the degree of analysis of the causes of defects in castings. It has also led to targeted optimization, improving the qualification rate of casting products, and reducing the number of trial mold modifications [6].

Jadao et al. in their article titled “Review of Simulation Based Casting” discuss casting simulation, its importance, types of casting simulation software, applications and a case study on feeder optimization. With casting simulation, the casting process and design can be optimized with minimum effort and time [14].

Hong Xu et al. simulated the die casting process of the right crankcase cover of ADC12 aluminum alloy and investigated the effects of pouring temperature, initial mold temperature and injection speed on the filling and solidification process of the casting of the right crankcase cover of ADC12 by orthogonal test method. The results showed that the porosity and shrinkage of the right crankcase cover are mainly concentrated in the thick wall part. The sequence of process parameters that affect the residual melt

modulus is pouring temperature, initial mold temperature and injection speed. By analyzing the filling process and the simulation results of the temperature field, the casting structure, mold structure and cooling system were optimized, and the process design was improved. The production verification was carried out according to the optimized process design. The casting quality is good and there are no obvious defects, which meets the actual production needs [15].

Sunil Umarane and colleagues investigated the defects in gravity casting of aluminum alloy using simulation software. The observed defects included solidification shrinkage, cracks, unfilled protrusions, and incomplete mold cavities, and were caused by improper selection of process parameters or improper design of gates and protrusions. The mold was modified based on the simulation results, and then the casting was carried out, and no defects were observed [16].

Rajulapati Ganesh and his colleagues in their work show the velocity variations, pressure variations, solidification behavior and its effect on various defects such as porosity, cold blockage, etc. in sand casting. Based on the results obtained in Click2cast simulation, relevant changes can be made to prevent defects [17]. Rohini U. Kendre et al. investigated the factors affecting sand casting defects such as speed, pressure, and temperature using Click2cast software, which will be a preventive tool for the manufacture of real parts [18].

2. Materials & Method

The casting simulation is based on the actual casting, i.e., three-plus branches made using the (genus), and the software used is SolidWorks and Click2Cast. The process parameters used in casting are as follows. SolidWorks software was used to create a comprehensive 3D model of the drive shaft's tripod. For automotive applications, the model was adjusted to meet weight and dimension requirements while improving structural rigidity and strength as can be seen in Figure 1.

To simulate the casting of the part, a simulation environment was used. Melting in the simulation environment was performed using a metal mold with H13 material. The preheating temperature of the mold was considered to be 150 degrees Celsius. Also, the material of the part was considered to be austenitic stainless steel 316, which has good corrosion resistance according to the application of the part. A casting core was also used in the casting process to create the center hole(Table 1).

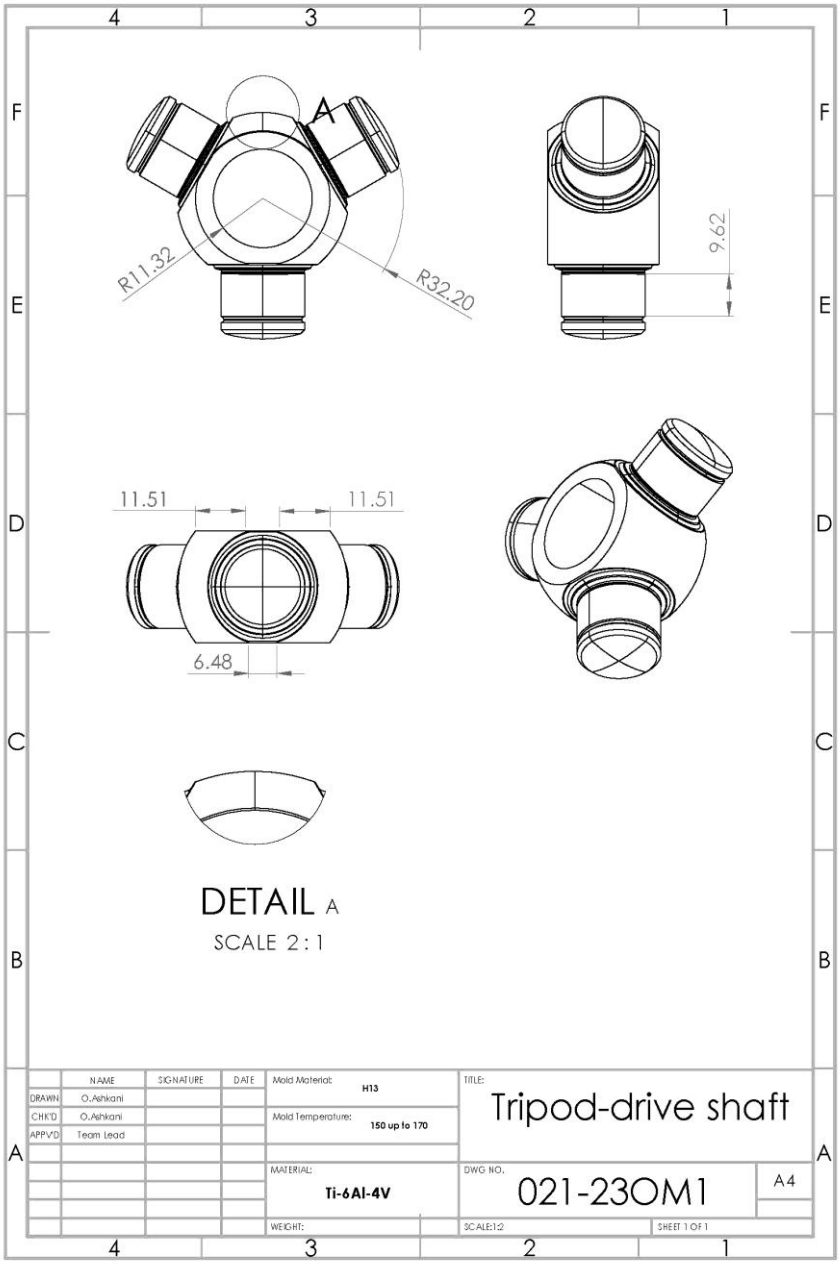

Figure. 1: Design in CAD software.

Table1: Simulation parameters

Main Materials	
Part materials	
Group	Stainless
Type	316L
Temperature(°C)	1537
Mold Material	
Type	Steel-H13
Temperature(°C)	150.0

Process Params			
Gravity direction		X	
Basic	●	Advanced	○
●	Ingate Vel.	[m/s]	0.98
○	Filling Time	[s]	0.16

3. Results and Discussion

One of the main challenges in the field of casting is mold temperature (Figure 2), as high mold temperatures can lead to serious damage to the mold. As can be seen, the arrow indicates the location of the melt entry in the simulation environment. Due to this, one of the branches has a higher temperature in the mold, which may lead to mold damage in this part in mass production. This is a key point to consider in mold design.

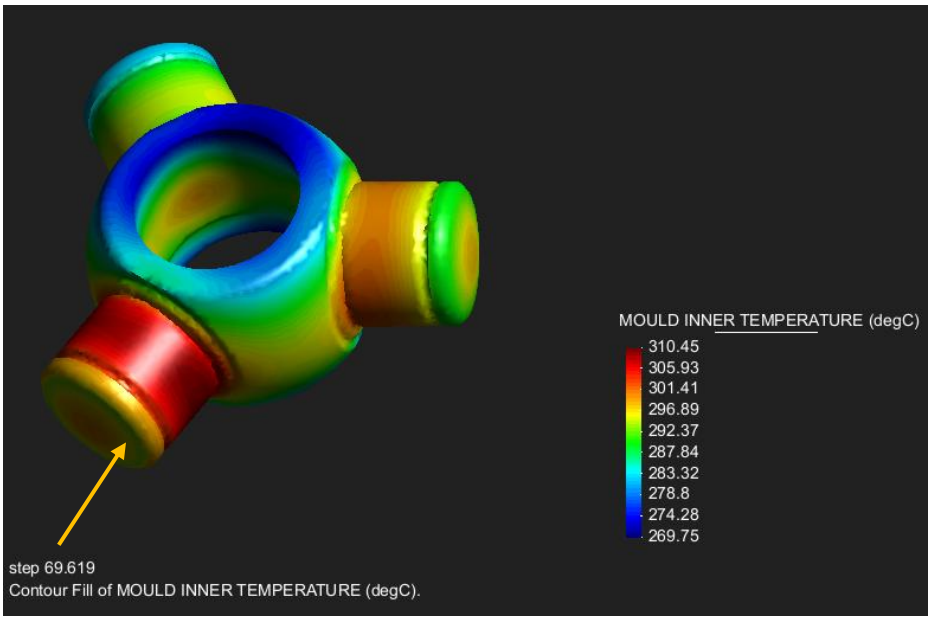

Figure. 2: Mold Temperature results.

It is noteworthy that the simulation results show the part temperature exactly as opposed to the mold temperature, with the temperature being highest in the branch where the melt arrives later. This is important because the mold design should be such that the temperature drop is uniform. However, in the design of the actual part, local mold cooling can be used to achieve a uniform temperature drop rate. Figure 3 shows the part temperature in the casting process.

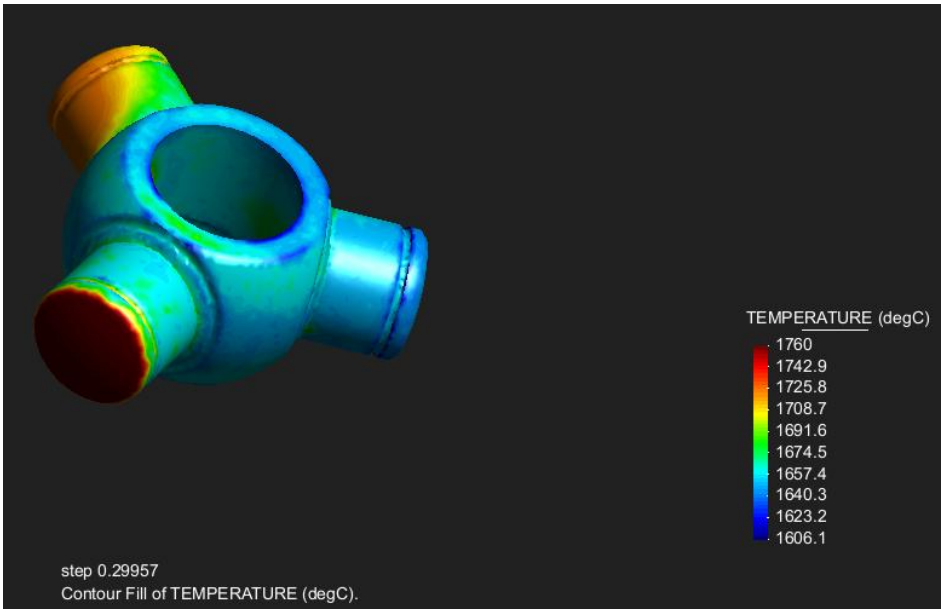

Figure. 3: Part temperature in the casting simulation.

One of the key issues is macro-voids, the presence of which can lead to reduced part quality and even corrosion on the part surface. Figure 4 shows the holes. As is clear, by defining the precise process parameters, minimal holes are created in the part, which is an important aspect in the design of this part. Also, reducing the holes can facilitate the machining process and is considered an important issue in manufacturing.

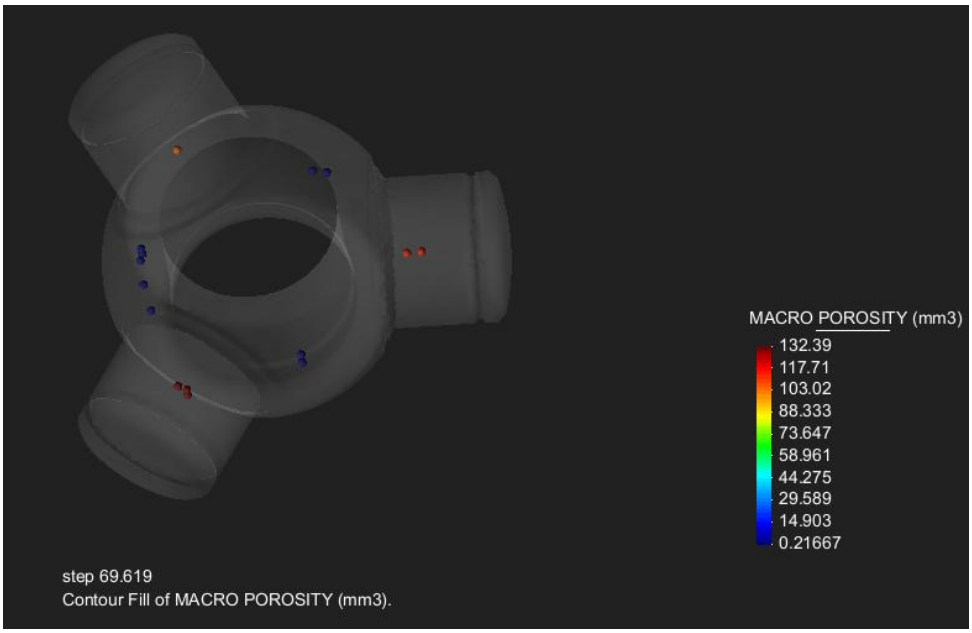

Figure. 4: Macro porosity after casting simulation.

Air entrapment is also a design consideration. Melt degassing and mold air management can help reduce this. Figure 5 shows areas where air is trapped. These areas are generally surface areas that can lead to reduced part quality.

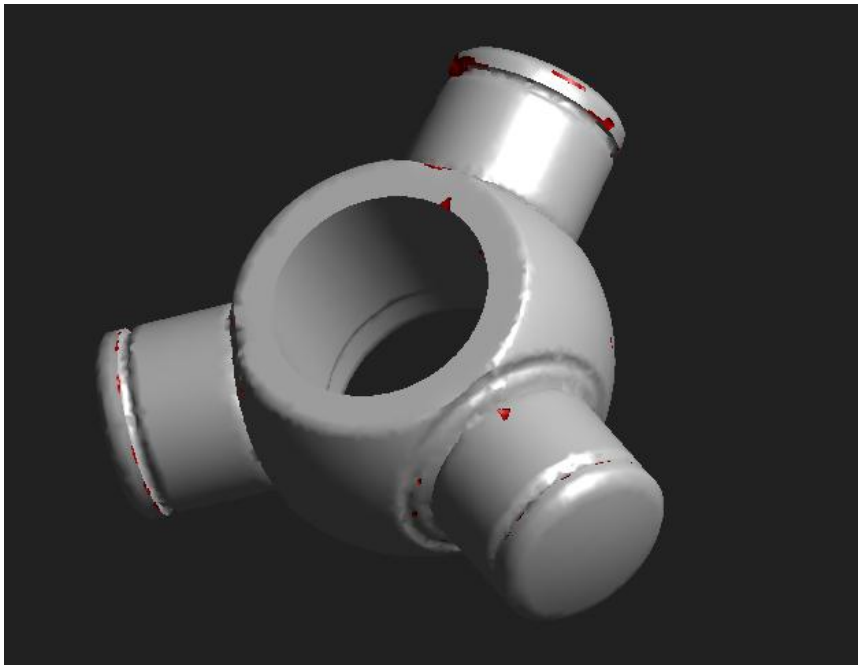

Figure. 5: Air trapping is shown in the areas with red dots.

The Niyama factor, or Niyama criterion, is a parameter used in casting simulations to predict the formation of shrinkage porosity defects in metal castings, particularly in steel. It is calculated by dividing the local thermal gradient by the square root of the local cooling rate. A low Niyama value indicates a higher probability of shrinkage porosity, while a high value suggests a lower risk. Figure 6 shows the Niyama factor for this part. As can be seen, based on the simulation results, there is lower risk for this part.

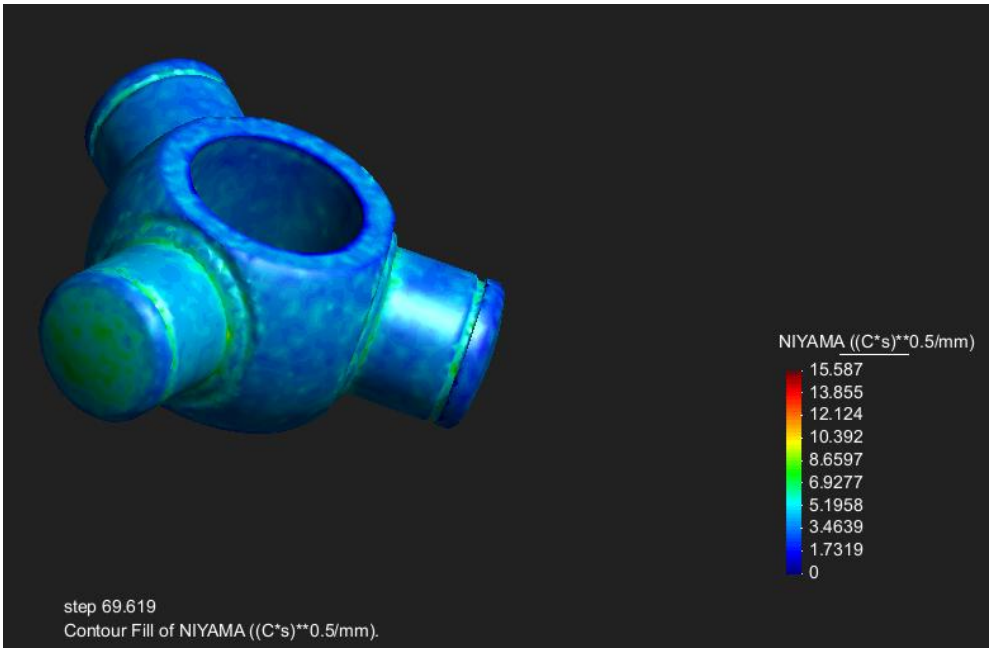

Figure. 6: Niyama Factor after simulation.

4. Conclusion

The present study was conducted with an emphasis on the high importance of casting simulation and the results showed that simulation is an important ability in the manufacture and production of parts. The results of the tripod casting simulation showed that gas cavities can be easily observed. Also, mold temperature control is of great importance, and this can lead to the identification of defects created in the part because increasing the mold thermal gradient may lead to damage to the mold design. Also, identifying the Niyama coefficient in steel parts and analyzing it plays an effective role in identifying defects.

5. Acknowledge

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Development of quantum dots in pharmaceuticals and biotechnologies: A mini review

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ABSTRACT

Quantum dots (QDs) are semiconductor Nano-crystals that possess unique optical and electronic properties due to their quantum mechanical behavior. Their size-tunable light emission, high brightness, and photo-stability make them invaluable in various fields, particularly in pharmaceuticals and biotechnology. Below, we explore some of the key applications of quantum dots in these areas.

Keywords : Quantum dots, Biology, QDs, pharmaceuticals.

1. Introduction

Quantum materials are used in new technologies such as solar cells, water purification, drug delivery, and bio imaging due to their unique properties. Graphene quantum dots are among the main materials in this field. Carbon and zinc sulfide quantum dots are also of great interest. In this poster, the latest achievements in this field are categorized.

2. Applications of QDs in Pharmaceuticals and Biology

2.1. Imaging and Diagnostics

One of the most significant uses of quantum dots in pharmaceuticals is in imaging and diagnostics. QDs are employed as fluorescent labels in various imaging techniques, including fluorescence microscopy, confocal microscopy, and in vivo imaging. Their ability to emit light at specific wavelengths allows for multiplexing, where multiple targets can be visualized simultaneously. This is particularly beneficial in cancer diagnostics, where quantum dots can be conjugated to antibodies that bind specifically to tumor markers, enabling early detection and characterization of tumors.

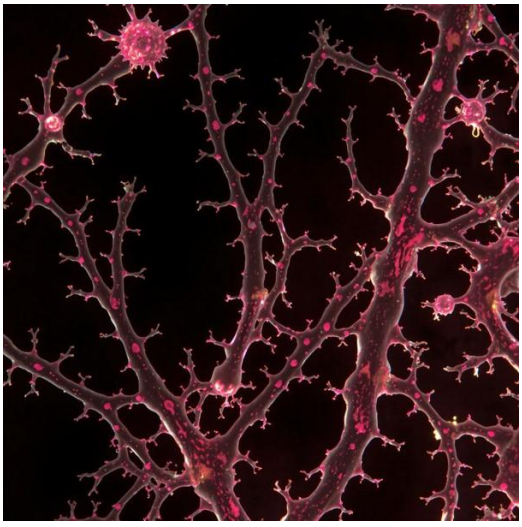

Figure 1- The images are hypothetical and refer to the development of quantum dots in improving imaging clarity. Higher transparency is important.

2.2. Drug Delivery Systems

Quantum dots can be integrated into drug delivery systems to enhance the efficacy and targeting of therapeutic agents. By attaching QDs to drug carriers, researchers can utilize the unique optical properties of quantum dots to track the distribution of drugs within the body in real time. The surface of QDs can be functionalized with ligands that target specific cells or tissues, ensuring precise delivery of therapeutic compounds while minimizing side effects.

2.3. Bio-sensing

The unique optical properties of quantum dots make them excellent candidates for bio-sensing applications. They can be used to develop highly sensitive biosensors for detecting biomolecules such as proteins, DNA, and viruses. These biosensors leverage the fluorescence of QDs, which can change in response to interactions with target analytes, allowing for rapid and sensitive detection of diseases. Researchers are encouraged to do more work in this area in the future.

2.4. Development of herbal medicines

Herbal medicines, derived from plants and their extracts, have been utilized for centuries across various cultures for their therapeutic properties. These natural remedies are often used to promote health, alleviate symptoms, and support the body's healing processes, treating conditions ranging from mild ailments like colds and digestive issues to more complex health concerns. Herbal medicines can come in various forms, including teas, tinctures, capsules, and topical applications, allowing for versatile usage depending on individual preferences. While many people find them beneficial, it's important to approach herbal remedies with caution, as their effectiveness can vary based on dosage, preparation, and individual health conditions. Additionally, consulting healthcare professionals before using herbal medicines is advisable to ensure safety and avoid potential interactions with conventional treatments.

Herbal medicines incorporating carbon quantum dots are also among the significant applications of quantum dots in biology, which enable the treatment of certain diseases. In this regard, we suggest that researchers work more in the near future on developing a new generation of herbal medicines with QDs.

3. Conclusions

Quantum dots represent a transformative technology in the fields of pharmaceuticals and biotechnology, offering innovative solutions for diagnostics, drug delivery, and therapeutic applications. As research continues to advance, the integration of quantum dots into various biomedical applications holds great promise, potentially leading to improved healthcare outcomes and revolutionary approaches to disease management. The ongoing exploration of QDs could unlock new frontiers in precision medicine, paving the way for more effective and personalized therapies.

4. Future perspective & suggestions

In the field of QDs, we suggest shortly researchers focus on these topics:

1. Imaging and Diagnostics: As mentioned before, Quantum dots can be used as fluorescent markers in imaging techniques such as fluorescence microscopy. Their size-tunable emission enables multiplexing, allowing for the simultaneous visualization of multiple biomarkers in biological samples, thereby improving diagnostic accuracy. Bio-imaging is a very good field for conducting more research.

2. Targeted Drug Delivery: By conjugating QDs with therapeutic agents, they can be developed as targeted drug delivery systems. They can be designed to release drugs in response to specific stimuli (like pH or temperature changes) or to target specific cells, such as cancer cells, minimizing side effects and enhancing treatment efficacy.

3. Bio sensing and Biomarker Detection: Quantum dots can be employed in biosensors to detect specific biomarkers associated with diseases. Their high photostability and brightness make them suitable for real-time detection of biomolecules, such as proteins or nucleic acids, aiding in early disease diagnosis.

4. Photo thermal Therapy: Due to their excellent light absorption properties, QDs can be used in photothermal therapy for cancer treatment. When illuminated with specific wavelengths of light, they can convert light into heat, selectively killing cancer cells while preserving surrounding healthy tissue.

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Simultaneous effect of temperature and torque on a bolt made of Ti-8Al-1Mo-1V alloy

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ABSTRACT

Light alloys with high strength-to-weight ratios should be of more interest to researchers today. Screws and bolts are typically made of steel alloys. The present study has shown that although steel alloys are traditionally used in screw and bolt manufacturing, the use of light alloys with a density half that of steel can be effective. The results of the present study showed that a bolt designed with a titanium alloy can exhibit adequate strength and, due to beta stabilizers, the formation of intermetallic compounds, and solid solution hardening, is a suitable material for manufacturing such parts while maintaining strength.

Keywords : Bolt manufacturing, Solid solution hardening, titanium alloys, light alloys.

1. Introduction

Mechanical joints have always been a vital aspect of the construction industry. They are used to transfer load, which involves compression between connected objects whilst relative motion occurs simultaneously [1] . Mechanical joints are typically categorized as permanent or non-permanent. Permanent joints (for example, welding, brazing, or riveting) create a fixed connection that cannot be disassembled without damaging the parts. Non-permanent (or temporary) joints—such as bolted or screwed connections—allow parts to be assembled and later taken apart without breakage.

In mechanical engineering, non-permanent joints play a crucial role in machine design. These joints are essential in applications where maintenance, adjustments, or part replacements are frequently required. This article explores the key types of non-permanent joints, their applications, advantages, and considerations to ensure effective design [2] . The most common mechanical joints are adhesive joints, bolted joints, riveted joints and clinching joints. In practice, threaded fasteners (bolts/screws) dominate the non-permanent category.

A screw is an externally helical threaded fastener capable of being tightened or released by a twisting force (torque) to the head. The most common uses of screws are to hold objects together and there are many forms for a variety of materials. Screws might be inserted into holes in assembled parts or a screw may form its own thread [3]. The difference between a screw and a bolt is that the latter is designed to be tightened or released by torquing a nut. A screw joint is a one-degree-of-freedom kinematic pair used in mechanisms. Screw joints provide single-axis translation by utilizing the threads of a lead screw to provide such translation [4]. This type of joint is used primarily on most types of linear actuators and certain types of cartesian robots [5]. A screw joint is sometimes considered as a separate type but it is actually a variation of bolted joint. The difference is that a screw is used rather than a bolt, thus requiring an internal thread in one of the jointed parts. This can save space; however, continuous reuse of the thread would probably damage the coils, making the whole part unsuitable.

Two primary parameters govern bolt selection, ensuring prevention of bolt failure and its detrimental consequences:

Bolt Grade

The bolt grade is a standardized classification system that defines the mechanical properties of bolts, nuts, and related fasteners. It indicates the maximum tensile stress and yield stress per unit inch or millimeter (depending on the reference standard). By consulting the standard and its tables, additional mechanical properties such as hardness, torsional strength, and maximum shear stress can be determined. [6, 8].

Notable Bolt Grading Systems

ISO Standard ➔ For steel bolts, two numbers are marked (e.g., 8.8 or 10.9), categorized into ranges: [9]

Low-Strength Bolts (4.6 to 6.4) :

Made of low-carbon steel, suitable for light-duty applications. [10]

High-Strength Bolts (8.8 to 12.9) :

Composed of high-carbon steel and heat-treated, used in industrial, construction, and aerospace applications. [11, 12]

Interpreting ISO Grades:

First Number × 100 = Ultimate Tensile Strength (MPa)

Example: 8 × 100 = 800 MPa

Second Number × (First Number × 100) = Yield Stress (MPa)

Example: 8 × 100 × 0.8 = 640 MPa

ASTM Standard ➔ Another well-known bolt grading system is ASTM. Like other systems and standards, it has its specific classification and is marked in this way (such as A2-50 or A4-80). [13]

An example for understanding the numbers on bolts in the ASTM standard:

(A2, A4) = indicates the alloy type

The second number ➔ 80 × 10 = 800 MPa

A bolt is considered standard only if its grade and the governing standard (e.g., ISO or ASTM) are permanently marked on it. [14,16]

The geometry of screw threads plays a critical role in the performance and reliability of mechanical fasteners. Several dimensional parameters define the shape and size of threads, and these are standardized to ensure proper function and interchangeability.

The major diameter (d) is the largest diameter of the external thread and typically corresponds to the nominal size of the fastener. The minor diameter (dr), also known as the root diameter, is the smallest diameter and is important for determining the tensile strength of the screw. The pitch diameter (dp) lies between the major and minor diameters and is the effective diameter where the thread thickness equals the thread space. This diameter governs the load distribution between mating threads.

The pitch (p) is defined as the axial distance between adjacent threads. For single-start threads, the lead (L)—the distance a nut moves along the screw axis in one full revolution—is equal to the pitch. Multi-start threads have leads that are multiples of the pitch. The included thread angle (θ) is typically 60 degrees for standard Unified and ISO metric threads.

For strength calculations, the tensile-stress area (At) is used to estimate the cross-sectional area resisting axial load. It can be approximated using the expression:

$$A_t \approx 0.7854 \left(d - \frac{0.9743}{p}\right)^2$$

This area provides a more accurate basis for stress analysis than the major or minor diameter alone.

The helix angle (α), which defines the angle of the thread's incline, is calculated from:

$$\tan(\alpha) = \frac{L}{\pi d_m}$$

where dm is the mean diameter of the thread. This angle affects how the thread behaves under load, particularly in terms of friction and torque.

The length of thread engagement is also important. For steel components, an engagement length equal to the nominal diameter of the screw is generally sufficient. For softer materials, a longer engagement—typically 1.5 times the screw diameter—is recommended to prevent thread stripping.

Lastly, the geometry of the screw head influences how torque is applied and how load is distributed under the head. Common head types include hex, socket, and pan heads, each with standardized dimensions for height, wrench size, and bearing surface [17].

Standards and Geometry of ISO Metric Screw Threads

The geometry of ISO metric screw threads is established through a series of well-defined international standards, each covering specific aspects of thread form and dimensional control. One of the defining features of these threads is their symmetrical shape, characterized by an included flank angle—commonly referred to as the pressure angle—of 60 degrees. This angle is standard across ISO metric and Unified Thread Series (UTS) profiles and plays an important role in how loads are distributed along the thread flanks [18,19].

The full thread profile is described in ISO 68-1, which defines a V-shaped form with flanks inclined at 30 degrees relative to the thread axis [20]. This standard provides the fundamental geometry for screw threads, including parameters such as thread height and pitch-to-diameter relationships. These serve as the basis for tolerance and fit standards used in production and inspection [21].

The principal thread dimensions—major diameter, minor diameter, and pitch diameter—are specified in DIN 13-1 [22]. This standard covers both coarse and fine pitch ISO metric threads and includes definitions for important characteristics like thread pitch, lead, and thread depth. It also distinguishes between internal and external threads, ensuring proper fit and compatibility in mating components [23].

At the termination points of threaded elements, such as the ends of bolts or the bottoms of tapped holes, DIN 76-1 defines the geometry of thread run-outs and undercuts. These features are not part of the functional thread but are essential for tool clearance and to prevent stress concentrations [24,25]. DIN 76-1 provides standardized values for these reliefs based on the thread pitch and nominal diameter.

Although DIN 76-1 does not define tolerances for the pressure angle itself, the 60-degree flank angle is assumed throughout ISO thread standards. For accurate analysis and design, engineers are advised to consult both DIN 13-1 and ISO 68-1, especially when evaluating load capacity, fatigue resistance, or manufacturing requirements related to thread geometry [26].

2. Materials and Method

In the present study, a long-base bolt sample was designed using SolidWorks software. Figure 1 shows a schematic of the bolt. Then, the same software was used to simulate and apply temperature and torque simultaneously to the bolt. Figure 2 also shows a schematic of the sample meshing.

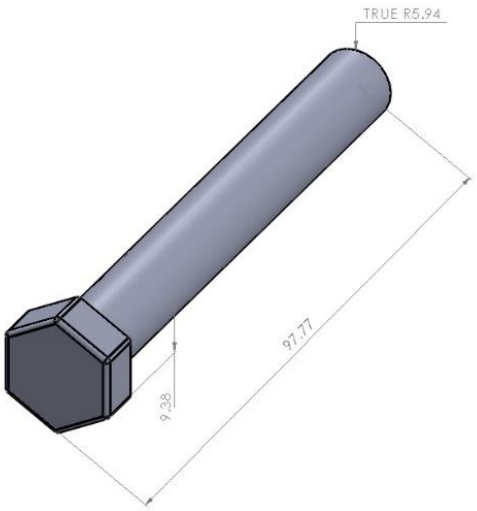

Figure 1- Schematic of bolt.

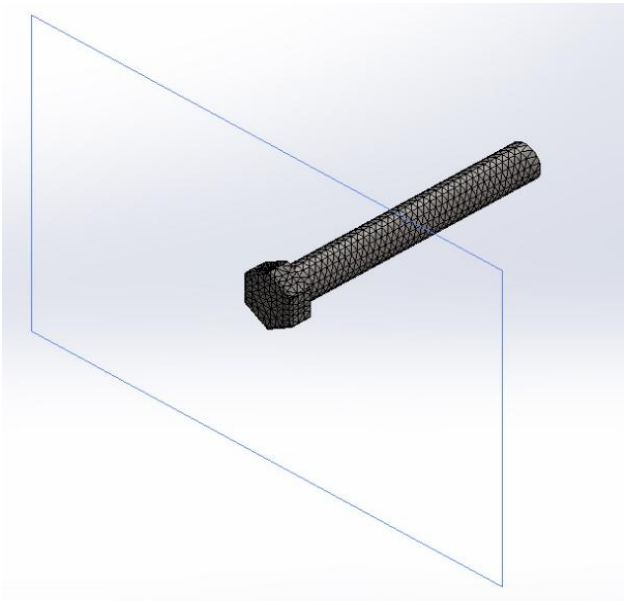

Figure 2- Schematic of the meshing of the sample.

For the simulation, a torque of 100 N.m was applied to the sample. The sample temperature was also assumed to be 273 degrees Kelvin. This temperature was assumed to be equal to zero degrees Celsius because the working conditions were assumed to be at zero temperature.

3. Results and Discussion

Figure 3 shows the displacement after the test. As is clear, the hex portion of the bolt showed the highest displacement, probably due to the freedom of that portion. However, the results show that the alloy had sufficient resistance to torsional force and the ability of this alloy to be used in specific applications is questionable.

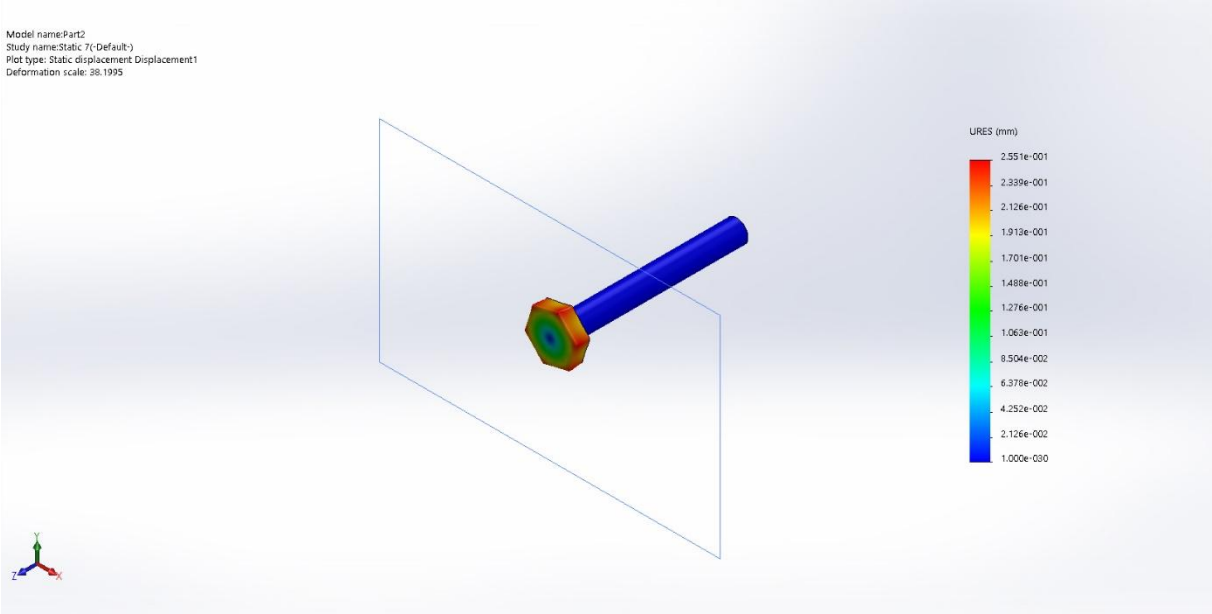

Figure 3- Results of displacement.

Figure 4 and Figure 5 also show the results of strain and strength changes, respectively. As is clear, when applying this torque and at a temperature of zero degrees Celsius, the material did not become brittle and maintained its strength. This is probably due to the formation of titanium-aluminum intermetallic compounds and also due to the presence of one percent by weight of molybdenum. Molybdenum, as a beta stabilizer, can lead to an increase in strength through solid solution hardening.

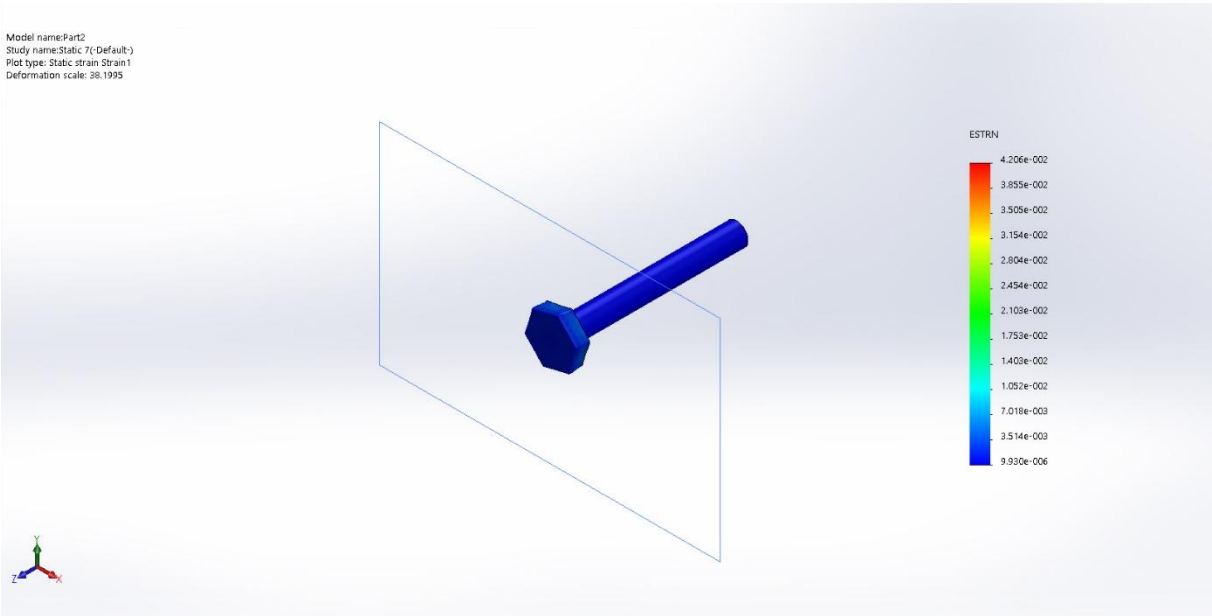

Figure 4- Strain results.

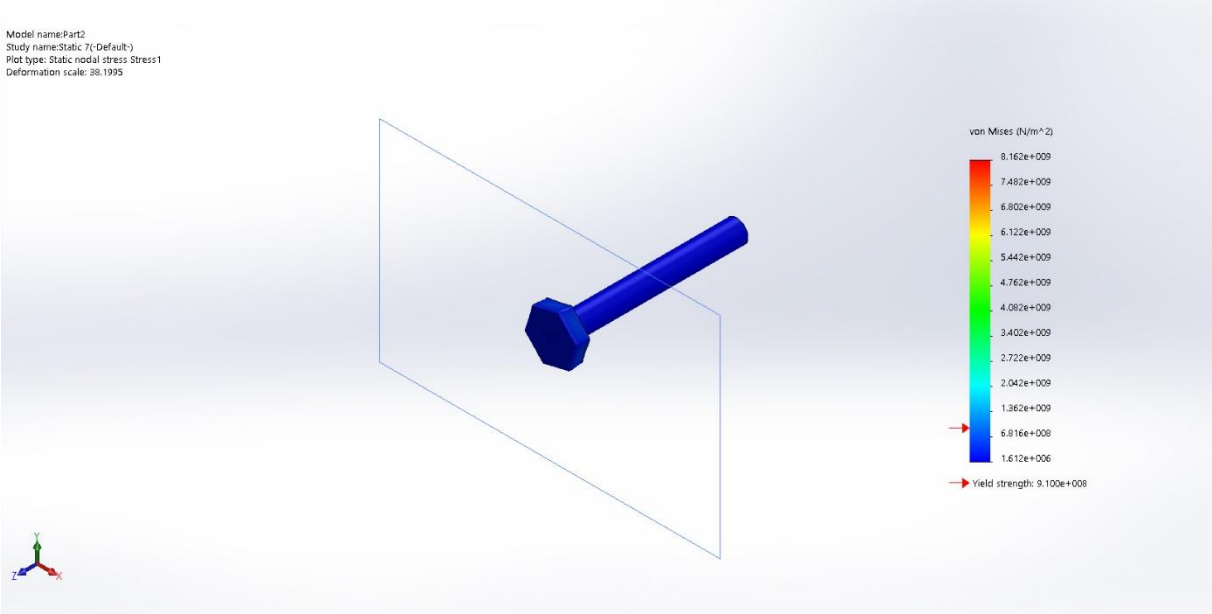

Figure 5- Stress results.

4. Conclusions

In general, the results of the present study can be categorized as follows:

1- The investigated titanium alloy has the potential to be used in various screws.

2- Solid solution strengthening, which is due to beta-stabilizing elements including molybdenum and vanadium, can be effective in the strength of the alloy.

3- This alloy can be considered because it is lighter than conventional alloys such as steel.

It is suggested that in the future, more focus should be placed on developing parts such as screws and bolts with light alloys such as titanium.

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Defect-Mediated Lithium-ion Migration in Li2OHCl Solid Electrolytes: Insights from EIS and EDS Analysis

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ABSTRACT

This study explores lithium-ion (Li^+) migration mechanisms in lithium halide and oxide materials by analyzing defect types such as Schottky, Frenkel, and interstitial defects. Samples were synthesized with controlled compositions to stabilize different structural phases, including orthorhombic, cubic, and Ruddlesden–Popper (RP) frameworks. Electrochemical impedance spectroscopy (EIS) and energy-dispersive X-ray spectroscopy (EDS) were employed to investigate ionic conductivity and elemental changes before and after thermal cycling. EIS results revealed distinct activation energies (E_a) linked to various migration mechanisms, such as 0.11–0.24 eV for Li^+ vacancy or interstitial dumbbell migration in low-temperature RP and cubic phases, and up to 2.48-1.54 eV at higher temperatures due to LiCl or Li_2O Schottky defect formation. EDS analysis confirmed an increase in oxygen vacancies post-EIS, supporting the formation of Schottky pairs, while high grain boundary resistance suggested additional barriers due to hydrogen-related defects.

Keywords : Lithium-ion conductivity; Defect formation energy; Solid electrolytes; Electrochemical impedance spectroscopy (EIS); Elemental analysis (EDS).

1. Introduction

Solid-state lithium-ion batteries (SSLIBs) have emerged as a transformative technology aimed at achieving safer, higher energy density storage compared to conventional systems that rely on liquid electrolytes. Among solid electrolytes, lithium-rich halide and oxide compounds, such as Li_2OHCl, hold particular promise due to their intrinsic safety, wide electrochemical stability window, and enhanced lithium-ion conductivity [1-3]. The realization of high-performance SSLIBs critically depends on a thorough understanding of lithium-ion (Li^+) migration mechanisms and the role of crystal defects in facilitating or impeding ion transport within these solids.

Solid electrolytes serve as the ion-conducting backbone of SSLIBs, influencing not only ionic mobility but also interfacial stability with electrodes. Inorganic solid electrolytes are especially attractive for their high Li^+ transference numbers, mechanical robustness, and suppression of dendritic lithium growth, thereby improving both battery safety and life cycle [4-6]. However, the absolute ionic conductivities of many solid electrolytes remain lower than those of liquid counterparts, particularly at room temperature. Fundamental to improving ionic conductivities

is an understanding of how structural features—especially various types of lattice defects and phase transitions—govern ion mobility.

Li^+ conduction in solid electrolytes, including Li_2OHCl, is predominantly mediated by point defects such as vacancies and interstitials. Defect types, including Schottky (paired cation and anion vacancies), Frenkel (a cation vacancy and a corresponding interstitial), and interstitial dumbbells, create pathways or barriers for ion movement across the lattice [7, 8]. The concentration and mobility of these defects are strongly influenced by synthesis conditions, compositional stoichiometry, and thermal history, which in turn regulate the phase stability—between orthorhombic, cubic, and layered (Ruddlesden–Popper, RP) frameworks—of the Li_2OHCl electrolyte [9-11].

The dynamic properties of the anion framework, especially in antiperovskite structures like Li_2OHCl, also play a vital role in promoting exceptional Li^+ transport. In this structure, a high cation vacancy fraction (~1/3 of Li sites are vacant) and the rotational disorder of OH^- anions have been shown to enhance cation transport, as the so-called "paddlewheel" rotation of molecular anions helps shuttle Li^+ ions rapidly through the cubic matrix [12, 13].

Electrochemical impedance spectroscopy (EIS) and energy-dispersive X-ray spectroscopy (EDS) are robust techniques for dissecting the complex interplay between structural defects, phase transitions, and ion conductivity. EIS provides quantitative activation energies for Li^+ migration and sheds light on the dominant conduction mechanisms across different temperature regimes and structural phases [14, 15]. For instance, studies of Li_2OHCl reveal that at low temperatures, RP and cubic phases facilitate migration via vacancy or interstitial mechanisms with low activation barriers (0.11–0.24eV), while higher temperatures favor the formation of Schottky defects, raising the activation energy and altering the conduction pathways [16, 17]. EDS analyses, particularly after thermal cycling, have confirmed increases in oxygen vacancies, strengthening the correlation between defect chemistry and ionic conduction [5].

Despite substantial progress, realizing optimal bulk and grain boundary conductivities in Li_2OHCl and related solid electrolytes requires a finer control over defect chemistry, microstructure, and interfacial engineering. High grain boundary resistance, often correlated with hydrogen-related or impurity-induced defects, poses significant bottlenecks for large-scale adoption [18]. Future advances are likely to be driven by a combination of advanced experimental methods and computational modeling, offering predictive tools for the rational design of next-generation solid-state conductors.

Achieving a comprehensive understanding of how defects and structural dynamics in Li_2OHCl solid electrolytes mediate lithium-ion migration will be central of this work for unlocking the full potential of all-solid-state lithium batteries and fostering the energy solutions of the future.

2. Experiment

2.1. Solid-State Synthesis

In this way, 1 mol LiCl (Ghatran Shimi, Iran, ≥99%), 2 mol LiOH (Merck, German, ≥99%), and 0.005 mol LiF (Merck, ≥99%) were weighed and well milled in a mortar and pestle. Then the mixture compacted in a 316L stainless-steel crucible, and heat treatment at 240 °C with a heating rate of 5 °C min^{-1}in a vacuum furnace for 48 h. The product cool neutrally.

2.2. Characterization

Structural characterization. The phase behavior was carried out by X-ray diffraction analysis (Philips PW 3710, German) with Cu Kα radiation (λ=1.5405 A°) in the 2θ ranges from 5° to 80° with step 0.02°. Quantitative evaluation of phases and lattice information were analyzed by Rietveld refinements with X'pert HighScore Plus version 2.2b (PAN analytical). Morphology characterization was carried out by ZIESS sigmaVP instrument equipped with an elemental MAP analyzer.

Impedance Spectroscopy. The powder was cold pressed in a stainless-steel mold under a uniaxial pressure 3000 bar. The thickness of the pellet was adjusted to 1 mm. The copper electrode was used as a unblocking electrode on both sides of the pellet for characterizing interfacial resistance. The symmetric cell was assembled by gold electrode as both working and reference electrodes. The Impedance measurements were taken using EG&G (parstat 2273) in a frequency range of 1 MHz to 100 mHz. The AC amplitude was selected 10 mV rms. The heating temperature was controlled by A KAEM MOD TU16(5) A250V. The cooling process was done naturally.

3. Results and Discussion

Figure 1a shows the XRD pattern of the synthesized $Li_2(OH)_{0.995}F_{0.005}Cl$. The phase structure exhibit cubic lattice with Pm3m symmetry. The main peak of the cubic pure Li_3OCl is observed at 32.22°. The domain phase formed are orthorhombic Li_2OHCl with Pban symmetry and a compressed lattice volume of 230 $Å^3$. Also $Li_4(OH)_3Cl$ phase formed as a second phase with lattice volume of 242 $Å^3$. Atomic coordination sites of LiH_2OCl indicates Li at position 3d rearrange at 4a and 4c positions, and H1 takes place at 16h occupying sites, leading to statistic distortion. The O-H1 and O2-H2 bonds length are calculated to be 0.945 Å and 0.788 Å, respectively.

The negative charge of the fluorine interior of the system might shortage the O-H bond distance as reduced the lattice parameter. These expansion and compaction give a slight distortion in octahedral Li_6O coordination.

Goldschmidt's tolerance factor, t, is likely used to interpret the structural stability. It is based on a geometrical situation of the atoms in the structure. For the general structure M_3BA, It is written as

$$t = \frac{r_B + r_M}{\sqrt{2}(r_A + r_M)}$$

where r_B is the ionic radius of B $(B = O, OH, \ldots; A = Cl, Br \ldots)$. If $t = 1$, the structure is ideally cubic. If t is far from unity, phase instability, tilt, and/or ion mismatch are possible. If the t-value is too large, [M3B] octahedrons may become face-sharing to provide a large space for A. If the t-value becomes smaller, [M3B] octahedrons may tilt to aid small A [19]. For the Li_2OHCl constitution, the t factor is calculated to be 0.90, meaning more regular with high symmetric structure.

The halide hydroxide structure in $Li_2(OH)_{0.995}F_{0.005}Cl$ is revealed by Fourier Transform-IR spectroscopy in Figure 1b. Some overlapped peaks within 3200-3632 cm^{-1} are referred to as OH^- free and OH^- stretching bonds, suggesting hydroxide functional groups. A sharp peak at 1645 cm^{-1} is referred to δ(HOH) of the water content. Moreover, two significant peaks at 586 and 826 cm^{-1} indicate halogen (Halo.) compounds like R-Cl bonds [20].

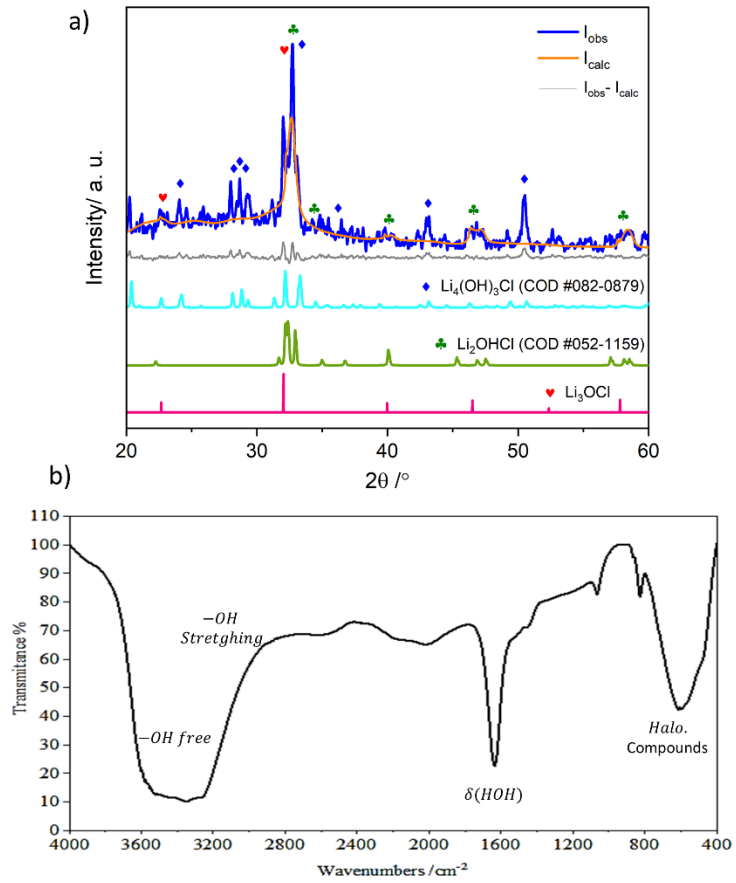

Figure 17. a) X-ray diffraction patterns. b) FTIR pattern.

Figure 2 shows the Nyquist curves from EIS measurements. Nyquist curves were modeled by an equivalent circuit includes an ohmic resistance in series with an RQ (referred to as total grain and grain boundary) in series with CPE to model the dielectric constant of the solid electrolyte in the space charge layer [21]. By fitting the Nyquist curves with an equivalent circuit and measuring the resistance in the electrolyte's pellet, ionic conductivity (σ_i) is calculated from

$$R_i = \frac{d}{\sigma_i A}$$

Ion conductivity has been monitored at both the heating and cooling processes. At 40°C, the measurements of the ion conductivity of $Li_2(OH)_{0.995}F_{0.005}Cl$ in symmetric unbloking Cu||Cu cell indicate the value of 3.2×10^{-6} S cm^{-1}. By rising temperature to 75°C, total ion conductivity is measured to be 1.2×10^{-5} S cm^{-1}. At 130 °C, the R_{g+gb} is abruptly reduced from 9489 Ω to 2 Ω. In this way, ion conductivity enhances to 10.7×10^{-3} S cm^{-1}. In contrast, ion conductivity of $Li_2(OH)_{0.995}F_{0.005}Cl$ in symmetric bloking Au||Au cell indicate the value of 2.2×10^{-4} S cm^{-1} at 25℃, 1.3×10^{-3} S cm^{-1} at 75 °C, and 3.4×10^{-3} S cm^{-1} at 110 °C. The difference is refered to interfacial polarization of Cu electrolde.

The substitution of F^- for an OH^- anion stabilizes the more favorable phase, in accordance with literature [22]. In orthorhombic phase, a non-ideal capacitance (CPE) of a double-layer shell at the interface between solid electrolyte and Cu electrode is observed. After transition from orthorhombic to cubic, CPE was replaced with Warburg because of the diffusion of Li^+ ions. During cooling below 65 °C, the Warburg impedance again is replaced with non-ideal

capacitance, and the grain resistance distinguishes from the grain boundary resistance (Fig. 2d). Cooling process causes to reduction σ_i because at high temperatures a soft phonon resonance provides more easily rotation of H-bonds into the structure, which results in high Li^+-ion conduction [23].

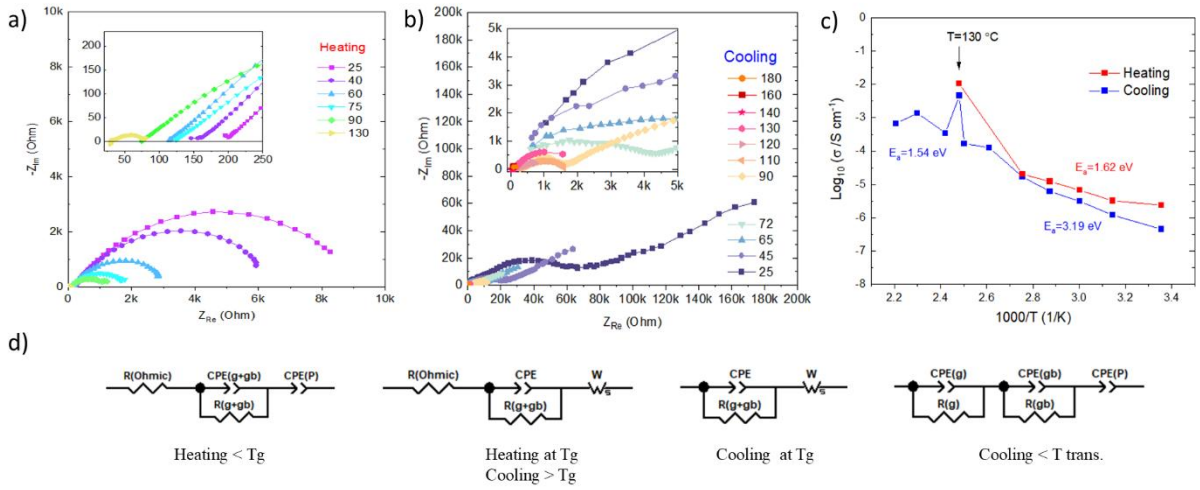

Figure 18. a-b) Impedance spectroscopy Nyquist curves in a symmetric cell with the non-blocking copper electrode during heating and cooling processes. Insets: high magnification of the Nyquist curves; c) Arrhenius plots of log(σ) versus 1/T with the measured activation energy; d) Equivalent circuits of Cu/ $Li_2(OH)_{0.995}F_{0.005}Cl$ /Cu symmetric cell.

The calculated activation energy of Cu/ $Li_2(OH)_{0.995}F_{0.005}Cl$ /Cu is equal to 1.54 eV during cooling and is 1.62 eV during heating, meaning Li_2O Schottky defects for migration mechanism.

Figure 3a-b show a surface morphology and elemental distribution in the SSE anti-perovskite $Li_2(OH)_{0.995}F_{0.005}Cl$ pellet before and after the EIS test. Before EIS, the surface of the pellet is smooth and dense with some grain boundaries. After EIS, the physical shape of the pellet distorts. Somewhere swell, pore forms, and grain boundaries become fissures, wrinkles appear a lot, and the smooth surface becomes full of defects. Free space saturates with the molten phase, and nucleation on the surface reveals the formation of new structures. Growth of internal anti-perovskite layers and rock-salt layer structures are like two-dimensional Ruddlesden–Popper structures (Fig 3b), as reported previously [24]. Whereas, no rock-salt layer structures observe on the surface of the grains before the EIS test (Fig. 3a).

Before EIS, substitution of 1.9 wt% F remains O content at 11.9%, and Cl content to 86.1% (Fig. 3c). It has to be noticed that the synthesized $Li_2(OH)_{0.995}F_{0.005}Cl$ is Cl-rich. However, the sample is composed of lithium halide hydroxide phases, and the concentration >1 for Cl is explicable. From the atomic weight of Cl (35.45 g per mol) and O (16 g per mol), the mole of Cl is calculated within ~2.42, and the mole of O is calculated within ~0.74. This differential of the oxygen concentration from the stoichiometry of $Li_2(OH)_{0.995}F_{0.005}Cl$ means formation of a full-of-defect anti-perovskite. Solid-state Li-ion superionic conductors have substantially disordered structures and high defect concentrations, due to incomplete filling of particular crystallographic sites. Althought, The perfect (defect-free) Li_3OCl is envisioned to be a poor Li^+ conductor, disordered halide hydroxides i.e, Li_2OHCl are considered to preserve the overall charge neutrality throught defect charge carriers. According to Kröger-Vink notations in the crystal-chemistry reaction, we will have

a) LiCl Schottky pair $(V'_{Li} - V^*_{Cl})$ leads to $Li_{3-x}OCl_{1-x}$

$\mathrm{Li}_{\mathrm{Li}}^{\times} - \mathrm{Cl}_{\mathrm{Cl}}^{\times} \rightarrow \mathrm{V}_{\mathrm{Li}}' - \mathrm{V}_{\mathrm{Cl}}^{*} + LiCl$

b) Li_2O Schottky pair $(2\mathrm{V}_{\mathrm{Li}}' - \mathrm{V}_{\mathrm{O}}^{**})$ forms $Li_{3-2x}O_{1-x}Cl$

$2\mathrm{Li}_{\mathrm{Li}}^{\times} - \mathrm{O}_{\mathrm{O}}^{\times} \rightarrow 2\mathrm{V}_{\mathrm{Li}}' - \mathrm{V}_{\mathrm{O}}^{**} + Li_2O$

c) Li_2O substitution by Cl $(\mathrm{O}_{\mathrm{Cl}}' - \mathrm{Li}_{\mathrm{i}}^{*})$ produces to $Li_{3+x}O_{1+x}Cl_{1-x}$

$Li_2O + \mathrm{Cl}_{\mathrm{Cl}}^{\times} \rightarrow \mathrm{O}_{\mathrm{Cl}}' + \mathrm{Li}_{\mathrm{i}}^{*} + LiCl$

d) Frenkel defect pair $(\mathrm{V}_{\mathrm{Li}}' - \mathrm{Li}_{\mathrm{Li}}^{*})$

$\mathrm{Li}_{\mathrm{Li}}^{\times} \rightarrow \mathrm{V}_{\mathrm{Li}}' + \mathrm{Li}_{\mathrm{i}}^{*}$

Wu estimated the defect formation energy of Li_2O and LiCl Schottky equal to 1.54 and 1.27 eV, respectively [25]. While Braga estimated defect formation energy of LiCl Schottky defect $(\mathrm{V}_{\mathrm{Li}}' - \mathrm{V}_{\mathrm{Cl}}^{*})$ equal to 4.75 eV [16].

From Fig. 2c, the calculated $\mathrm{E_a} = 3.19$ eV reveals that both Li_2O and LiCl Schottky defects may be formed beside interstitial dumbbell mechanism with $\mathrm{E_a} = 0.14 - 0.17$ eV [26]. According to EDS result in Fig. 3d, F content increase to 10.3% ,O content decrease 6.1%, and Cl content changes to 83.6%. It means that increasing oxygen vacancy in the $Li_2(OH)_{0.995}F_{0.005}Cl$ cause to formation of Li_2O Schottky pair $(2\mathrm{V}_{\mathrm{Li}}' - \mathrm{V}_{\mathrm{O}}^{**})$ [25]. An increase in O-vacancy concentration $(\mathrm{V}_{\mathrm{O}}^{**})$ after the EIS test approves the formation of the Li_2O Schottky pair in the structure. In addition, Recently, Zhao has mentioned that migration of Li interstitial along the edge of Li_6O octahedron follows a two dimensional Ruddlesden–Popper (RP) phase with a barrier 0.17 eV [27].

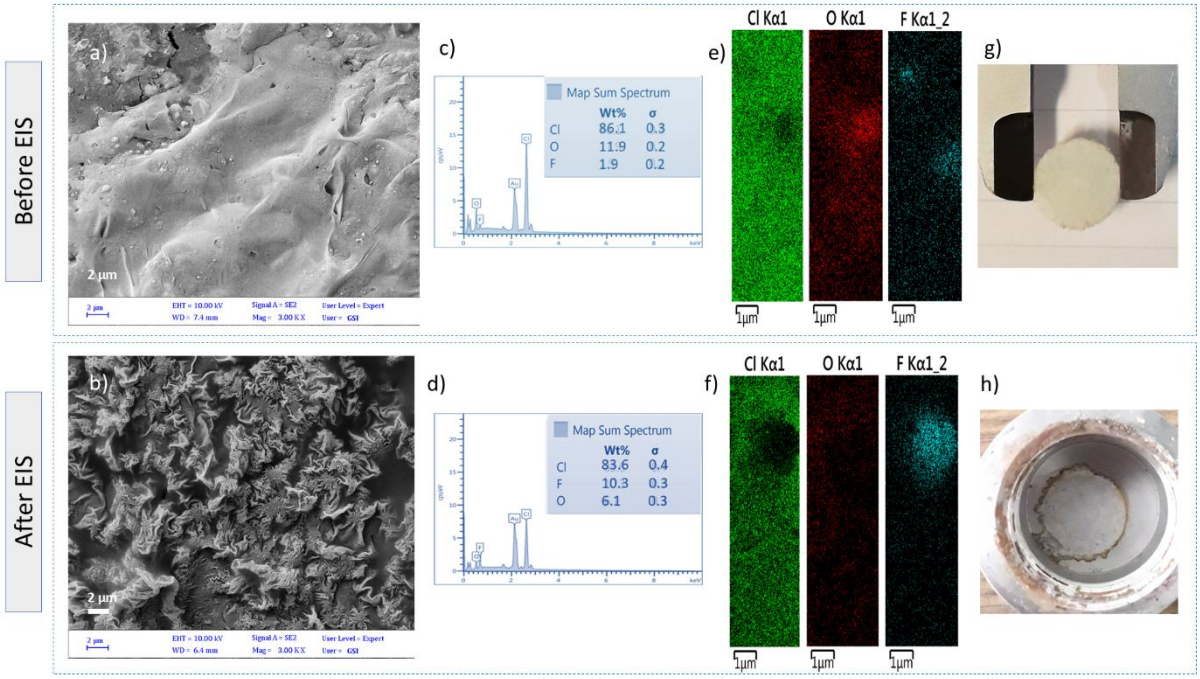

Figure 19. a-b) SEM images of the $Li_2(OH)_{0.995}F_{0.005}Cl$ pellet before and after Impedance spectroscopy; c-d) Elemental wight percentage taken from e and f images before and after EIS; e-f) elemental distribution from the EDS analysis; g-h) digital image of pellet before and after EIS.

4. Conclusion

This study provides a detailed examination of how defects govern lithium-ion migration in Li_2OHCl solid electrolytes. The synergy of EIS and EDS analyses reveals i) Distinct migration pathways in different structural phases; ii) Lower activation energies for vacancy/interstitial mechanisms in RP and cubic phases; iii) Enhanced defect formation and migration barriers at elevated temperatures, especially linked to increased oxygen vacancies and hydrogen-related grain boundary effects. EDS Results after EIS testing detects a rise in oxygen vacancies, confirming increased Schottky defect formation post-thermal cycling. EIS Findings show high grain boundary resistance, implying that barriers—likely due to hydrogen-related defects—impede Li^+ mobility at interfaces. Comprehending these migration and defect mechanisms is vital for the design of high-performance, robust solid-state electrolytes.

Acknowledgments

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Declaration of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Evaluation and simulation of mechanical properties of Gyroid TPMS-based Nitinol with Gradient Lattice Structure

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ABSTRACT

NiTi with triply periodic minimal surface (TPMS) lattice structures is a biocompatible material that is of great interest for biomedical applications due to its properties such as super elasticity (SE), shape memory effect (SME), and biomimetic lattice structure. In this study, the effect of porosity level on the mechanical properties, and shape memory behaviors of Gyroid TPMS-based NiTi lattice structures, which were fabricated by laser powder bed fusion (LPBF), were examined. To investigate the properties of the specimens, different techniques including uniaxial compression test, cyclic compression test, scanning electron microscope (SEM), and finite element method (FEM) by ANSYS Workbench 2023 were performed. It was revealed that as the amount of porosity increased due to the reduction of struts thickness, the compressive modulus (E) and ultimate strength (σmax) decreased by almost 50% and 70%, respectively. Also results showed that E and σmax of gradient lattice structures (GLS) were 25% and 15% less than uniform lattice structures (ULS). Cyclic compression results showed that as the porosity increased from 50-80%, the recoverable strain decreased by 22%, but GLS showed more recoverable strain than ULS. In the next step, FEM by The Auricchio constitutive model (for three-dimensional sample), simulated the SE and von Mises stress distribution of TPMS-based NiTi shape memory alloy. Finally, for predicting the relationships between relative density and mechanical properties, two equations based on the Gibson-Ashby models were introduced to describe E and σmax of Gyroid TPMS-based NiTi lattice structures fabricated by LPBF.

Keywords : NiTi, triply periodic minimal surface, shape memory alloy, Gyroid, Laser Powder Bed Fusion.

1. Introduction

In 1963 it was observed that the NiTi alloy would automatically recover to its original shape when it was deformed at room temperature in contact with a hot object [1]. Shape memory alloys (SMAs) like NiTi are widely used in the biomedical field duo to their remarkable function properties, including shape memory effect (SME) and super elasticity (SE). SME and SE enable large reversible deformation up to 8% by varying the temperature and loading, respectively [2-4]. Individually, the SME and SE make NiTi SMAs more useful than the conventional metallic biomaterials such as cobalt-chromium alloys, Ti-6Al-4V, stainless steels, etc. SME and SE of NiTi SMAs both originate from a reversible thermoelastic martensitic transformation between the austenite phase and martensite phase [1, 5]. SME is a phenomenon that the NiTi can return from a deformed shape to the original shape when heated above transformation temperature (TT). When Nitinol is cooled through TT range, the main properties such as elasticity, strength, and structure significantly change. The SME and SE of NiTi allow us to fabricate intelligent implants with very similar behavior to bone [7]. The TT range must be determined before any other test, because the test

temperature must be known to measure variables such as ultimate strength, yield strength, and elastic modulus. Han et al. showed the martensite start temperature (M_s) and austenite finish temperature (A_f) of $Ni_{50.8}Ti_{49.2}$ is 32.5^{o}C and 53.6^{o}C, respectively [6]. The SE is a phenomenon that the NiTi can recover a large nonlinear strain upon unloading because of elimination of stress-induced martensite. Due to the SE, NiTi SMAs exhibit mechanical behaviors similar to natural bones including high flexibility, easily deformable, and recover a large range of strain, which helps to decrease stress shield effect and promote bone healing [4, 7]. The SE can provide NiTi a low elastic modulus but it is still higher than the elastic modulus of human bones (0.5-25GPa) [8]. Thus, for reducing bulk modulus of NiTi (0.4–15GPa) new porous lattice structures introduced and developed recently [9]. A porous NiTi lattice structure with a suitable architecture can have an elastic modulus equivalent to target human bone [10].

Recent years, triply periodic minimal surface (TPMS) developed as and advanced biomimetic lattice structures with a special surface geometry variation in three coordinate directions and mean curvature radius of zero in the bone tissue engineering field. The main properties of TPMS are minimal surface area, a boundary that is defined by a closed curve and interconnected pores. TPMS structures are made from sharing each unit cell by giving a thickness to the surface and then combined to form 3D symmetrical structure [10, 11]. Studies have shown that TPMS structures have very advantages in bone tissue engineering field for bone regeneration. TPMS advantages include a) the same mechanical properties to bone for supporting bone regeneration [7] b) mimicking biological bone tissues by varying the shape and size of porosity, so they can integrate well with the others surrounding tissues [8] c) interconnected pores promote many cellular mechanisms such as oxygen diffusion, ion exchange, and nutrient transportation [9]. Engineers have been attracted to TPMS structures since they provide an optimized environment for bone regeneration [10]. Moreover, TPMS structures exhibit a good self-supporting property during AM process, consequently improving their manufacturability. Based on the above description, combination of NiTi and TPMS lattice structures has been regarded as a promising solution for bone replacement Yang et al. [11], by laser powder bed fusion (LPBF), showed that increasing the volume fraction of porous NiTi samples increases the elastic modulus and also decreases the superelasticity property.

NiTi structures are produced mainly using traditional manufacturing technologies such as powder metallurgy, self-propagating high-temperature synthesis, hot isostatic pressing, and metal injection molding. The problem is NiTi structures fabricated by traditional methods commonly have unintended pore distributions, inhomogeneous microstructures, internal defects, low dimensional accuracy, and limited desirable structure, causing an uncontrollable mechanical and biological performances [11, 12]. Nowadays, additive manufacturing (AM) technologies such as laser powder bed fusion (LPBF) have been developing due to design flexibility and fabrication of complex porous metallic products (e.g. TPMS structures).Therefore, fabrication of TPMS-based NiTi with excellent performance and precise control of internal topological architectures can now be achieved [13].

Mechanical behaviors of TPMS lattice structures significantly depend on the type of unit cell geometries and the material properties matrix [11]. In 2013, Wild et al. [14] succeeded in making a porous implant by LPBF. Wilde was able to prepare a porous structure with optimal parameters to be placed in the rabbit's body by performing a uniaxial pressure test and surface topography with the help of a computer. Result showed that porous structures with 80% porosity and 500-600µm size have a high potential for bone regeneration and strengthening, especially for complex bone structures. However, the studies about the effect of porosity on the mechanical behaviors of TPMS lattice structures-based NiTi are still hardly reported.

In this paper fabrication of TPMS lattice structures-based NiTi with different porosities (50-80%) that led to different pore size (250-540µm) by LPBF and clearly investigated their mechanical properties, superelastic effect, stress distribution and finite element analysis performances. The findings can help understand the relationship between mechanical behaviors and porosity in TPMS lattice structures-based NiTi.

2. Materials and Methods

Designand LPBF Processing of TPMS based NiTi

In this work, the Triply Periodic minimal surface (TPMS) with a gyroid unit cell was designed using MSLattice software, which is based on MATLAB code and the mathematical equation of the gyroid unit cell. This unit cell was selected because of its self-supporting structure and high fatigue resistance. In addition, the gyroid structure easily mimics the gradient pore characteristics of natural bones. The samples were designed with dimensions of 10mm×10mm×10mm and a unit cell size between 3-3.75. The combination of these parameters allowed design eight different groups of samples, four of which were uniform lattice structures (ULS), and four of which were gradient lattice structures (GLS). The ULSs contained G80-ULS, G70-ULS, G60-ULS, and G50-ULS. These structures were designed with unit cell sizes of 3.000, 3.125, 3.275, and 3.750, and relative densities of 20%, 30%, 40%, and 50% (0). GLS structures were designed using the unit cell size variation method. Thus, the maximum and minimum values of the unit cell were 3.75 and 3, respectively, and the relative density changed depending on the desired porosity. To design G80-GLS, G70-GLS, G60-GLS, and G50-GLS, their relative densities were 20%, 30%, 40%, and 50%, respectively. Further details of the two groups of ULS and GLS produced in this study are shown in0.

Table 1. MSLattice parameters for designing ULS of Gyroid TPMS-based NiTi.

Unit cell size	Porosity percentage (%)	Porosity size (micron)	ULS Code
3.000	79.9	540	G80 ULS
3.125	70.3	450	G70 ULS
3.275	60.2	350	G60 ULS
3.750	50.2	250	G50 ULS

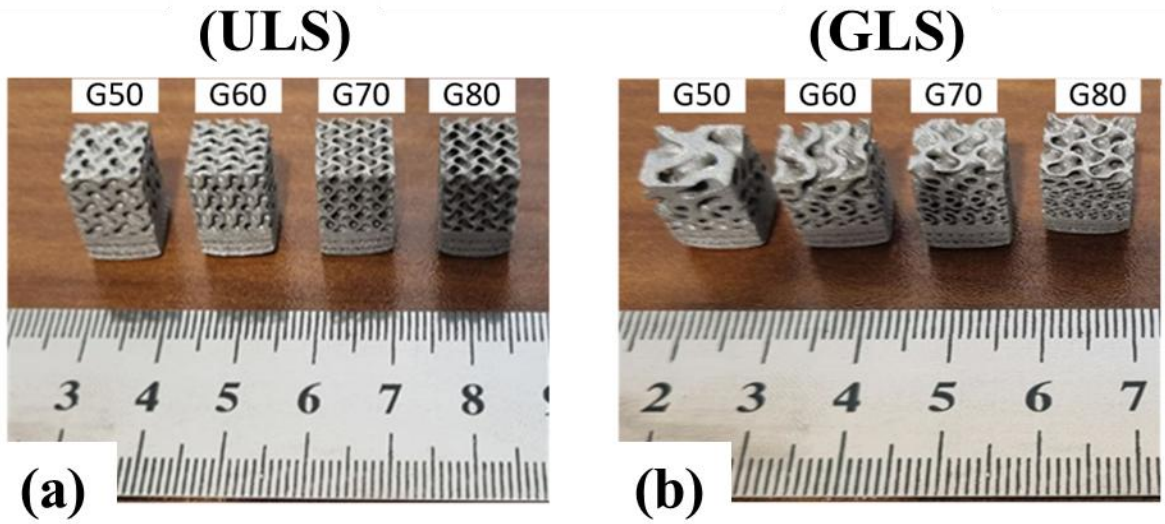

Figure 1. Illustration of the Gyroid TPMS-based NiTi samples fabricated by LPBF: a) uniform lattice structures (ULS) and b) gradient lattice structures (GLS). Eight Samples used in this study with porosity of 50, 60, 70 and 80% in each category.

All the samples were produced using pre-alloyed NiTi powder manufactured by TLS Technik GmbH (Bitterfeld). The particle size of the powder was 15–45µm, containing 50.8at%Ni and balanced Ti. The powder particle size distribution was measured to be D_{10}=22µm, D_{50}=33µm and D_{90}=44µm. scanning electron microscope (SEM) micrograph used for showing the morphology of powder particles (0a).

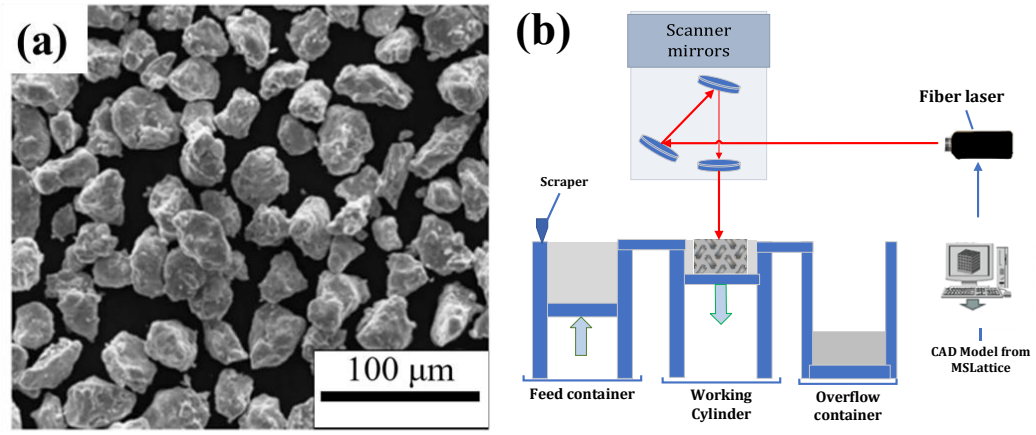

Figure 2. Illustration of a) SEM micrograph of pre-alloyed Ni50.8Ti49.2 powder produced by EIGA process, and b) The schematic of LPBF system.

Both the ULS and GLS samples were produced using a Sisma-Mysint 100 Powder Bed Fusion 3D printing machine equipped with an ytterbium fiber laser (cw, $P_{max,\,theor}$ = 200W, λ=1076.5nm). The parameters used in this study are listed in 0.

Table 2. LPBF process parameters used for fabrication of Gyroid TPMS-based NiTi

Parameter	Values
Laser power (P)	70-150 (W)
Scanning speed (V)	700-1100 (mm/s)
Hatch distance (dH)	60, 100 (µm)
Layer thickness (t)	20, 25 (µm)
Energy densities (E)	50-120 (J/mm^3)
Laser spot diameter (dL)	30 (µm)
Oxygen level	< 200 (ppm)

2.2 Mechanical Testing

A Zwick ZO50-5 tone testing machine (Zwick Company, Germany) was used to perform the uniaxial compression and cyclic compression tests. All uniaxial tests were conducted at an elastic strain rate of $10^{-4}s^{-1}$ at 70°C, according to the ISO 13314 (ISO 2011). The temperature was set above the austenite phase transformation temperature so that the samples were in a single-phase austenite state, and we could examine the behavior of the austenite phase under pressure. The total strain percentage was 80% to demonstrate the failure of the structure. The elastic modulus (E) and maximum stress (σ_{max}) was calculated according to this standard. Cyclic tests were performed in the force control mode of the testing machine. In this test, the same temperature and strain rate were used, but the total strain was 16% to demonstrate the superelastic effect in Gyroid TPMS-based NiTi. The recoverable and unrecoverable strains were measured by plotting the stress-strain curve of the cyclic test.

2.3 Finite Element Analysis (FEA)

To predict the stress distributions of the ULS and GLS samples under compressive loading, FEA models of the samples were created using ANSYS Workbench 2023. The objective of the FEA simulations is to

understand the deformation mechanism and stress distribution under compressive loading. A tetrahedral element type with edge length of 0.1 mm based on a mesh sensitivity study was used to mesh the FEA models. In total, approximately 5,000,000 elements were generated. For the simulation of compressive loading, a frictionless support was applied on the bottom surfaces, while a 2mm displacement was applied on the top surfaces. The FEA results included the elastic and plastic behaviors of the samples. For the simulation of cyclic loading, we used the Auricchio constitutive model, which can predict super elastic behavior. The Auricchio constitutive model has six parameters, as shown in 0. The first is the phase transformation forward stress at start, σ^{AS}_{s}; the second is the phase transformation forward stress at finish, σ^{AS}_{f}; the third is the phase transformation backward stress at start, σ^{SA}_{s}; the fourth is the phase transformation backward stress at finish, σ^{SA}_{f}; the fifth is the maximum recoverable strain, L; and the sixth is the difference between tension and compression, α[15, 16]. For simplification, two assumptions were made: first, the structures fabricated by LPBF were consistent with the CAD solid model; second, the samples at high temperature were completely in the austenite phase, and the final residual strain was zero.

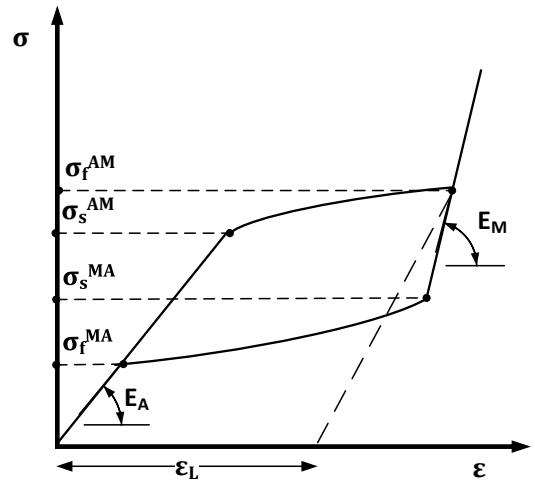

Figure 3. Idealized stress-strain diagram for superelastic behavior of NiTi according to Auricchio model.

2.4 Statistical methods

For all experiments, average values and standard deviations (SD) were calculated from 3 different measurements, and values were reported as average ± SD. The percent change (PC) method was used to see the differences between measurements. If PC is positive, it shows an increase in second values, and if PC is negative, it shows a decrease in second values. Equation 1 shows the PC method.

$$PC = \frac{V_2 - V_1}{V_1} \times 100 \quad \textbf{(1)}$$

3. Results And Discussion

3.1. Compressive Strength

0a and b show the compressive stress-strain curves of the Gyroid TPMS-based NiTi at different porosities with uniform and gradient structures, respectively. The samples with different porosities showed similar mechanical responses in four stages, but their overall mechanical properties had obvious differences. In the initial stage, known as elastic deformation, the stress increases linearly with the strain. The slope of this relationship represents the compressive modulus. The subsequent stage involved elastic-plastic deformation, which began when the stress-strain curve deviated from the linear response. The stress at which the axial loading curve deviated by 0.2% from the linear-elastic region was defined as the nominal yield strength. During the elastic-plastic deformation, the stress increased nonlinearly until it reached the

ultimate strength (σ_{Max}). Subsequently, a sharp drop in stress occurred, forming a short yield plateau. The stress-strain curves then entered a third stage, a long plateau with fluctuating stress. Finally, most struts in the lattice structure were destroyed and compressed, leading to a densification stage where stress increased sharply as strain continued to rise.

0c and d demonstrate the compressive modulus and ultimate strength of uniform and gradient Gyroid TPMS-based NiTi lattice structures with different porosity levels, which were extracted from the stress-strain curves. The results depicted that for the uniform lattice structures (ULSs), all the compressive modulus and ultimate strength significantly decreased as the porosity increased. In ULSs the compressive modulus and ultimate strength were only 2300MPa and 326.7MPa respectively in the lattice structure with 50% porosity, while they were 1004MPa and 100.3MPa respectively in the one with 80% porosity. For gradient lattice structures (GLSs), the compressive modulus and ultimate strength gradually decreased with the increase of the porosity percentage. The compressive modulus and ultimate strength were 1644MPa and 270.9MPa respectively in the GLS with 50% porosity, while they were 806MPa and 74.6MPa respectively in the one with 80% porosity. For a constant porosity (for example G50), changing the structure from ULS to GLS reduced the compressive modulus and ultimate strength by 28% and 17%, respectively.

The porosity percentage directly influence the mechanical properties of lattice structures. It is so helpful to derive a mathematical model between mechanical properties and the amount of porosity in ULS and GLS Gyroid TPMS fabricated by LPBF. It will help engineers design NiTi implants with desired mechanical properties. The experimental results can be utilized to derive nonlinear equations for predicting the mechanical behavior of lattice structures with varying amount of porosity. The Gibson–Ashby models express the elastic modulus and ultimate strength (Equations 2,3) [17].

$$\frac{E}{E_0} = C_1 \rho^n \quad \textbf{(2)}$$

$$\frac{\sigma_p}{\sigma_{p,0}} = C_2 \rho^m \quad \textbf{(3)}$$

Where ρ is the relative density of structure; E_0 and $\sigma_{p,0}$ are the elastic modulus and ultimate strength of the bulk materials, respectively; C_1, C_2, n and m represented the constant coefficients and exponents, which can be determined by fitting the experimental results using the formulas mentioned above.

The coefficients of determination or R squared (R^2) for E_{ULS}, E_{GLS}, $\sigma_{p,ULS}$ and $\sigma_{p,GLS}$ were 0.838, 0.939, 0.997 and 0.999, respectively, indicating a well fit using power-law models based on Equations (2) and (3) for the experimental results, see 0e and f. It is important to acknowledge that differences exist between the experimentally determined mechanical properties obtained from compressive tests and the estimated properties derived using Equations (2) and (3). These discrepancies may arise due to factors such as neglecting the impact of residual stress, powder adhesion, microstructure inhomogeneity and other defects when modeling the mechanical behavior of uniform or gradient Gyroid TPMS-based NiTi fabricated via 3D printing [18].

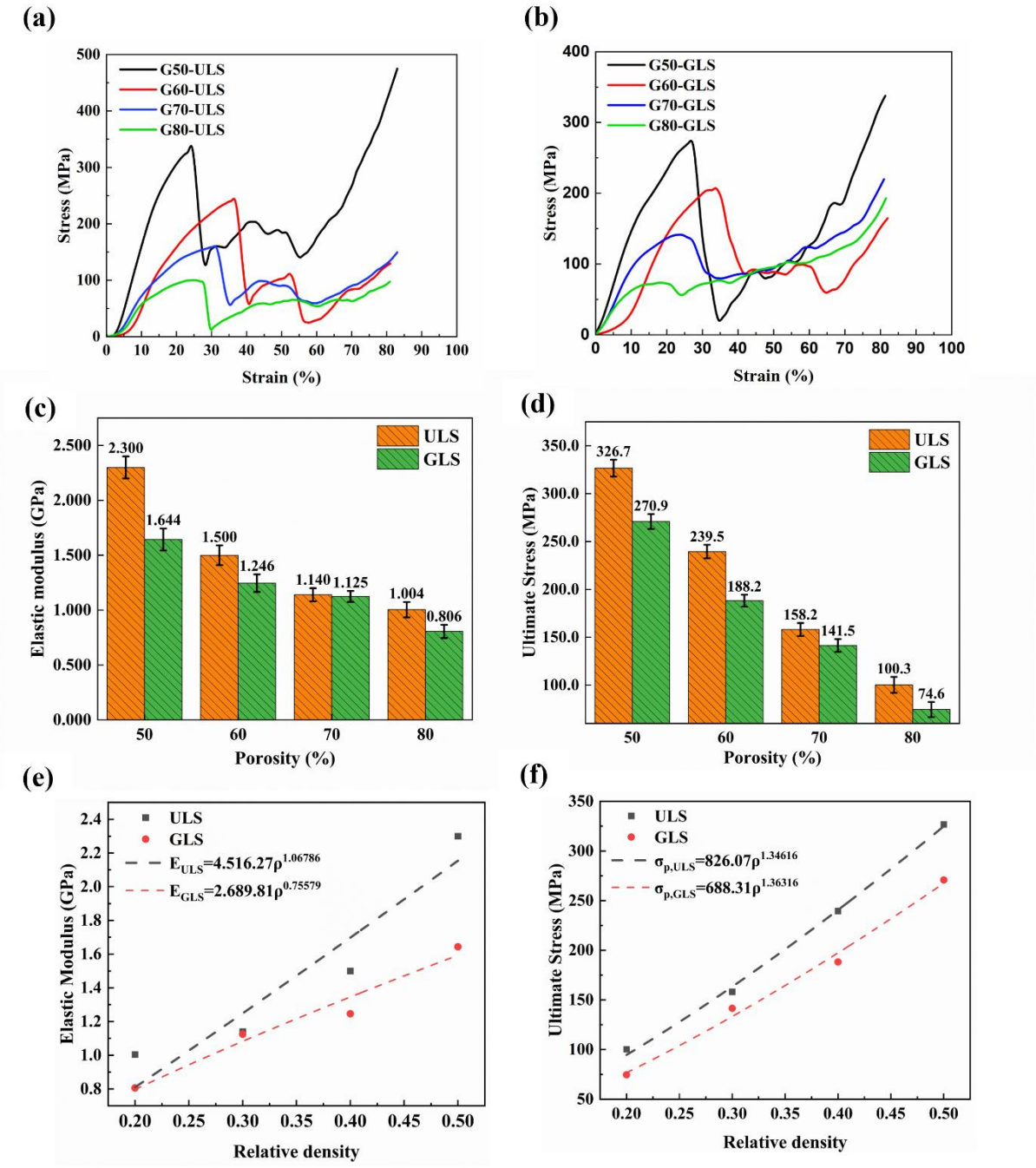

Figure 4. a) and b) illustrate the compressive stress-strain curves of the ULS and GLS Gyroid TPMS-based NiTi, respectively, where each colored curve represents an individual sample. c) Summary of the elastic modulus results, and d) shows the ultimate strength results of compressive test. e) and f) show fitting curves of elastic modulus and ultimate strength, respectively, based on Equation (2) and (3).

3.2 Superelastic properties

0a and b show the cyclic compressive stress-strain curves of the Gyroid TPMS-based NiTi with uniform and gradient structures, respectively, at different porosities. The percentage of recovered strains from the total strain during unloading extracted from the loading-unloading curves is shown in 0c. As shown in 0c, for the gradient Gyroid TPMS-based NiTi, the sample with 50% porosity exhibited the largest recovered strain during unloading. For GLSs, as the porosity increased from 50% to 80%, the percentage of recoverable strain from the total strain decreased from 65% to 50%. In addition, for uniform Gyroid TPMS-based NiTi, as the porosity increased from 50% to 80%, the percentage of recoverable strain from the total strain decreased from 59% to 46%. In general, the amount of recoverable strain decreased with increasing porosity percentage. It should be noted that at any percentage of porosity, the amount of recoverable strain of the gradient structures was greater than or equal to that of the uniform structures. All Gyroid TPMS-based NiTi fabricated by LPBF exhibited a good shape-memory effect.

As the porosity increased, the proportion of superelastic response decreased in the Gyroid TPMS-based NiTi fabricated by LPBF. This change occurred even though the percentage of recovered strain from the total strain remained affected. The underlying reason is the combined axial compressive deformation and bending deformation of the struts along the vertical axis. While the overall deformation at 16% remained consistent across the ULS and GLS Gyroid TPMS with varying porosities, the local strut deformation differed. An increase in the porosity led to a significantly higher local strain in the struts. This increased strain broadened the stress-induced martensite bands and enhanced collisions between stress-induced hcp martensite bands, resulting in a greater driving force for the reverse transformation of stress-induced martensite. Therefore, the martensite phase was more stable than before. Consequently, A_s and A_f temperatures increased, the interval between them broadened, and the amount of stress-induced martensite that could retransform to austenite after unloading the samples spontaneously at the testing temperature decreased.

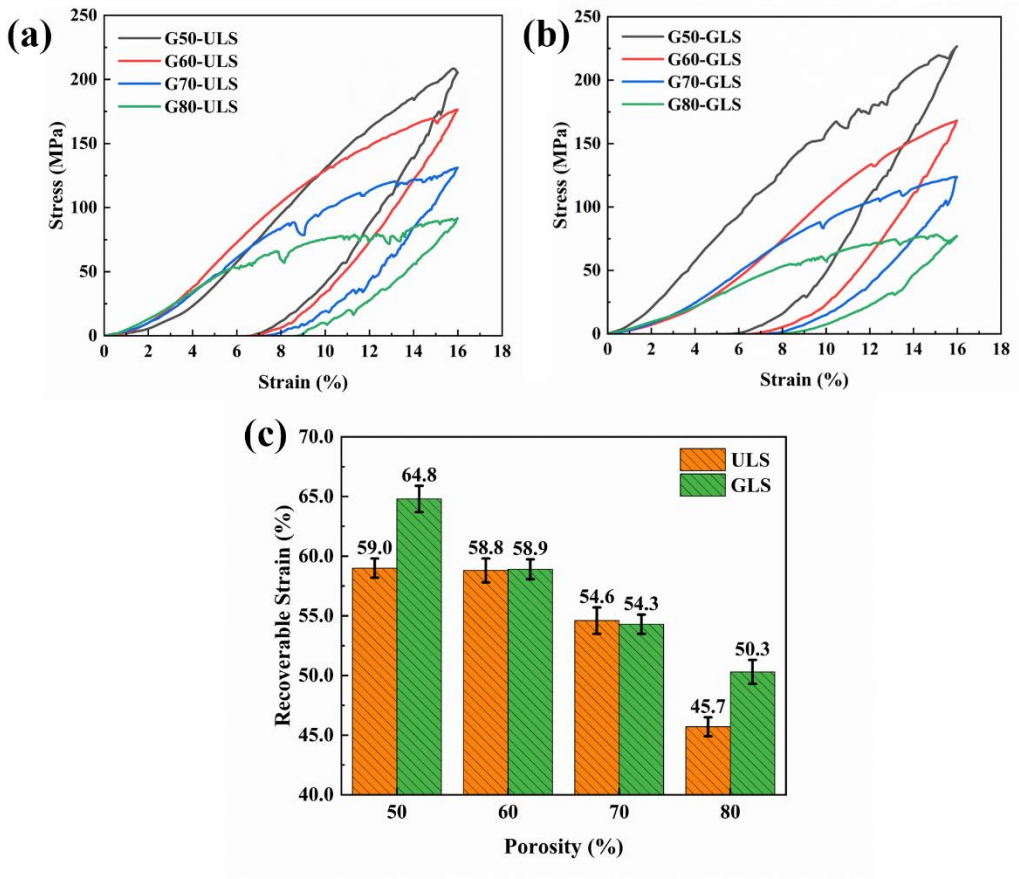

Figure 5. a) and b) illustrate the cyclic stress-strain curves of the ULS and GLS Gyroid TPMS-based NiTi, respectively, where each colored curve represents an individual sample. c) show the percentage of recovered strains from the total strain during unloading for ULS and GLS samples.

3.3 Finite element analysis result

Finite element analysis was used to determine the von Mises stress distributions for ULS and GLS. For this regard a simple elastic-plastic model was used to simulate the Gyroid TPMS-based NiTi. 0 shows the von Mises stress distribution of samples with 50% porosity under compressive loading in the direction of reducing porosity and perpendicular to reducing porosity. For a better understanding of the deformation mechanisms and stress concentration at the macroscopic level within the Gyroid TPMS-based NiTi samples. As shown in the 0, the stress concentrated strongly on the center of the curved strut in all the structures, where cracks could more easily initiate and propagate. For the uniform structure, it was found that the stress concentrated on the yellow parts, exhibiting a higher stress concentrated in the thicker lattice structure region. Thus, for the ULS, the stiffer and higher-density parts acted to shield the lower-density parts from some of the applied stress. For the gradient structure with compressive loading perpendicular to the reducing porosity direction, the FEA showed almost no concentrated stress. These results show that the deformation mode was not significantly influenced by the porosity gradient perpendicular to the compressive loading direction. For the gradient structure with compressive loading in the direction of reducing porosity, the stress distribution at the bottom layer with a high porosity percentage was found to experience a stress concentration higher than other points, and that stress decreased layer-by-layer with increasing density. The significant stress concentration distribution along the building direction caused a larger strain in this structure, where several layers at the bottom collapsed, and the top parts remained consistent. Therefore, the stress distribution corresponded to the layer-by-

layer collapse mechanism shown in 0.

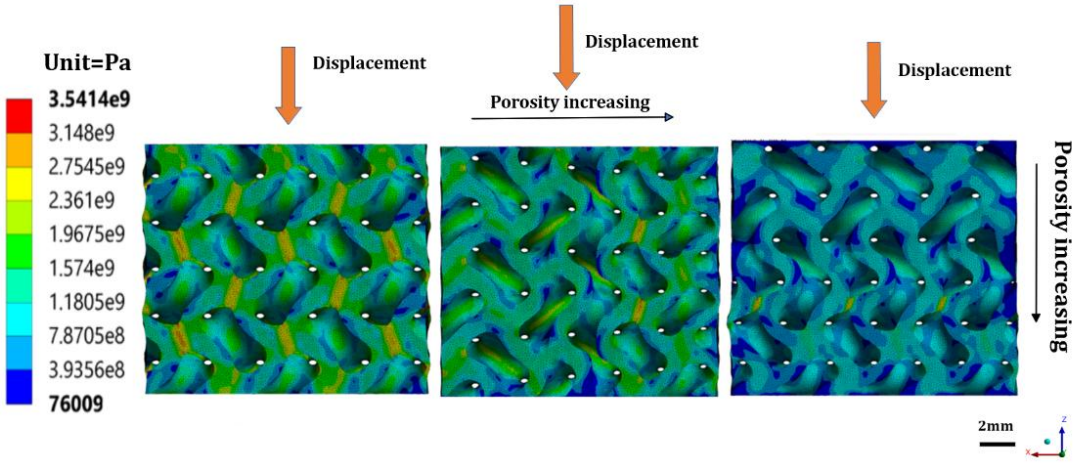

Figure 6. Von-Mises stress distribution from left to right for G50-ULS, G50-GLS displacement perpendicular to the direction of increasing porosity and G50-GLS displacement in the direction of increasing porosity.

After analyzing the output results from the ANSYS software, the elastic modulus and yield stress for each sample in both the experimental and simulated modes were compared (0).

Table 3. Comparison of elastic modulus and yield strength of experimental compressive test and FEA.

	Sample	E^{Exp} (Mpa)	E^{FE} (Mpa)	σ_y^{Exp} (Mpa)	σ_y^{FE} (Mpa)
ULS	G50	2300±100	2242	228.2±4.8	198.9
	G60	1500±90	1397	101.9±3.1	137.3
	G70	1140±60	995	65.0±2.8	101.3
	G80	1004±70	601	51.4±2.3	62.0
GLS	G50	1644±100	2229	117.7±4.9	203.7
	G60	1246±80	1385	133.9±2.4	149.6
	G70	1125±50	989	83.6±2.8	94.0
	G80	806±60	549	42.0±3.7	59.7

As previously mentioned, the Auricchio constitutive model relies on six key parameters to create a stress-strain hysteresis loop. In the initial step, the properties of all eight Gyroid TPMS-based NiTi were adjusted to closely align the simulation results with the experimental data. 0 presents the superelastic parameters of the Gyroid TPMS-based NiTi fabricated using the LPBF method. Notably, the unrecoverable strain observed in the experimental results differed from the simulation outcomes because of the model's assumption of full strain recovery, which influenced the parameter definitions.

Table 4. Material properties of cyclic test for FEA of Gyroid TPMS-based NiTi in ANSYS.

E_A	E_M	σ_s^{AS}	σ_f^{AS}	σ_s^{SA}	σ_f^{SA}	ε	ν
11000 MPa	16000 MPa	601.25 MPa	720 MPa	219.141 MPa	50 MPa	0.09	0.33

0 shows the experimental stress-strain diagrams along with the simulation of G50, G60, G70, and G80 related to the ULS and GLS categories. In almost all samples (except G50), the values of the elastic modulus of austenite and martensite in the simulation results were lower than the actual values. However, the simulation results of the elastic modulus of austenite and martensite have high errors until the error

reaches its maximum value of 50% in the G80-ULS sample (0). This result makes the simulation of super-elastic behavior questionable and shows that more research is needed on the simulation of these types of samples.

00 compares the stress required to transform austenite to martensite and martensite to austenite in the porous ULS and GLS Gyroid TPMS-based NiTi samples under experimental conditions with the stress required to perform the transformation under simulated conditions. Similar to the elastic modulus, the austenite-to-martensite transformation stress decreases with increasing porosity. By increasing the percentage of porosity from 50% to 80% for ULS samples, the starting stress of austenite to martensite transformation and the starting stress of martensite the martensite-to-austenite transformation have decreased by 57% and 76 %, respectively. For the GLS samples, with an increase in porosity percentage, the starting stress of austenite to martensite and the starting stress of martensite to austenite decreased by 61% and 69%, respectively. Owing to the residual strain in the Gyroid TPMS-based NiTi super-elastic graphs, the transformation stress of martensite to austenite could not be measured correctly, and errors were encountered in the relevant data.

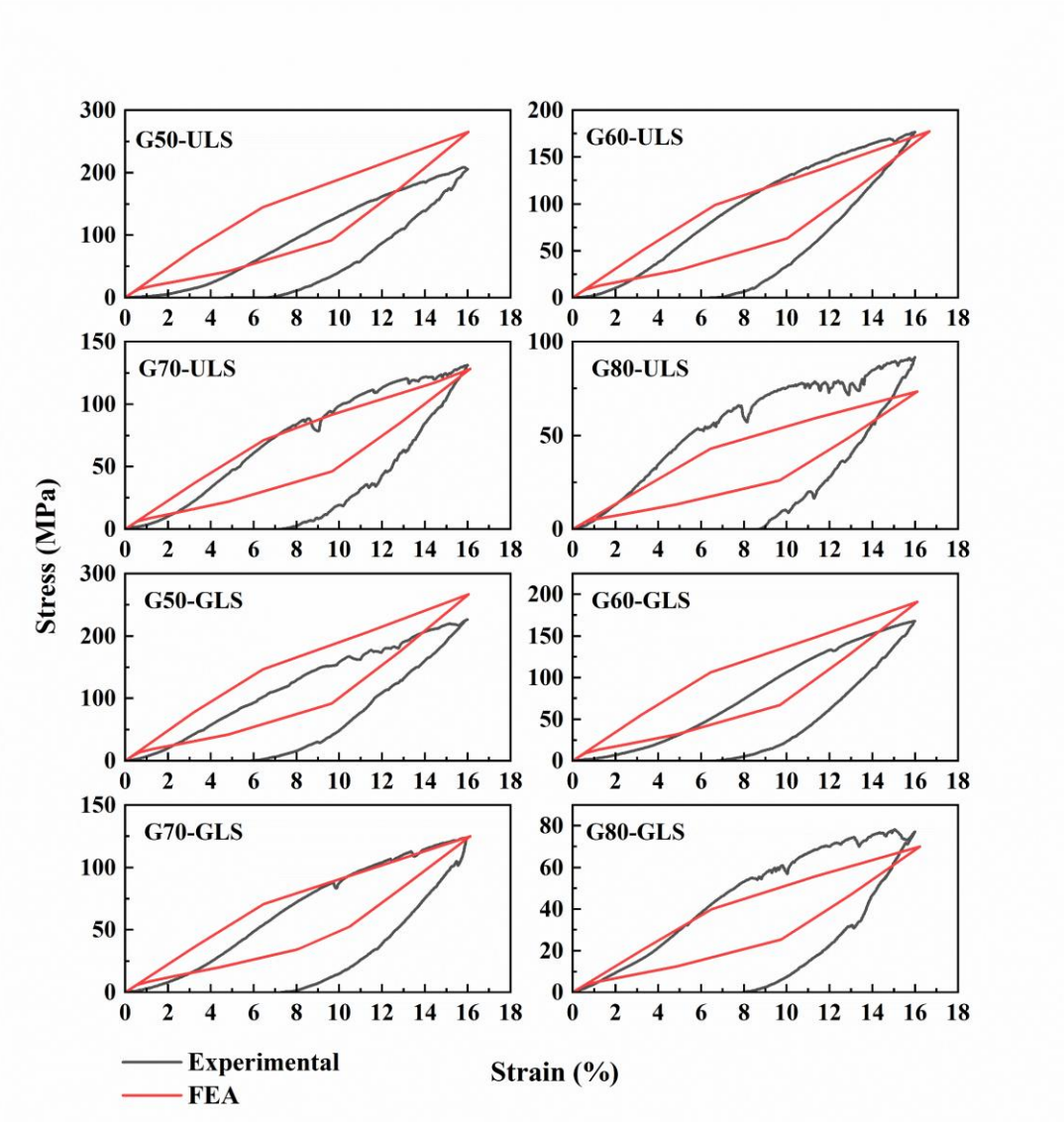

Figure 7. Comparison of experimental and FEA results of cyclic tests to determine superelastic behavior.

Table 5. The austenite and martensite modulus at experimental and simulated cyclic compression test.

	Sample	E_A^{Exp} (MPa)	E_A^{FE} (MPa)	E_M^{Exp} (MPa)	E_M^{FE} (MPa)
ULS	G50	1797±111	2404	2886±165	2814
	G60	1773±120	1491	2528±153	1724
	G70	1382±71	1143	2092±117	1271
	G80	1226±85	663	1439±91	706
GLS	G50	1719±121	2333	2663±100	2847
	G60	1507±168	1723	2379±143	2008
	G70	1278±113	1125	1982±86	1298
	G80	831±66	625	1561±121	716

Table 6. The austenite to martensite transformation stresses at experimental and simulated cyclic compression test.

	Sample	σ_s^{AM-Exp}(Mpa)	σ_s^{AM-FE}(Mpa)	σ_s^{MA-Exp}(Mpa)	σ_s^{MA-FE}(Mpa)
ULS	G50	123.5±4.7	143.1	102.1±4.3	96.5
	G60	111.7±2.3	98.2	83.2±3.1	67.9
	G70	79.6±2.6	70.3	59.2±2.8	49.7
	G80	53.6±4.3	43.6	24.1±2.6	26.4
GLS	G50	136.9±4.0	144.2	101.1±3.8	98.2
	G60	109.9±3.7	103.5	24.9±2.1	72.2
	G70	75.6±5.4	68.4	33.8±2.7	34.8
	G80	53.1±3.9	38.7	31.7±2.9	27.0

4. Conclusion

The main goal of this study was to introduce a structure and material similar to trabecular bone, in this regard, Gyroid TPMS-based NiTi with Gradient Lattice Structures with pore size between 250-540µm are designed and printed by MSLattice and LPBF, respectively. The results of the uniaxial pressure test showed that the elastic modulus of Gyroid TPMS-based NiTi with porosities of 50%, 60%, 70%, and 80% are between 2300MPa and 800MPa. Considering that the elastic modulus of the spongy part of the bone (trabecular) is between 150MPa and 1650MPa [19], except for the G50-ULS structure, the other tested structures can be used as implants. This result shows that the choice of Gyroid structure with porosities of 50%, 60%, 70%, and 80% together with nitinol is completely mimic the mechanical properties of trabecular bone. For ULS samples, increasing the porosity from 50% to 80% decreases the elastic modulus by 56%, the yield strength by 77%, and the ultimate strength by 69%. On the other hand, increasing the porosity from 50% to 80% for GLS samples, decreases the elastic modulus by 51%, the yield strength by 64%, and the ultimate strength by 72%.

The results of the cyclic pressure test showed that increasing porosity from 50% to 80%, decreases the recoverable strain by 22%. It should be noted that in this research, only porosities of 50%, 60%, 70%, and 80% were studied, and other studies have shown that in porosities less than 50% with an increase in porosity the recoverable strain increase [11]. On the other hand, the comparison of the ULS and GLS

structures showed that structures with gradient porosity show more recoverable strain than uniform porous structures. This result has helped make GLS structures more popular and has shown that these structures have good recoverable strain (high superelastic property) in addition to being very similar to the bone structure and having an elastic modulus closer to it.

In the von Mises stress distribution on the ULS and GLS samples, the points of stress concentration from which the probability of failure and crack growth are higher are clearly shown. In the ULS parts, stress concentration points are distributed symmetrically and uniformly in the part, whereas in the GLS parts, stress concentration points are more located in the part that has more porosity and lower relative density. Therefore, it can be said that during the failure of the ULS parts, a continuous crack is created throughout the part; however, in the GLS parts, the crack starts from the layers with low relative density, and after the failure of that layer, it spreads to the next layers.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Parameter affecting the lightening of the rotor of the vehicle under torsional force, a simulation study

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ABSTRACT

In response to the growing demand for energy efficiency and sustainability in the automotive industry, reducing weight and optimizing key powertrain components like rotors and shafts has become increasingly important. These components operate under complex torsional loads and must resist fatigue, vibration, and high-speed rotation. This study uses numerical simulation and finite element analysis (FEA) in Abaqus to investigate the torsional behavior and structural performance of automotive rotors, focusing on advanced materials and optimized geometries. Traditional materials like standard steel are compared with advanced alternatives such as carbon fiber-reinforced polymers (CFRPs), titanium alloys, and high-strength steels. Modal and harmonic analyses show that hollow shafts made from these advanced materials offer significant weight reduction while maintaining or improving torsional stiffness and vibration damping. This research presents a framework for designing lightweight, high-efficiency rotors that support emission reduction and enhanced vehicle performance.

Keywords : rotor, analysis, Abaqus, mechanical properties, torsional force, Ti-6Al-4V.

1. Introduction

The global push for sustainability in the automotive industry has necessitated the development of more energy-efficient vehicles. One of the most effective approaches to achieving this goal is the reduction of vehicle weight, which directly contributes to improved fuel economy and reduced greenhouse gas emissions [1] . Among the many components of a vehicle, the shaft or rotor is a key element responsible for transmitting mechanical power and is subjected to complex torsional loading conditions, especially under dynamic operation [2] . The lightweighting of automotive shafts, while maintaining or enhancing their structural performance, presents significant engineering challenges. Engineers must ensure that the shaft can withstand high torsional loads, fatigue, and vibrations without failure. Achieving this balance often involves selecting advanced materials and employing innovative design strategies that reduce mass without sacrificing mechanical integrity [3].

Advanced materials such as high-strength steels, titanium alloys, and composite materials like carbon fiber-reinforced polymers have been widely explored for use in automotive and aerospace shaft

applications. These materials provide superior strength-to-weight ratios, making them highly effective for reducing the mass of rotating components while maintaining or improving structural integrity [4]. Their inherent properties, such as excellent corrosion resistance, high fatigue strength, and thermal stability, make them ideal candidates for harsh operating environments where traditional materials may fail [5]. Among these, carbon fiber-reinforced polymers (CFRPs) have gained significant attention due to their remarkable mechanical properties and flexibility in design. CFRP shafts, for example, can be manufactured with directional stiffness, allowing engineers to tailor the mechanical response to specific loading conditions. This characteristic not only improves performance but also enhances vibration damping capabilities [6]. Titanium alloys, while more expensive, offer excellent strength and resistance to fatigue, especially under high-cycle loading typical in high-speed rotating systems.

Geometric design plays a pivotal role in enhancing the torsional behavior of shafts. Parameters such as wall thickness, outer diameter, and shaft length directly influence stiffness and mass distribution. Studies have shown that employing hollow configurations and applying optimization techniques like topology optimization and response surface methodology (RSM) can significantly improve dynamic performance and durability of shaft systems.[7, 8]

Computer-aided engineering (CAE) platforms such as Abaqus are extensively employed to simulate stress fields, torsional deflection, and failure mechanisms in composite shaft systems. These simulations enable engineers to refine material and geometric configurations under realistic operational loads, offering cost-effective insights into dynamic behavior and structural integrity[9]. In the analysis of automotive rotor behavior under dynamic loading, CAE plays a crucial role—especially in evaluating the effects of unbalanced rotation, which can lead to increased vibration and fatigue. Accurate modeling using Abaqus enables prediction of stress distribution and system dynamic response under nonlinear and time-dependent loads[10] .The use of hollow and composite shafts has gained popularity in automotive design to reduce weight and enhance drivetrain efficiency. CAE-based simulations are critical in optimizing shaft geometry and material selection by enabling comparison of stress performance, buckling modes, and natural frequencies across different configurations [11].

Moreover, torsional vibration analysis plays a significant role in evaluating the operational stability of shafts. Excessive torsional vibrations can lead to noise, harshness, and even mechanical failure over time. Through modal and harmonic analysis, engineers can predict natural frequencies and identify critical speeds that may pose risks during operation.[12]

Despite numerous studies, there is still a gap in understanding the combined impact of material choice, geometric configuration, and boundary conditions on the torsional performance of lightweight shafts. Many studies focus on isolated factors, but few investigate the integrated effects using comprehensive simulation frameworks [13]

This study, through numerical simulations and advanced engineering tools, analyzed the torsional performance of an automotive rotor under dynamic loading conditions. By evaluating different geometric configurations and comparing conventional materials with advanced options such as carbon fiber-reinforced polymers and titanium alloys, the results showed that optimized designs using these materials can achieve significant weight reduction while maintaining or improving torsional stiffness, fatigue resistance, and vibration damping. These findings can play an important role in the development of lightweight, high-efficiency powertrain systems aligned with goals of fuel economy and emission reduction.

2. Materials & Method

In this study, a finite element simulation framework was developed using Abaqus to investigate the torsional performance of automotive drive shafts with an emphasis on structural optimization and weight reduction. The shaft was modeled as a hollow cylindrical structure with precisely defined dimensions,

enabling a detailed sensitivity analysis of geometric parameters such as wall thickness and outer diameter. Boundary conditions were applied by fully constraining one end of the shaft while subjecting the opposite end to a gradually increasing torsional moment, simulating realistic operational loading conditions. The primary aim of this research is to evaluate the torsional response and dynamic behavior of shafts constructed from advanced engineering materials under rotational loading. Selected materials include high-strength steel, titanium alloy (Ti-6Al-4V), and carbon fiber-reinforced polymer (CFRP)—chosen for their superior specific strength, fatigue resistance, and vibration damping characteristics. Accurate material properties were extracted from validated literature and incorporated into the simulation environment for high-fidelity modeling. To gain deeper insights into the dynamic response of each shaft configuration, both modal analysis and harmonic response analysis were conducted. These analyses allowed for the identification of natural frequencies, mode shapes, and resonance risks, as well as the characterization of stress distribution under cyclic torsional loads.

Table 1. Chemical composition of materials used in simulation

Material Name	Chemical composition												
	C	Cr	Mn	Si	Max S-P	Fe	Al	Ti	V	Cu	Zn	Mg	Zr
1-0762	0.45	0	1.5	0.4	S: 0.3 P: 0.06	0	0	0	0	0	0	0	0
Ti-6Al-4V	0	0	0	0	0	0.25	6	90	4	0	0	0	0
AL 7075	0	0.23	0.3	0.4	0	0.5	88.32	0.2	0.2	1.6	5.5	2.5	0.25

The following table presents the chemical composition and key properties of the selected materials, which serve as the foundational dataset for comparative evaluation and multi-objective optimization of material–geometry combinations in the lightweight shaft design process.

For analysis, first a 3D model was designed in CAD software and in CAE software, the part and the torsional force were shown before simulation (Figure 1) and Abaqus software was selected. Then, 7075 aluminum and titanium alloy were selected for comparison. Tables 1 and 2 show the mechanical properties and chemical compositions.

Table 2. Mechanical properties of materials used in simulation

Material	Young's Modulus (GPa)	Yield Strength (MPa)	Density (kg/m³)	Notes
1-0762	200	700-850	7850	High strength-good resistance to impact
Ti-6Al-4V Titanium Alloy	113	96	4430	Lightweight, corrosion-resistant
Aluminum Alloy 7075-T6	70	560	2810	Common lightweight aerospace alloy

Following the presentation of the chemical compositions of the engineering materials in Table 1, Table 2 outlines the key mechanical properties of the selected alloys. These include Young's modulus (indicating stiffness and resistance to elastic deformation), yield strength (reflecting the material's resistance to plastic deformation), and density (a critical factor in optimizing the strength-to-weight ratio). These parameters are essential for assessing the mechanical performance of materials under operational conditions. The table compares three widely used industrial materials: medium-carbon steel (1-0762), known for its high strength and reasonable ductility; titanium alloy (Ti-6Al-4V), offering excellent mechanical strength and corrosion resistance; and aluminum alloy (7075-T6), valued for its lightweight

nature and good fatigue resistance. Understanding the differences in mechanical behavior among these alloys provides a foundation for selecting the most appropriate material in structural design—especially in fields such as aerospace and automotive engineering, where optimizing both mechanical performance and structural weight is crucial.

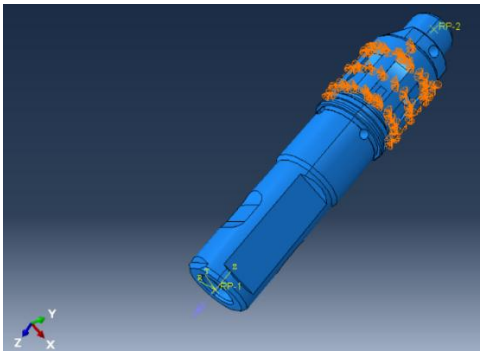
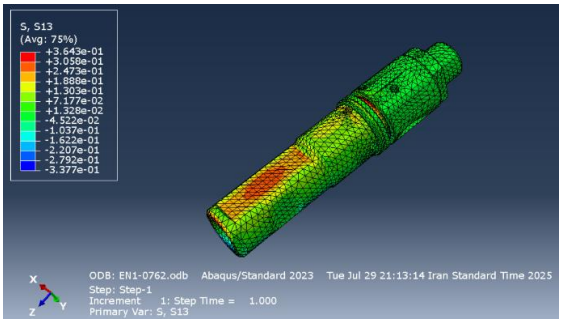


Figure 1. Design in CAE software.

3. Results and Discussion

The rotor is currently made of 1-0762 material, which has high tensile strength. Titanium alloy has a higher strength than the material used, and aluminum 7075 has a lower strength than the material used. Rotors are usually made of high-strength alloy materials to ensure that they can withstand the significant stresses and strains they encounter during operation. In this design, special attention has been paid to changing the material by two common materials. The materials used have a lower modulus of elasticity than the previous material.
During operation, the rotor is subjected to considerable **torsional loads** as it transfers torque within the drivetrain. This torsional stress can lead to deformation or fatigue failure if the material lacks sufficient strength and stiffness. Therefore, material selection plays a critical role in ensuring both mechanical integrity and long-term durability.

The materials most commonly used in rotors are 1-0762 and **Ti-6Al-4V**, which offer good **strength**. Ti-6Al-4V, in particular, combines high specific strength with excellent corrosion resistance and thermal stability. While its density is higher than that of aluminum, it remains lighter than steel and delivers superior mechanical performance, making it well-suited for high-stress, weight-sensitive rotor applications(Figure 2).



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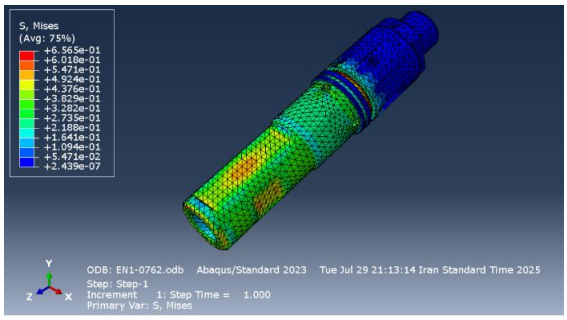

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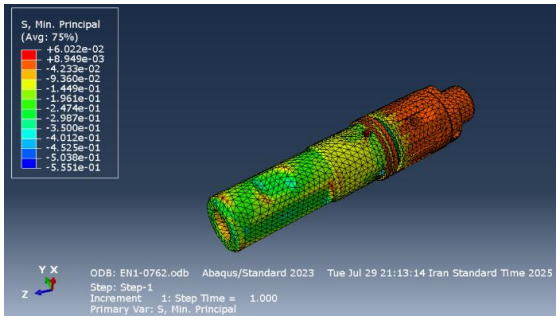
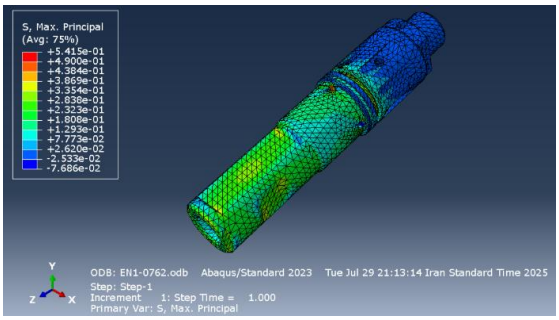


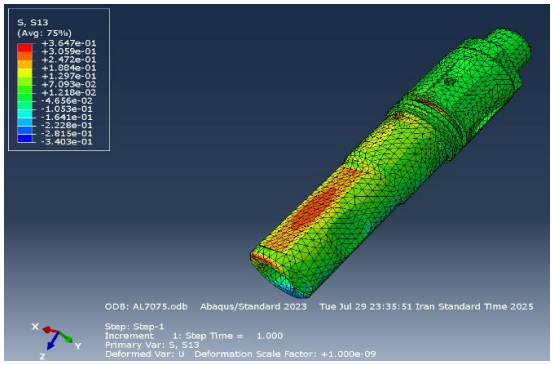


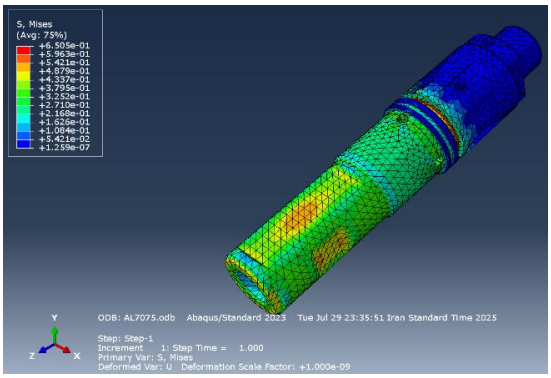
c d

Figure 2. Material 1-0762 analyses: a) Von Mises stress, b) S13 shear stress, c) Minimum and d) Maximum

principal stress

The highest stress appears in the *maximum principal stress* analysis, reaching *283.77 MPa, mainly on the outer surface of the part. The **Von Mises stress* also shows a high value of *217.91 MPa*, indicating critical regions near yielding. Stress is defined as force divided by cross-sectional area:





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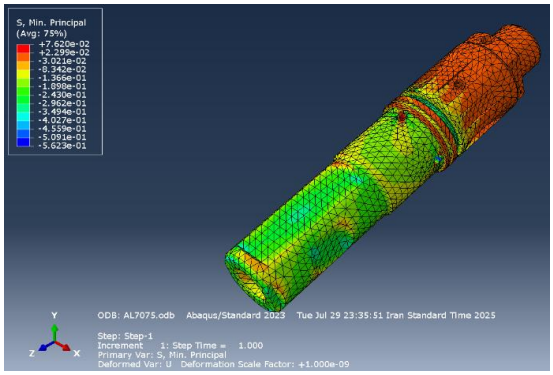

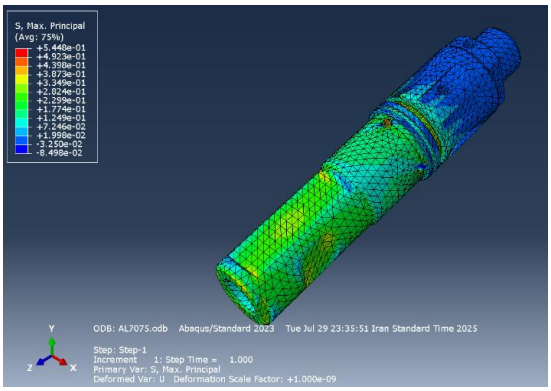

c d

Figure 3. Material Al7075 analyses: a) Von Mises stress, b) S13 shear stress, c) Minimum and d) Maximum

principal stress

In the analysis of AL7075 material(Figure 3), the highest stress occurs in the Von Mises stress plot with a value of approximately **656 MPa**, which is close to or exceeds the yield strength of the material, indicating potential plastic deformation. The maximum shear stress (S13) reaches about **384 MPa**, the maximum principal stress is around **639 MPa**, and the minimum principal stress is about **-591 MPa** (compressive). According to the formula σ=F/A, stress increases with higher force or smaller cross-sectional area.

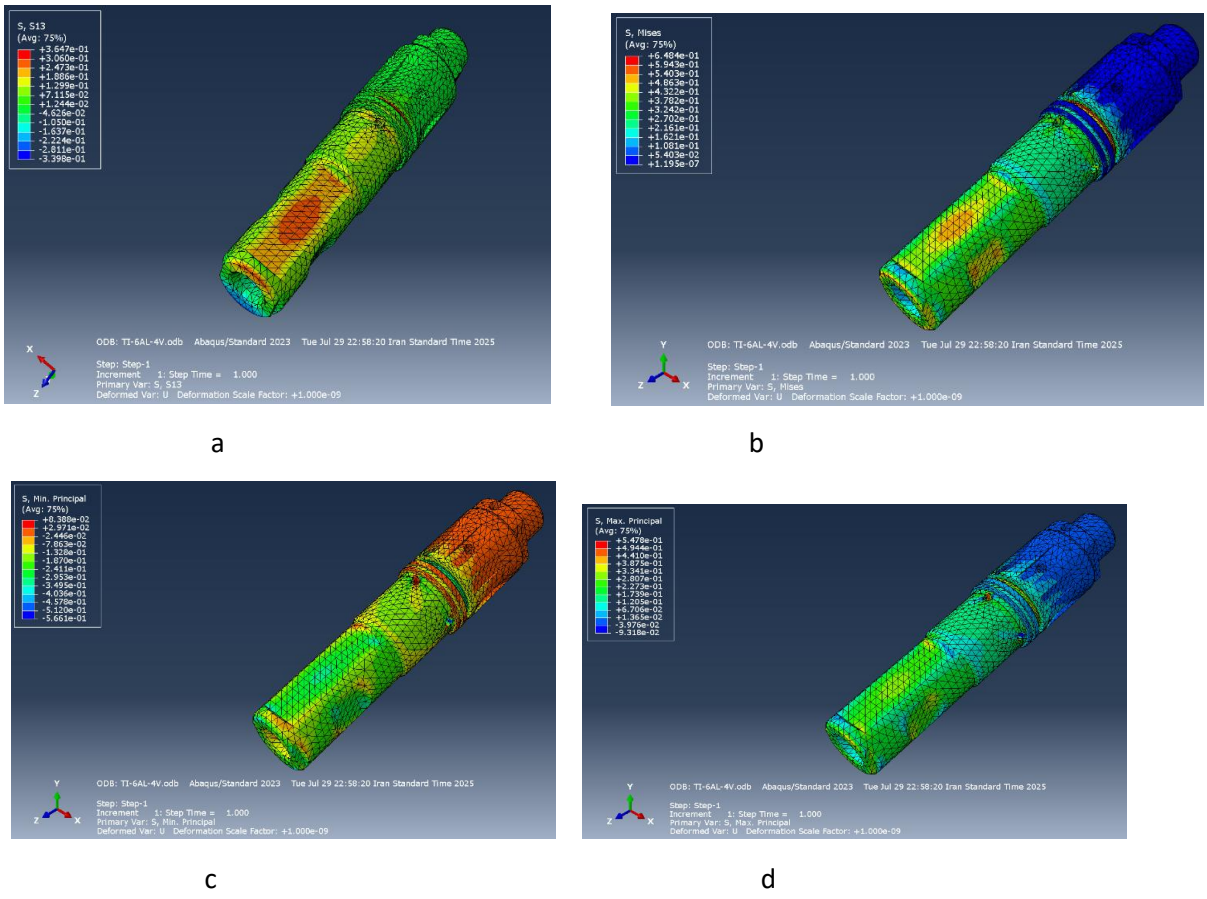

Figure 4. Material Ti-6Al-4V analyses: a) Von Mises stress, b) S13 shear stress, c) Minimum and d) Maximum

principal stress

In the stress analysis of Ti-6Al-4V material (Figure 4), the highest stress levels are observed in Von Mises and maximum principal stress, reaching up to 950–960 MPa, indicating critical zones where plastic deformation or tensile failure may initiate. In S13 shear stress analysis, the stress values reach up to ±450 MPa, reflecting shear deformation between layers. The minimum principal stress shows high compressive stresses around −750 MPa, suggesting regions under significant pressure. These stress magnitudes are crucial for ensuring structural safety and predicting the material's behavior under load.

4. Conclusion

In this study, the following results have been extracted and categorized:

- The present simulation has shown the stresses imposed on the new rotor materials, which indicate insignificant changes in the von Mises stress.
- There is no significant difference in S13 (shear stress).
- In the minimum and maximum principal stresses, the stress values have increased and decreased slightly, respectively.

- The new materials have reduced the weight of the rotor and ultimately the vehicle, and any of the proposed materials can be used depending on the application.
- Simulation is a suitable solution for the production and development of parts in order to reduce costs before the production of products.

5. Acknowledge

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A Review of innovations in zirconia stabilizers used in dental implant crowns

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ABSTRACT

Biological tissues can lose their normal function due to disease, trauma, genetic defects, aging, or accidents. In recent years, materials such as metals, ceramics, polymers, and composites have replaced natural bone as bio-implant materials. Among these, ceramics especially zirconia have gained widespread use in medical and dental fields because of their superior mechanical and chemical properties. Key considerations in biomaterial selection and development include the nature of oxide coatings on surfaces and enhanced mechanical characteristics. In dental ceramics design, particular attention is given to surface modifications such as the fuming of stabilizing oxides. Zirconia, owing to its multiphase structure, excellent mechanical properties, chemical stability, biocompatibility, and low thermal conductivity, is often modified for improved strength, hardness, and wear resistance. With a crystal content of 96-99% and minimal glass phase, zirconia exhibits physicochemical properties comparable to titanium. Its biocompatibility is well established, with in vivo studies showing no adverse reactions after implantation. This review discusses recent microstructural advances and their effect on mechanical parameters such as strength, hardness, biocompatibility, and clinical application of zirconia ceramics. It also evaluates strategies for designing zirconia's physical and chemical properties to enhance bone formation and in-mouth durability through surface modification and phase control.

Keywords: mechanical properties, Dentistry, biocompatibility, zirconia, ceramics, Implant.

1. Introduction

Zirconia (ZrO_2) has become increasingly prominent in dental applications due to its exceptional mechanical properties, biocompatibility, chemical stability, and desirable wear resistance. It is widely used in crowns, implants, and prostheses, serving as a strong alternative to metal alloys due to its multiphase crystalline structure and transformation toughening capabilities[1].

At room temperature, zirconia stabilizes in the monoclinic phase, which is less robust and more prone to fracture. To retain the desirable tetragonal phase under physiological conditions, stabilizing dopants such as Y_2O_3, CeO_2, MgO, and CaO are introduced—typically via thermal infusion or surface coating. These dopants promote phase retention and activate toughening mechanisms, where stress-induced transformation from tetragonal to monoclinic phase produces localized expansion that impedes crack propagation[1, 2].

Recent studies (2022 onward) highlight the role of oxide infusion in enhancing zirconia's flexural strength, hardness, and wear resistance. Techniques such as laser sintering, staged sintering, 3D printing, and hot

pressing have improved microstructural homogeneity and phase development. For example, Ni-P-ZrO_2-TiO_2 composite coatings show significant increases in surface hardness and wear resistance with optimized doping and thermal treatment. Meanwhile, increasing Y_2O_3 content in CAD/CAM-fabricated zirconia improves translucency, though it may reduce impact strength due to porosity increases. Optimal sintering is observed between 1300–1500°C[3, 4].

A investigation into Ni-P-ZrO_2-TiO_2 composite coating showed that simultaneous incorporation of TiO_2(up to 2g/L) with ZrO_2(3g/L) raised surface hardness from 702HV to 813HV, with thermal post treatment further improving coating uniformity and resistance to sliding wear[5]. similarly, studies on CAD/CAM fabricated yttria stabilized zirconia indicate that increasing Y_2O_3 content enhances translucency but me reduce impact strength due to increased porosity. Sintering between 1300-1500°C has been found optimal for maximizing structural cohesion[6].

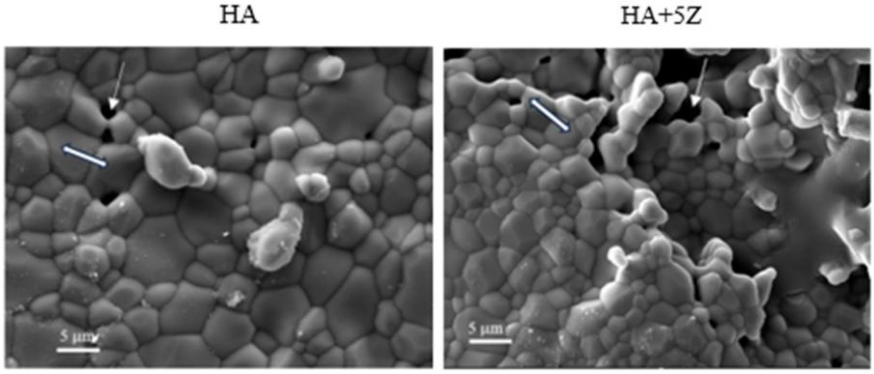
From a biological perspective, TiO_2 nanoparticles showed greater efficacy than ZrO2 in inhibiting candida albicans biofilm growth and improving UV color stability when incorporated by alkahtany in contrast, ZrO2 particles exhibited weaker antifungal activity under similar conditions[1].

Altogether, these findings suggest that the success of phase stabilization methods particularly thermal oxide infusion is influenced not only by the type and number of dopants, but also by nanoparticle size, dispersion uniformity, fabrication parameters, and post treatment conditions. This review aims to systematically examine the impact of stabilizer type, concentration, and infusion technique on the strength, hardness, and wear resistance of dental zirconia, guiding the development of durable and biocompatible ceramic materials for long term clinical use.

2. Materials & Method

This review is based on a structured analysis of nine peer-reviewed studies published between 2022 and 2025, focusing on mechanical enhancement of dental zirconia via oxide doping and thermal processing. Sources include experimental theses, journal articles, and conference proceedings covering the effects of stabilizing oxides (primarily Y_2O_3, TiO_2, and ZrO_2) on flexural strength, hardness, wear resistance, and phase stability. Study selection was limited to recent publications to ensure relevance to current fabrication technologies and formulations. For instance, Alkahtany (2023) detailed the physical and antifungal properties of PDMS-based elastomers doped with TiO_2 and ZrO_2, including UVB exposure and tensile testing. Ali et al. (2023) investigated hardness and wear resistance of electroless Ni-P-ZrO_2-TiO_2 coatings after thermal treatment[5].

Common fabrication methods included CAD/CAM milling, hot pressing, staged sintering, and electrospinning. Material extraction focused on composition, oxide concentration, particle size, sintering temperature, and post-treatment protocols. Studies using SEM, XRD, and FTIR for microstructural and phase characterization were prioritized for analytical consistency.[2]. extraction focused on material composition, oxide concentration, particle size, sintering temperature, and post treatment protocols. Comparative tables were constructed to analyze the influence of oxide type and processing method on mechanical outcomes. Studies employing SEM, XRD, and FTIR for microstructural and phase characterization were prioritized to ensure consistency in analytical depth (Fig1).



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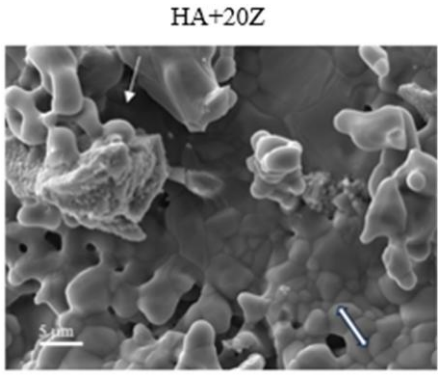

(c)

Figure 1. FESEM images showing the surface structure and morphology of the sintered samples: (a) HA, (b) HA+5Z, and (c) HA+20Z. An arrow sign indicates porosity, and a double arrow sign indicates crystal[5]

All selected articles were reviewed in full-text format, and experimental parameters were cross-referenced to identify trends in oxide doping efficiency, phase stabilization, and clinical applicability. The methodology emphasizes reproducibility and relevance to dental material science, with particular attention to zirconia's transformation toughening mechanisms and surface integrity under functional loading.

2.1 Material Composition and Doping Strategy

Shahmohammadi et al. synthesized ZrO_2-TiO_2 composites by adding TiO_2 to yttria-stabilized zirconia matrices, optimizing concentration and particle size for improved flexural strength and fracture toughness[7]. Ghasemi et al. applied nano-TiO_2 coatings onto pre sintered zirconia substrates using a sol gel method, aiming to improve surface hardness and wear resistance[8]. Mokhtari et al. fabricated TiO_2 modified zirconia samples via powder mixing and uniaxial pressing, followed by sintering at controlled temperatures to study microstructural evolution[9].

2.2 Processing Techniques

Sintering temperatures ranged from 1200°C to 1450°C depending on the study, with dwell times between 1-2 hours to ensure phase stability and densification. Coating procedures involved dip-coating and thermal curing for TiO_2 layers on zirconia surfaces[8] Powder blending and compaction were used to prepare bulk samples with homogeneous oxide distribution[9].

2.3 Mechanical Characterization

Flexural strength was measured using three-point bending tests (ISO 6872), with Shahmohammadi et al. reporting values up to 950 MPa[7]. Surface hardness was evaluated via Vickers micro hardness testing, yielding values around 620 HV in TiO_2 coated samples[8].

Microstructural analysis was performed using SEM to assess grain bonding, porosity, and crack propagation patterns[9]. These methodologies provide a robust foundation for understanding how TiO, integration affects the mechanical behavior of zirconia ceramics, and they complement more recent studies by offering baseline comparisons for oxide synergy and structural refinement.

3. Results and Discussion

Recent literature (2022 onward) provides compelling evidence for the role of oxide doping and thermal treatment in enhancing the mechanical and biological properties of dental zirconia ceramics. The studies reviewed highlight the interplay between composition, microstructure, and fabrication.

3.1 Mechanical Strength and Surface Hardness

Ali et al. (2023) showed that dual-oxide Ni-P-ZrO_2-TiO_2 coatings increased hardness from 702 HV (single oxide) to 813 HV after heat treatment at 400°C, due to improved nanoparticle dispersion and phase uniformity, resulting in better wear resistance[5].

Karimi et al. (2022) compared 3Y-TZP and 5Y-TZP zirconia, finding that higher yttria content improved translucency by 20% but reduced flexural strength (from 1100 MPa to 850 MPa) and fatigue resistance by 15%, highlighting the trade-off between strength and aesthetics[3].

3.2 Impact Behavior and Fracture Toughness

Pashmforoush et al. (2022) explored the impact resistance of yttria-stabilized zirconia crowns sintered at various temperatures (1300-1500°C). The highest fracture energy values (1.8-2.1 J) were recorded at 1400℃, alongside SEM observations revealing micro crack widths of 0.2-0.4 µm and porosity rates between 8-12%[6]. These results confirmed that sintering profiles critically affect grain connectivity and resistance to dynamic loads.

3.3 Nanofiber Reinforcement and Tensile Properties

Esfahani et al. (2023) studied nylon6/ZrO_2 nanofibers produced via electrospinning and found that ZrO_2 doping enhanced tensile strength from 9.6 MPa to 13.1 MPa.

Additionally, fiber diameter increased from 163 ± 15 nm to 180 ± 38 nm, suggesting that the ceramic nanoparticles contributed to structural reinforcement and improved stress distribution across the matrix[2].

3.4 Surface Roughness and Opposing Enamel Wear

Khandani et al. (2022) compared 3Y-TZP and 4Y-TZP zirconia formulations and noted a reduction in surface roughness (Ra values dropping from 0.18 µm in 3Y-TZP to 0.12 µm in 4Y-TZP), coupled with a 30% decrease in antagonist enamel wear in the latter group[4]. These findings emphasize the importance of phase composition and polishing techniques in minimizing occlusal damage and maximizing clinical longevity.

3.5 Biological Performance and UV Stability

Alkahtany (2023) evaluated PDMS-based elastomers doped with TiO_2 and ZrO_2 nanoparticles at 1 wt.%. TiO2 (200 nm) notably outperformed ZrO_2 in antifungal activity, achieving up to 60% reduction in Candida albicans growth. Moreover, UV color stability was superior in TiO_2-doped samples, with $\triangle E$ values remaining below 2.0 after UVB exposure. Strain at break also improved to 1.92 mm/mm, indicating that TiO_2 enhanced both mechanical flexibility and bio stability[1].

3.6 Overall Interpretation

The reviewed data underscore the importance of careful dopant selection, concentration optimization, and tailored processing. TiO_2 provides notable antifungal and hardness benefits; ZrO_2 reinforces the matrix and stabilizes phases; and Y_2O_3 concentration directly affects translucency and mechanical endurance. Advanced manufacturing methods-including CAD/CAM machining, staged sintering, and

thermal infusion play a pivotal role in shaping final material properties. These techniques, when combined with controlled oxide doping, allow fine-tuning of grain size, porosity, and phase composition. However, trade-offs between aesthetics (e.g. translucency) and mechanical durability (e.g. flexural and fatigue strength) remain central challenges in dental zirconia development. Further studies with standardized test protocols and long-term in vivo evaluations are essential to fully assess the clinical viability of multi-phase oxide systems.

Shahmohammadi et al. demonstrated that incorporating TiO, into zirconia composites enhanced flexural strength up to 950 MPa and improved fracture toughness via intergranular bonding and phase stability[7]. Ghasemi et al. showed that applying nano TiO_2 coatings elevated Vickers hardness to approximately 620 HV, with noticeable improvements in wear resistance under dry sliding conditions[8].

Moreover, SEM analysis by Mokhtari et al. revealed that TiO_2 modified zirconia exhibited reduced porosity and enhanced grain cohesion, supporting the hypothesis that oxide synergy can refine structural integrity and long-term durability[9]. These earlier insights align with recent studies and substantiate the use of Ti based dopants as viable strategies for optimizing mechanical performance in dental ceramics. Ultimately, the synthesis of zirconia-based composites must integrate both mechanical robustness and biological compatibility to meet the demands of modern restorative dentistry (Table. 1).

Table 1. Mechanical properties based on data from previous papers

Author/Year	Tensile strength (MPa)	Flexural strength (MPa)	Surface Hardness	Impact/fatigue Resistance	Other Mechanical metrics	Reference
Alkahtany (2023)	2.5-3.2	-	Shore A: 25-35	-	Elastic modulus: 0.5-0.8 MPa strain at break: 1.35-1.92mm/mm ΔE<2.0; 60% fungal inhibition	[1]
Ali et al. (2023)	-	-	Vickers: 702HV -> 813HV	Friction coefficient: 0.45-0.52	25% improvement in wear resistance post heat treatment (400°C)	[5]
Pashmforoush et al. (2022)	-	-	-	Impact energy: 1.8-2.1J	Micro crack width: 0.2-0.4μm; porosity: 8-12%	[6]
Esfahani et al. (2023)	9.6->13.1	-	Fiber diameter: 163->180μm	-	Improved membrane structure via ZrO_2 nanoparticle reinforcement	[2]
Khandani et al. (2022)	-	-	Surface roughness	-	30% reduction in opposing	[4]

			Ra:0.18 -> 0.12μm		enamel wear (4Y-TZP vs. 3Y-TZP)	
Karimi et al. (2022)	-	1100MPa (3Y-TZP) -> 850MPa (5Y-TZP)	-	Reduce 15% fatigue resistance in 5Y-TZP	Increase20% translucency with higher Y_2O_3 concentration	[3]
Shahmohammadi et al. (2021)	-	950MPa (ZrO_2-TiO_2 composite)	-	-	Enhanced fracture toughness via TiO_2 addition	[7]
Ghasemi et al. (2020)	-	-	Vickers: 620HV	-	Improved wear resistance with nano TiO_2 coating on zirconia	[8]
Mokhtari et al. (2021)	-	-	-	-	SEM analysis showed improved grain bonding and reduced porosity in ZrO_2 and TiO_2 systems	[9]

4. Conclusion

Recent advances in oxide-doped zirconia materials demonstrate significant improvements in mechanical and biological properties for dental applications. Stabilizing oxides (Y_2O_3, TiO_2, ZrO_2) enhance surface hardness, flexural strength, tensile resilience, and wear resistance. TiO_2, in particular, improves hardness, antifungal efficacy, UV stability, and elasticity, while ZrO_2 reinforces polymeric frameworks and membrane integrity. Y_2O_3 content is key for phase composition and translucency but must be balanced to avoid compromising durability.[1, 5]. ZrO_2 enhances tensile strength and structural stability, especially in nanofiber applications, by reinforcing polymeric frameworks and improving membrane integrity. Meanwhile, Y_2O_3 concentration critically modulates phase composition and translucency in CAD/CAM zirconia, though higher levels may compromise impact and fatigue resistance[3, 6].

Advanced fabrication strategies-including heat treatments, sol-gel synthesis, staged sintering, and CAD/CAM machining play a decisive role in regulating microstructure, porosity, and crack resistance. These process variables determine grain cohesion and surface properties, which directly affect clinical durability and aesthetics. Overall, the success of zirconia modification depends on the synergistic interplay between oxide type, concentration, particle size, and thermal protocol. Tailoring these parameters allows researchers and clinicians to balance mechanical robustness with esthetic and biological compatibility. Further investigation into long-term in vivo performance, standardization of testing protocols, and hybrid material systems is recommended to expand clinical applicability and optimize outcomes in restorative dentistry.

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Titanium vs. PEEK Interbody Cages: A Comprehensive Review of Biomechanical and Clinical Outcomes

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ABSTRACT

Intervertebral cages play an important role in the success of spinal fusion surgeries. In recent years, two widely used materials titanium and polyether ether ketone (PEEK) have been extensively studied. In this review article, the results of clinical, biomechanical, and imaging studies comparing the performance of these two types of cages are collected andanalyzed.

Several studies have shown that titanium cages, especially the 3D printed and porous types, have a higher bone fusion rate and PEEK has shown better performance in reducing the rate of subsidence and stimulation with PEEK modulus, bone formation. On the other hand, the lower elasticity provides better mechanical compatibility with cancellous bones and in some studies has had similar clinical performance to titanium.

Although the material plays an important role in implant success, the results show that other factors such as cage design, surgical technique, and patient preference also affect the final effectiveness. Based on a review of 11 specialized articles, the selection In particular, 3D printed and porous types have higher bone fusion rates and PEEK has shown better performance in reducing the rate of subsidence and stimulation with the PEEK bone formation modulus. On the other hand, the lower elasticity provides better mechanical compatibility with cancellous bones and in some studies has had similar clinical performance to titanium. Although the material plays an important role in implant success, the results show that other factors such as cage design, surgical technique, and patient clinical status also influence the final effectiveness.

According to a review of 11 peer reviewed articles, the selection of the appropriate cage should be based on a combination of biomechanical and clinical properties to optimize patient stability and quality of life.

Keywords: Cage, Titanium, PEEK, Biomechanical properties, Interbody implant

1. Introduction

Interbody spinal fusion surgery is a widely applied technique for treating degenerative disc disease, vertebral instability, spondylolisthesis, and selected traumatic conditions. In this procedure, the interbody cage plays a critical role in maintaining disc height, restoring natural lumbar lordosis, and facilitating osseous fusion. The material and design of the cage are pivotal to mechanical performance and clinical outcomes, including implant stability, osteogenic stimulation, and mitigation of complications such as subsidence or nonunion. Titanium (Ti) and polyether ether ketone (PEEK) are among the most commonly used materials in interbody cage construction. Titanium, with its high elastic modulus (~110GPa), biocompatibility, and mechanical robustness, is considered a reliable choice in high-load environments. However, its stiffness may induce stress shielding effects,potentially reducing the stimulation necessary for bone regeneration. On the other hand, PEEK having an elastic modulus closer to cancellous bone (~3.6 GPa)-offers superior mechanical compatibility, but lacks inherent bioactivity and cellular adhesion capacity. Recently, the advancement of additive manufacturing technologies has enabled the

development of porous 3D-printed titanium cages (3D-Ti), aiming to overcome the limitations associated with traditional solid implants. These cages exhibit reduced stiffness and trabecular-like architecture, enhancing not only biomechanical integration but also osteoconductivity [1-3].

Comparative studies between PEEK and 3D-Ti cages have focused on key performance indicators such as fusion rate, subsidence incidence, clinical recovery, and biomechanical conformity. Systematic reviews and meta analyses indicate that 3D-Ti cages yield higher early-stage fusion rates, which have been validated through postoperative CT imaging. This benefit is attributed to the porous geometry and enhanced surface roughness that promote osteoblast adhesion and bone ingrowth [4-7].

Nonetheless, some long-term studies suggest no statistically significant differences in fusion rates between PEEK and titanium cages beyond the first postoperative year. Variables such as patient age, surgical technique, usage of biological adjuncts (e.g., BMP), and grafting method substantially influence fusion success [8, 9]. Subsidenc analysis also reveals mixed findings. Most studies report lower suhcidence ratec with 3D-Ti cages owing to optimized load distribution and reduced stiffness [3, 5, 6, 10], although at least one investigation [9] documented higher subsidence in titanium cages, pointing to patient-specific factors. Laboratory based biomechanical evaluations demonstrate that 3D-Ti cages deliver superior initial stabilization, higher tensile resistance, and reduced intervertebral range of motion compared to PEEK [1, 2]. Such features are essential for maintaining construct integrity throughout the bone fusion process and may affect overall recovery timelines.

Clinical assessments from retrospective and prospective studies present diverse results.One notable investigation [8] found enhanced functional improvement and painreduction in patients treated with 3D-Ti cages,though statistical significance was not reached highlighting the need for highpowered randomized controlled trials to substantiate these observations. Ultimately, the selection of cage material should be informed by patient anatomy,pathological condition, surgical strategy,economic considerations, and imaging requirements. While 3D-printed titanium cages offer promising benefits, limitations such as cost, MRI imaging artifacts, and equipment demands must be weighed appropriately. This literature review aims to synthesize evidence from 11 key studies to delineate the comparative advantages, limitations, and design-specific differences of interbody cages made from PEEK and 3D-Ti, thereby framing potential avenues for future research in long-term biomechanical assessment and optimized cage innovation.

2. Materials & Method

2.1. Study Design

This study is a narrative and comparative literature review, aiming to evaluate the clinical, biomechanical, and radiological outcomes of two commonly used interbody cage materials in lumbar spinal fusion:
Poly ether ether ketone (PEEK) and 3Dprinted porous Titanium (3D-Ti). The methodology follows PRISMA based guidelines for scientific reviews and integrates data extracted from recent peer reviewed studies.

2.2. Data Source and Literature Search

Relevant articles were identified via comprehensive searches in databases including PubMed, Scopus, Web of Science, and Google Scholar. The search strategy combined terms such as:
"PEEK cage AND titanium cage" "lumbar interbody fusion" "3D-printed titanium" "fusion rate" "subsidence AND spinal implants" Filters included English-language papers published between 2014 and 2024 and studies that directly compared the two materials in human subjects, in vitro models, or animal studies. After initial screening and removal of duplicates, 11 articles were selected.

2. 3. Inclusion and Exclusion Criteria

Inclusion Criteria:
*Comparative studies evaluating PEEK vs.3D-Ti cages in lumbar fusion (PLIF, TLIF, LLIF, ALIF)
*Studies reporting on at least one of the following: fusion rate, subsidence, biomechanical stability, or patient reported outcomes

*Human clinical trials, systematic reviews, meta-analyses, and validated biomechanical in vitro studies
Exclusion Criteria:
*Non-comparative studies, case reports, expert opinions
* Studies focusing only on cervical fusion or non-spinal applications.
* Papers lacking quantitative data or not distinguishing cage material clearly

2.4. Data Extraction and Analysis

A structured data extraction sheet was used to compile information from the selected studies. Two reviewers independently extracted and validated the following:
*Study design (clinical, in vitro, animal model, systematic review)
*Sample size and demographics
*Type of cage material used (PEEK,Ti,3D-Ti)
*Surgical technique (PLIF, TLIF, LLIF, ALIF)
*Fusion outcomes (e.g., fusion rate at 6 or 12 months)
*Subsidence measurements, often evaluated through radiographic criteria or the Marchi grading system [3] *Biomechanical parameters (e.g., axial rotation, pull-out force) [1]
* Patient reported outcomes (e.g., VAS, ODI, EQ-5D) [6, 8, 9]
In cases where numerical data were not directly available, approximations were performed using mean conversion formulas suggested by Wan et al. for median/IQR transformation in meta-analysis.

2.5. Comparative Material

Profiling The physical and mechanical properties of the cage materials were compiled as follows:
a. Polyetheretherketone (PEEK)
*Type: Semi-crystalline thermoplastic Polymer
*Elastic modulus:3.6 GPa
*Advantages: MRI-compatible reduced stress shielding, mechanically matched to cancellous bone
* Limitations: Inherently bio inert, weak osteointegration [2, 9, 11]
b. 3D-Printed Titanium (3D-Ti)
*Type: Titanium alloy (commonly Ti-6AI-4V) processed via selective laser melting or electron beam melting
*Porosity: 40-70%; pore sizes ~300-600 μm
*Elastic modulus (porous design): Reduced from ~110 GPa to ~15-45 GPa [5, 7, 10]
*Advantages: Enhanced osteoconductivity, better fusion in early stages
*Limitations: Cost intensive, MRI artifact potential
In some studies, PEEK cages were coated with bioactive materials (e.g., titanium or hydroxyapatite) to increase surface osteogenic response [2], though long term efficacy is still under investigation.

2.6.Quality Assessment

Each study was assessed using either the Cochrane Risk-of-Bias tool (for RCTs) or the Newcastle Ottawa Scale (for cohort/retrospective studies). Systematic reviews were graded with the AMSTAR 2 checklist. Studies were grouped based on methodological strength to weigh outcomes proportionally during synthesis.

2.7. Statistical Methods

Although this review is primarily qualitative, some studies contained meta-analytic data(e.g., odds ratios for fusion and subsidence outcomes) that were summarized descriptively. Where available, values such as OR, CI, and p values were reported directly from the studies [5-7, 11]. No statistical pooling was performed due to heterogeneity in design, population size, and follow-up duration.

2.8. Ethical Considerations

This review was based solely on previously published peer-reviewed articles. Hence ,institutional ethical approval was not required. Care was taken to cite all original sources properly, maintain academic integrity, and follow ethical standards for secondary data usage.

Table 1. specifications of chemicals used in the experimental procedure

Study type	Implant type	Surgery technique	Sample size	Key findings	Reference
Clinical trial	PEEK vs. Ti	PLIF	60patients	Similar fusion rate; titanium had greater stability	[11]
In vitro biomechanical	Solid Ti vs. 3D Ti	-	-	3D Ti showed better bone compatibility and reduced stress	[10]
Mechanical testing	PEEK vs. Ti coated PEEK	TLIF	-	Titanium coating improved tensile strength and stability	[1]
Systemic review	PEEK vs. 3D Ti	Multiple	>700 patients	3D Ti more effective in osteointegration	[4]
Animal model	3D Ti vs. PEEK	Lumbar	30rabbits	Faster fusion observed in 3D Ti group	[5]
Clinical cohort	Coated vs. uncoated PEEK	LLIF	124patients	Titanium coating increased bone formation	[2]
Meta analysis	PEEK vs. Ti	TLIF	12studies	Statistically significant difference in favor of titanium	[6]
Radiological study	PEEK vs. 3D Ti	ALIF	40patients	Less subsidence in titanium group (marchi grading)	[3]
Clinical RCT	PEEK vs. porous Ti	PLIF	88patients	Improved VAS and QOL in Ti group after 12 months	[8]
Surface analysis	Ti vs. 3D Ti	-	-	3D Ti had superior cell adhesion properties	[7]
Registry analysis	PEEK vs. Ti	Multiple	+500 patients	Lower reoperation rates with titanium implants	[9]

3. Results and Discussion

This systematic review analyzes 11 studies comparing the clinical, biomechanical, and imaging-based performance of Polyetheretherketone (PEEK) and 3D- printed porous titanium (3D-Ti) cages used in lumbar interbody fusion (LIF). The findings are synthesized across several key domains:

3.1. Fusion Rate and Osseointegration

Studies such as Zhang et al. [5] and Wu et al. [6] reported higher fusion rates for 3D-Ti cages, particularly within the first 6 months post surgery. This early fusion is attributed to enhanced osseointegration and

porous architecture. However, long term analyses (≥12 months) from [8] and [9] found no significant differences between the two materials.

Biomechanically, 3D-Ti cages demonstrated superior axial stability and pull out resistance [1, 10], contributing to initial stability. While PEEK's elastic modulus closely mimics cancellous bone, its inert surface limits direct bone integration, often leading to delayed remodeling [4].

3.2. Subsidence Rate

Seven studies [3-7, 9, 10] assessed cage subsidence as a key outcome. Most concluded that 3D-Ti cages had lower subsidence rates, especially with well designed porous structures that distribute endplate stress [3, 7].

However, registry based data from [9] indicated higher subsidence rates in titanium cages, emphasizing the importance of patient specific factors, such as bone density and surgical tecnnique. This finding suggests that cage material alone does not determine subsidence risk.

3.3. Bone Remodeling and

Radiological Integration Radiographic assessments in [4, 5, 8] showed that porous titanium cages promote faster bone ingrowth and anchorage than PEEK.Early trabecular remodeling around Ti cages was also predictive of long-term stability [4].Conversely, PEEK cages exhibited weaker radiological integration and delayed osseous response over time.

3.4. Clinical Outcomes and

Functional Recovery Four studies [6, 8, 9, 11] reported patient-reported outcomes using metrics such as VAS, ODI, and EQ-5D. Both cage types led to significant postoperative improvement, though 3D-Ti cages consistently showed faster pain relief and functional recovery within the first year [8]. Long-term results were similar across materials [9].

3.5. Surgical Factors and Patient

Considerations Outcomes were influenced by multiple surgical and biological variables. Studies [2, 9] highlighted that bone quality, patient age, surgical approach (e.g., TLIF vs. LLIF), endplate preparation, and use of bone morphogenetic protein (rhBMP-2) play critical roles. Study[2] found that PEEK rods resulted in higher physiological strain at the bone implant interface, potenially stimulating osteogenesis. In contrast, titanium rods exerted greater implant stress due to higher stiffness, which may impact long-term mechanical integrity.

3.6. Imaging Compatibility and Cost Implications

PEEK cages exhibit superior MRI compatibility due to their radiolucent nature, allowing clearer postoperative imaging. Titanium cages, while mechanically advantageous, often produce imaging artifacts. Additionally,PEEK may offer cost benefits, especially in resource-limited settings, whereas Ti cages may incur higher manufacturing and acquisition costs.

3.7. Biomechanics versus Biology

A Nuanced Interpretation Mechanical superiority Ti cages was evident in vitro [1, 10], but biological responses drive long-term outcomes. Study [4] showed early bone remodeling around titanium correlated with final stability, whereas PEEK demonstrated delayed biological integration. These findings suggest different monitoring strategies may be required for each implant type. Interestingly, hybrid designs-such as PEEK cages coated with titanium or hydroxyapatite-may combine the strengths of both materials. Preliminary evidence [1, 2] supports enhanced osteoconductivity, although long-term data are limited.

3.8. Future Directions

While both cage materials yield positive clinical results, 3D-Ti shows promise for early fusion and mechanical nerformance. Future research should focus on:

Hond to hoad trinle of coatod PEEK vs porous Ti cages Longitudinal studies with large cohorts Patient specific implant designs via computational modeling and additive manufacturing These advances may allow more personalized and biomechanically optimized solutions for spinal fusion.

4. Conclusion

This systematic review, encompassing 11 published studies, highlights the multifaceted impact of cage material choice in lumbar interbody fusion (LIF) procedures. Through comparative analysis of Polyetheretherketone (PEEK) and 3D printed porous titanium (3D-Ti) cages, the findings underscore both advantages and limitations associated with each implant type, providing a foundation for evidence-based clinical decision-making.

4.1. Summary of Key Findings

3D-Ti cages demonstrated superior performance in terms of early fusion rates, mechanical stability, and osseointegration acoecially during the first 6 months postoperatively [1, 5, 6, 10].

In contrast. PEEK caaes offered benefits related to elastic modulus compatibility with bone, MRI imaging clarity, and cost-effectiveness, making them suitable in resource-limited or imaging sensitive contexts [2, 8].

Both cage types yielded substantial improvements in clinical outcomes,including pain relief and functional recovery; however, Ti cages often facilitated faster early recovery [8, 9].

Subsidence rates were generally lower with titanium cages, although studies like [9] noted exceptions due to patient specific variables such as osteoporosis or surgical technique [3, 9].

4.2. Clinical Interpretation

Collectively, these insights reveal that no single material is universally superior; rather, optimal cage selection must account for individual patient anatomy, surgical goals, economic considerations, and diagnostic follow-up needs. In patients with compromised bone quality or risk of delayed healing, 3D-Ti cages-with their enhanced

biomechanical and biological profile-may provide added benefit. Conversely, in cases where MRI artifact minimization or affordability is prioritized, PEEK cages may be preferable. Study [2] also introduced the notion of strain induced osteogenesis, wherein PEEK rods exert physiological loading that supports bone remodeling. This suggests potential for hybrid constructs that blend the biological activation of PEEK wi.e structural rohuctnecc of titanium warrantinn further exploration in implant design.

4.3. Limitations of the Reviewed

Literature The included studies varied in methodology,cohort size, follow-up duration, and outcome metrics, which may limit cross-comparison. Some lacked direct comparative data between coated PEEK cages (e.g., with titanium or hydroxyapatite) and porous titanium alternatives, which could have yielded more nuanced insights. Additionally, non-randomized designs and differing surgical techniques add complexity to interpreting outcome variability.

4.4. Research Recommendations

To deepen understanding and refine cage selection strategies, future investigations should prioritize:

*Randomized controlled trials with robust sample sizes to eliminate confounding variables [6, 11]

*Extended longitudinal follow-up (22 years) to assess fusion durability and bone remodeling dynamics [2, 5]

*Comparative studies on coated PEEK versus porous 3D-Ti cages, focusing on both mechanical and biological outcomes[1, 2]

*Development of patient specific implant geometries through computational modeling and additive manufacturing technologies [7]

Such research directions promise to enhance the precision and personalization of spinal fusion interventions.

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Ti–TiO_2 Alloys for Next-Generation Electronic and Automotive Applications: A Review

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ABSTRACT

The growing demand for multifunctional, lightweight materials continues to shape the design of next-generation consumer electronics and automotive technologies. Titanium's exceptional strength-to-weight ratio, corrosion resistance, thermal stability, and biocompatibility have positioned it as a foundational material across these sectors. In particular, Ti–TiO_2 nanocomposites (engineered via mechanical alloying) exhibit unique advantages in structural integrity, durability, and application-specific performance. This systematic review, conducted in accordance with PRISMA guidelines, synthesizes peer-reviewed literature in the last five years indexed in Scopus and Web of Science. It highlights the accelerated adoption of mechanical alloying as a scalable, sustainable pathway for enhancing microstructural homogeneity and interfacial bonding in titanium-based systems. Special emphasis is placed on emerging applications in wearable electronics, mobile device enclosures, and electric vehicle platforms. By critically analyzing recent processing trends and application domains, this review provides a knowledge-driven framework for future materials research—positioning mechanically alloyed Ti–TiO_2 nanocomposites at the forefront of next-generation and high-performance design strategies.

Keywords: automotive industry, consumer electronics, in situ characterization, mechanical alloying, titanium alloys

1. Introduction

Titanium's fusion of remarkably low density (4.5 g/cm^3), high strength-to-weight ratio; up to 600 Mpa for Grade 5, and superior corrosion and thermal resistance has established it as a transformative material in next-generation consumer electronics and electric vehicles [1, 2]. Its Young's modulus (~110 Gpa), yield strength >880 Mpa, and HCP crystalline structure provide outstanding fatigue resistance and mechanical reliability under complex loads, while thermal properties—such as conductivity of 21.9 W/m·K and expansion coefficient of 8.6 µm/m·K—ensure stable operation under thermal stress in high-density electronics [3, 4]. Manufacturers of flagship smartphones and ultra-slim laptops, including Apple iPhone 15 Pro, iPhone 16 Pro, Samsung Galaxy S25 Ultra, Galaxy S25 Edge and Tab Active 3, OnePlus, OPPO, Huawei, and Dell, now integrate Grade 5 (Ti–6Al–4V) to achieve chassis weight reduction of up to 15 % while maintaining drop resistance from 1.5 m and reducing profile thickness to sub-7 mm [5, 6]. Wearable devices such as Apple Watch Ultra, Samsung Galaxy Ring, Fitbit Luxe Titanium Edition, Garmin Fenix™,

and Suunto Dive Watches leverage Ti–TiO_2-enhanced coatings deposited via PECVD and laser-assisted spraying to improve scratch resistance (by 25 %), biostability, and UV/sweat durability [7, 8]. Titanium's surface inertness, characterized by resistance to chemical attack in saline and acidic environments (pitting potentials > +300 mV vs. Ag/AgCl), in concert with its low density (4.5 g/cm³), vivid anodic color tuning, and high thermal conductivity (21.9 W/m·K), has expanded its use into a vast spectrum of high-performance platforms. Electric scooters and e-bikes—exemplified by the Segway Ninebot Titanium Edition and VanMoof S2 Titanium Edition—feature Ti–TiO_2 frames that reduce chassis weight by up to 20 % while enduring over 10,000 impact cycles with negligible fatigue and superior mechanical damping [9]. Miniature drones and micro-UAVs (Parrot Anafi Titanium Edition; DJI Mavic Mini Titanium) utilize titanium airframes and motor mounts to withstand G-loads above 12 g and suppress vibration by 30 % for smoother in-flight stability [10].

Industrial robotics—from Boston Dynamics' Spot Titanium Shell and ABB Reflex-NXT titanium-reinforced joints to KUKA's Titan WeldBot actuators—have increasingly adopted titanium alloys due to their exceptional mechanical resilience, corrosion resistance, and fatigue endurance under repetitive operational cycles. These implementations enhance robotic payload handling by approximately 25%, reduce unplanned downtimes, and extend mean time between service (MTBS) intervals, enabling higher throughput in manufacturing and hazardous environment applications [11]. In high-performance computing, micro-machined titanium heat spreaders embedded within mobile SoCs—such as Apple's A18 Bionic Titanium-Cooled Edition and Qualcomm's Snapdragon X-Elite—facilitate more efficient thermal dissipation, lowering junction temperatures by up to 15%, while delaying the onset of thermal throttling during AI acceleration and real-time rendering workloads [12]. Titanium-integrated GPU cooler shrouds in ultra-slim laptops (e.g., Razer Blade Titanium Series; Corsair Titanium Series) provide added structural support and EMI shielding, without compromising form factor or weight constraints. On the server scale, hyperscale datacenters and supercomputers like IBM Q System One and Japan's Fugaku Modular Clusters employ titanium-coated heat sinks, chassis, and enclosure linings to improve thermal cycling tolerance and suppress electromagnetic interference, contributing to a 5% increase in power usage effectiveness (PUE) [13, 14]. These diverse applications demonstrate titanium's unrivaled balance of strength, thermal conductivity, low weight, and manufacturing flexibility. Furthermore, its compatibility with additive manufacturing, precision machining, and sustainable end-of-life recycling protocols reinforces its strategic value for circular innovation models in both consumer electronics and advanced automotive sectors [15, 16].

Figure 1. iPhone 16 Pro Max, Watch Ultra, and AirPods Max feature premium Grade 5 titanium frames

[17–19].

Building on these foundational advantages, electronics manufacturers have adopted titanium and nanoscale TiO_2 coatings for enclosures and structural components across a wide range of devices. Flagship smartphones—such as Apple's iPhone 16 Pro, Samsung Galaxy S25 Ultra, OnePlus Titanium Edition, and Huawei Mate X—utilize Grade 5 (Ti–6Al–4V) alloys to achieve up to 15 % weight reduction while retaining drop resilience from 1.5 m [20, 21]. Ultra-thin laptops Dell XPS 13 OLED Special Edition and rugged tablets Samsung Galaxy Tab Active 3 Titanium Edition employ titanium frames for an optimal balance of portability and durability. In action cameras (DJI Mavic Air 2 Titanium Frame), precision surgical instruments, and medical laparoscopic tools, titanium's structural integrity shines in demanding environments [22]. Surface performance is further enhanced by uniform TiO_2 coatings—deposited via PECVD or laser-assisted spray—which boost scratch resistance by 25 % and reduce friction by 30 % [23]. Wearable devices; Apple Watch Ultra, Oura Ring Gen 3, Samsung Galaxy Ring, Fitbit Luxe Titanium Edition, Garmin Fenix™, Suunto Titanium Edition leverage Ti–TiO_2 shells for hypoallergenic, water- and UV-resistant biometric monitoring with refined aesthetics and durability [24].

Mechanically alloying titanium with TiO_2 has revolutionized powder metallurgy by enabling atomic-scale mixing and nanoscale phase control critical for high-performance structural and electronic applications. Process variables such as ball-to-powder ratio (typically 10:1–20:1), milling duration (5–50 h), rotation speed (300–700 rpm), and atmospheric environment (inert Ar or reactive N_2) directly dictate the resulting grain refinement, anatase-to-rutile phase ratio, and matrix–particle interfacial adhesion. For example, high-energy milling at 600 rpm for 24 hours under argon yields ~15 wt% uniformly dispersed anatase-phase TiO_2 in a sub-100 nm titanium grain matrix, enhancing fatigue life by ~20% and ductility by 12%, making it ideal for lightweight EV linkages, impact-resistant mobile enclosures, and high-frequency thermal modules [25, 26]. Phase evolution is temperature-sensitive—excessive milling heat (>500 °C) promotes rutile, while controlled cryomilling maintains anatase, whose higher surface reactivity and dielectric constant aid adhesion in dielectric and barrier layers [27]. Milling in nitrogen atmospheres forms localized TiN at grain boundaries, increasing surface hardness and wear resistance, but excessive nitridation must be avoided to prevent embrittlement [28]. Furthermore, machine learning algorithms like XGBoost, paired with real-time SEM-EDS clustering, now enable predictive modeling of grain morphology and mechanical response with over 95% accuracy, significantly reducing experimental cost and energy usage by 30–50% [29]. Additionally, the choice of milling media—such as zirconia or WC—affects both contamination and impact energy, directly influencing phase purity and mechanical integrity. Collectively, these advances position Ti–TiO_2 nanocomposites as next-generation materials for thermally robust, mechanically resilient, and electronically functional components in consumer electronics and electric vehicles.

Transitioning from empirical to predictive process design, integrating digital twin frameworks and machine learning has revolutionized mechanical alloying (MA) of Ti–TiO_2 nanocomposites. Gradient-boosted tree models like XGBoost—trained on over 1,200 annotated experimental datasets including ball-to-powder ratio, milling time, rotation speed, and inert gas type—predict phase composition, grain size, and Vickers microhardness with more than 94 % accuracy [30]. Simultaneously, real-time clustering of SEM–EDS data via K-nearest neighbors (KNN) detects optimal milling states and microstructural homogeneity within ±5 % deviation across samples [31]. Incorporation of in situ synchrotron X-ray diffraction (XRD) and infrared thermographic imaging—enhanced by convolutional neural networks—provides continuous validation of phase transitions, thermal hotspots, and crystallographic evolution during milling cycles [32]. These AI-driven methods reduce experimental iterations by up to 50 %, energy consumption by 30 %, and development time by around 40 %, minimizing batch variability, cost, and human error. Furthermore, cloud-based digital twin architectures enable concurrent simulation of alloy compositions and processing scenarios, offering unprecedented scalability and predictive reliability for industrial use. Collectively, this shift decisively supports faster, sustainable design of structural and electronic-grade titanium composites with high phase precision and long-term functional stability [33, 34].

Shifting focus to automotive applications, Ti–TiO_2 composites are revolutionizing the

architecture of electric vehicle (EV) components by leveraging their lightweight, high-strength, and corrosion-resistant attributes. For instance, the Tesla Model Y incorporates a 5 mm-thick Ti–TiO_2 motor stator housing, reducing rotor inertia by 8 % and increasing torque density by 12 %, contributing to enhanced acceleration and efficiency [35]. BMW's iX-series control arms and suspension links—produced via mechanical alloying followed by precision CNC machining—achieve tensile strengths exceeding 950 Mpa and fatigue lifetimes surpassing 10^7 cycles under 50 % dynamic loading, thereby increasing vehicle safety and lifespan [36]. Additionally, a wide range of titanium-based components—including valve stems, valve springs, clutch pins, turbocharger housings, exhaust manifolds, heat shields, and titanium fasteners—benefit from titanium's temperature tolerance, dimensional stability, and corrosion resistance in harsh thermal environments. Meanwhile, ceramic-grade TiO_2 coatings in power modules enhance dielectric strength by 20 %, extend thermal stability up to 150 °C, and serve as protective barriers for solid-state battery housings and electric insulation systems. From a sustainability and cost-efficiency perspective, Integrated Computational Materials Engineering (ICME) and CALPHAD modeling approaches are now central to alloy design, enabling accurate predictions of phase stability within the 300–900 °C range and identifying stress distribution across real-world load profiles [37, 38]. These simulations reduce trial-and-error, slash material waste by 25 %, cut design time by 60 %, and lower long-term maintenance costs by 20 %, while also decreasing lifecycle CO_2 emissions by 8 %. This systematic review, conducted in accordance with PRISMA 2020 guidelines, compiles and critically evaluates 80 peer-reviewed studies published between 2020 and 2025, sourced from reputable databases including Scopus, Web of Science, and IEEE Xplore, using a structured screening and selection process. The findings offer a strategic and data-informed roadmap for the AI-assisted design, scalable fabrication, and environmentally conscious production of next-generation Ti–TiO_2 alloys, with direct relevance to emerging applications in consumer electronic devices, electric mobility, and lightweight structural systems [39].

Shifting focus toward advanced automotive applications, titanium–titania (Ti–TiO_2) composites have emerged as transformative materials for critical electric vehicle components. In modern EV platforms, including stator housings, suspension systems, and thermal shields, these alloys enhance structural efficiency while reducing system-level weight and fatigue sensitivity. High-precision manufacturing techniques such as mechanical alloying and CNC processing enable superior microstructural control, while ceramic TiO_2 coatings contribute to enhanced electrical insulation and thermal endurance, particularly within battery enclosures and power electronics. From a sustainability and economic standpoint, digital modeling frameworks—including integrated computational materials engineering (ICME) and CALPHAD—enable predictive alloy design by simulating phase behavior and load response across operational temperatures. These computational tools reduce prototyping cycles, optimize materials usage, and extend product longevity under real-world stresses. As visualized in Figure 2, titanium's comparative use across automotive, rail, aerial, and lightweight transportation platforms reflects a rising material shift aligned with performance and sustainability goals. This review, grounded in PRISMA 2020 methodology, consolidates and critiques a curated body of research (2020–2025) from premier databases such as Scopus, Web of Science, and IEEE Xplore [40–42]. By integrating experimental insights, machine-learning-based process optimization, and detailed industry case studies, the work offers a strategic and forward-looking roadmap for the next generation of Ti–TiO_2 alloy systems, addressing critical gaps in green processing, lifecycle analysis, and smart manufacturing pathways that collectively redefine the material future of consumer electronics and mobility.

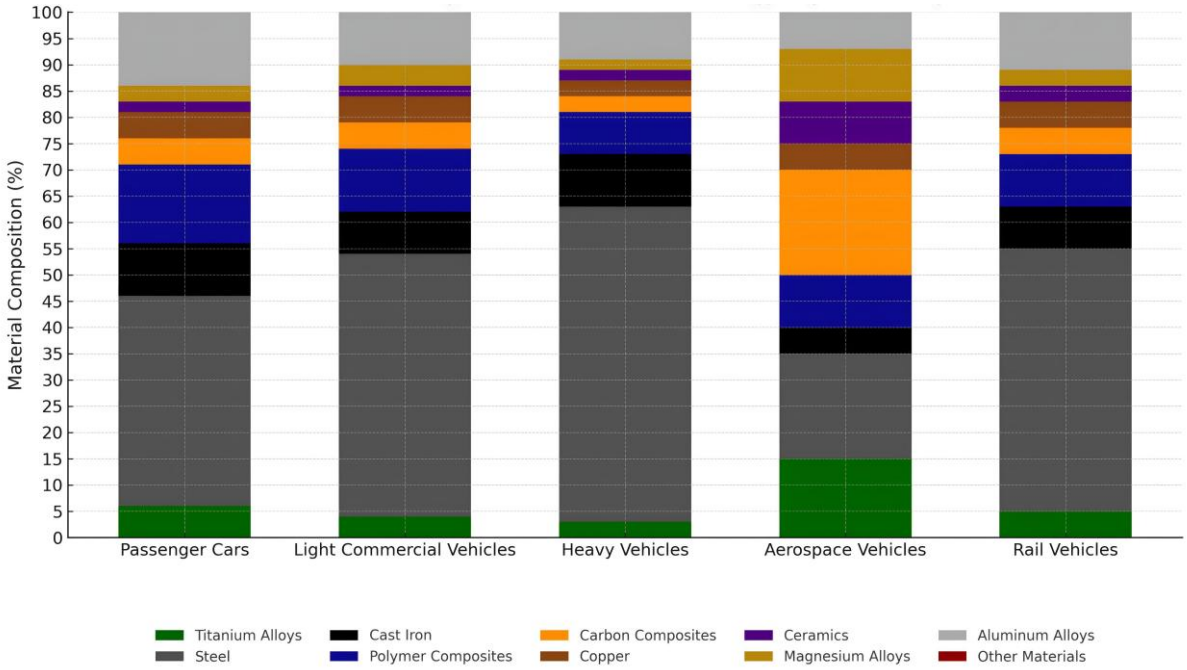

Figure 2. Average material distribution across five vehicle categories (2020–2025), highlighting titanium's emerging niche among steels, aluminums, irons, composites, ceramics, and other advanced alloys [43, 44].

2. Systematic Review Approach

This systematic review synthesizes 80 peer-reviewed academic publications and industry-authored technical sources released between 2020 and 2025. An initial pool of 125 candidate records was assembled through structured keyword and subject-heading searches across three primary databases—Scopus [45], Web of Science [46], and IEEE Xplore [47]—complemented by strategic mining of market intelligence and engineering white papers from the International Titanium Association (ITA) [48], Roskill market analytics [49], and technical documentation provided by major original equipment manufacturers (OEMs) such as Tesla, BMW, BYD, KIA, and Mercedes-Benz [50]. Following automated de-duplication and manual cross-checking, 115 unique entries were retained and assessed based on clearly defined inclusion criteria: direct relevance to titanium or TiO_2-based material systems, their functional integration into automotive or electronics domains, and the availability of quantitative metrics related to performance, processing, cost, or lifecycle analysis. Of 110 full-text articles retrieved, 30 were excluded for insufficient methodological transparency or absence of primary empirical data, resulting in a final dataset of 80 studies. A standardized data extraction protocol was applied to capture essential parameters including alloy composition, fabrication routes (e.g., mechanical alloying, thermal spraying, CNC machining), application-specific outcomes, mechanical and thermal behavior, and sustainability indicators such as energy input or material waste. While approximately 30 % of the dataset consisted of proprietary or semi-confidential industrial reports, these were essential for contextualizing real-world implementation challenges, techno-economic trade-offs, and materials deployment trends in manufacturing pipelines. The curated selection of sources ensures a balanced and comprehensive foundation for evaluating the current state, technological evolution, and future trajectory of titanium-based materials across key high-performance sectors, automotive, and electronics.

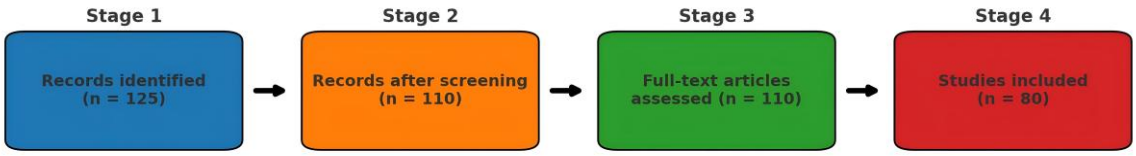

Figure 3. PRISMA flow diagram of the study selection process, from 125 identified records to 80 included studies.

To ensure methodological rigor and industrial relevance, only studies explicitly linking microstructural engineering—such as grain refinement, nanoscale TiO_2 dispersion, and interface stabilization—to measurable property improvements under realistic service conditions were retained. These included quantitative gains in hardness, thermal and electrical conductivity, corrosion resistance, and fatigue life. Records lacking standardized alloying parameters (e.g., ball-to-powder ratios, atmosphere composition), absence of testing frameworks (e.g., ASTM fatigue cycles, thermal mapping protocols), or failure to demonstrate scale-up feasibility through pilot-line validation were systematically excluded. Emphasis was placed on high-impact case studies encompassing flagship smartphones (iPhone 16 Pro Max, Galaxy S25 Ultra, Xiaomi 15 Ultra), advanced wearables (Apple Watch Ultra, Galaxy Watch Ultra), and electric vehicle components (BMW, BYD, KIA), which provided engineering-grade data on failure modes, thermal degradation, and mechanical fatigue under cyclic and harsh environments [51, 52].

Thematic synthesis of 80 rigorously screened academic and industrial studies (2020–2025) revealed three strategic pathways for optimizing Ti–TiO_2 alloy utilization. First, in the electronics sector, in-situ nanoparticle incorporation via high-energy ball milling enables ultra-lightweight chassis, EMI-shielded battery housings, and thermally robust heat sinks with extended fatigue performance and mechanical durability. Second, in mobility applications, closed-atmosphere mechanical alloying under argon or nitrogen minimizes oxidation and energy waste while producing corrosion-resistant linkages, engine valves, and battery-cooling plates suitable for salt-exposed environments. Third, in aerospace and biomedical fields, hybrid alloying coupled with nano-coating processes significantly improves high-temperature oxidation resistance and biocompatibility. These sector-specific findings inform a forward-looking roadmap centered on digital-twin frameworks, AI-driven parameter optimization, and sustainable process design—ultimately enabling scalable, circular-economy manufacturing of high-performance titanium components for next-generation consumer electronics and electric vehicles [53–55].

3. Technological Trends and Supply of Titanium

The global titanium value chain is governed by an asymmetric distribution of mineral resources and a growing demand across strategic industries. As demonstrated in Figure 4, major ilmenite and rutile concentrations—two principal titanium-bearing minerals—are localized in regions such as eastern Australia, the Ural Mountains in Russia, and select North American provinces—each exceeding a deposit density of 1 Mt km^{-2} [56]. These deposits are typically hosted in heavy mineral sand systems or stratiform complexes associated with ancient igneous and metamorphic belts, which often require advanced exploration technologies and beneficiation techniques. Medium-scale reserves, predominantly along West Africa and inland Brazil, are illustrated in green, while low-density zones persist across Central Asia and northern Canada, where infrastructural challenges and limited geological surveying have hindered development. These distribution patterns, corroborated by borehole mapping and mineralogical studies [56], align with the assessments by García and Lopez on critical mineral geographies [57], who highlight titanium's concentration risk and its implication for long-term supply stability. As further quantified in Figure 7, Australia commands over one-third of total global reserves, significantly surpassing the collective reserves of China, India, and Canada [56], which underlines the geopolitical sensitivity embedded in the upstream segment of the value chain. This reinforces the strategic need for bilateral exploration incentives, cross-regional resource-sharing frameworks, and diversification strategies to mitigate disruption risks and ensure secure access to feedstock for the growing aerospace, defense, and consumer electronics sectors.

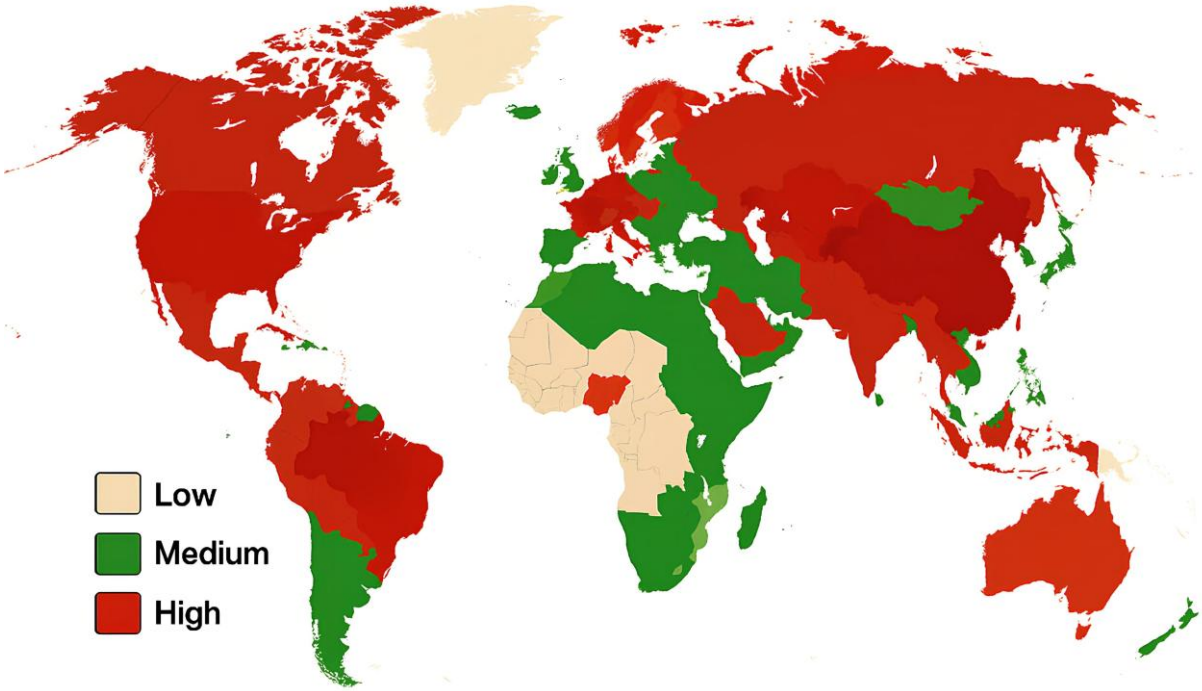

Figure 4. Global map of titanium resource intensity: deep red denotes the most richly endowed provinces, muted green marks moderate concentrations, and pale beige highlights areas of scarcity [58–62].

Figure 5 traces the material lifecycle of titanium, showing that primary production has steadily expanded since 2000, primarily driven by demand from aerospace and automotive sectors where titanium's high specific strength, low density, and exceptional corrosion resistance make it ideal for turbine blades, structural components, and exhaust systems [63]. This expansion is further supported by national stockpiling programs and rising private-sector investments in lightweight metal initiatives. Concurrently, advances in mechanical separation and hydrometallurgical recovery have accelerated the growth of secondary flows [64], with key progress observed in techniques like plasma arc melting, gravity separation of mill scrap, and solvent-extraction-based purification of chloride solutions. These developments have resulted in a tripling of recycling's contribution to titanium feedstock availability compared to the early 2000s. Such circularity efforts are reinforced by EU and East Asian directives on resource efficiency, which mandate closed-loop recovery from both pre-consumer and post-consumer titanium streams. These improvements are particularly evident in ilmenite chlorination and low-temperature reduction pathways, including the FFC Cambridge process, which minimizes environmental impact by reducing the reliance on carbon-intensive Kroll refining [65]. As depicted in Figure 6, global titanium prices have nearly tripled between 2000 and 2030, propelled not only by declining ore grades and high energy consumption in legacy processes, but also by increasingly concentrated ownership of upstream assets and logistical bottlenecks during geopolitical crises [66]. To address these cost pressures and enhance supply chain resilience, there is growing interest in distributed, modular processing units, including transportable chlorination reactors and micro-refining systems sited closer to demand hubs such as aerospace clusters and advanced manufacturing zones [67]. These innovations collectively signal a paradigm shift toward more agile, decentralized production networks that enable just-in-time refinement, reduce dependency on distant suppliers, and foster greater material circularity across the titanium value chain.

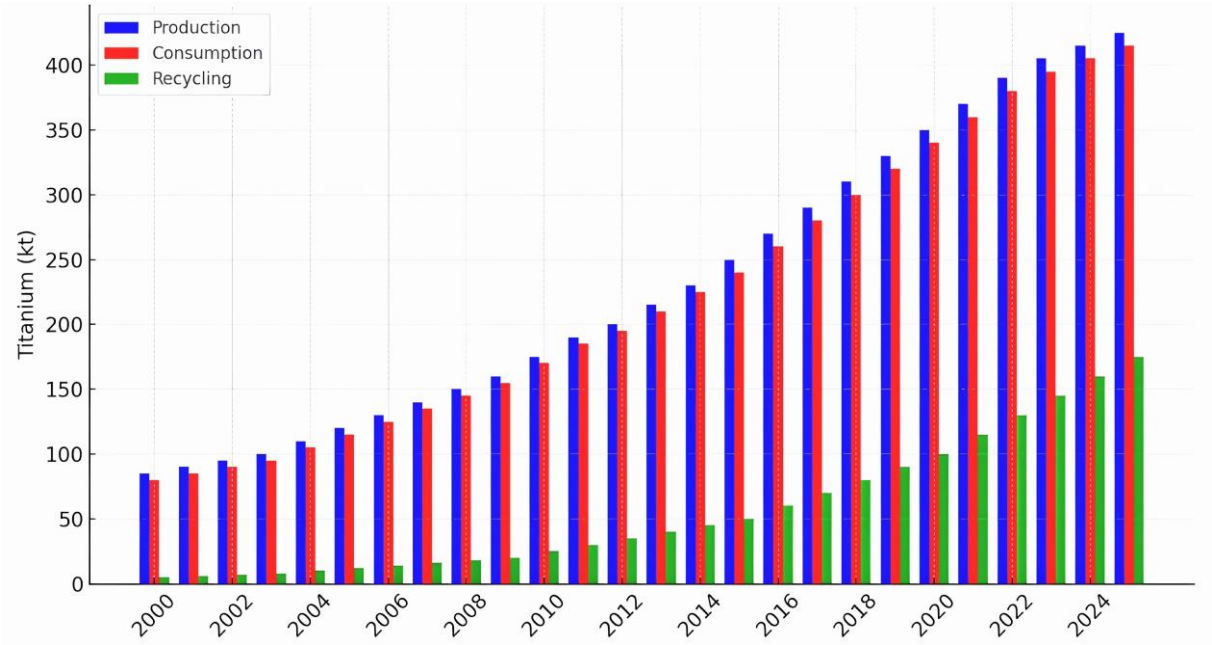

Figure 5. Global titanium sponge production, consumption, and recycling trends (2000–2025) [68–70].

Figures 8 and 9 provide a sectoral breakdown of titanium consumption, highlighting the dominant position of aerospace, where titanium alloys are increasingly used in airframes, turbines, and propulsion modules [71]. Automotive applications, particularly in electric vehicles, show exponential growth in components such as suspension systems and battery cooling modules [72]. The medical sector has expanded significantly post-2015, leveraging titanium's corrosion resistance and biocompatibility in orthopedic implants and dental fixtures [73]. In electronics, though absolute volumes remain lower, demand is steadily rising in high-performance computing (HPC), especially in thermal dissipation elements [74]. These evolving sectoral dynamics reinforce the rationale for standardized alloy qualification schemes and fully digitally integrated manufacturing pipelines [75].

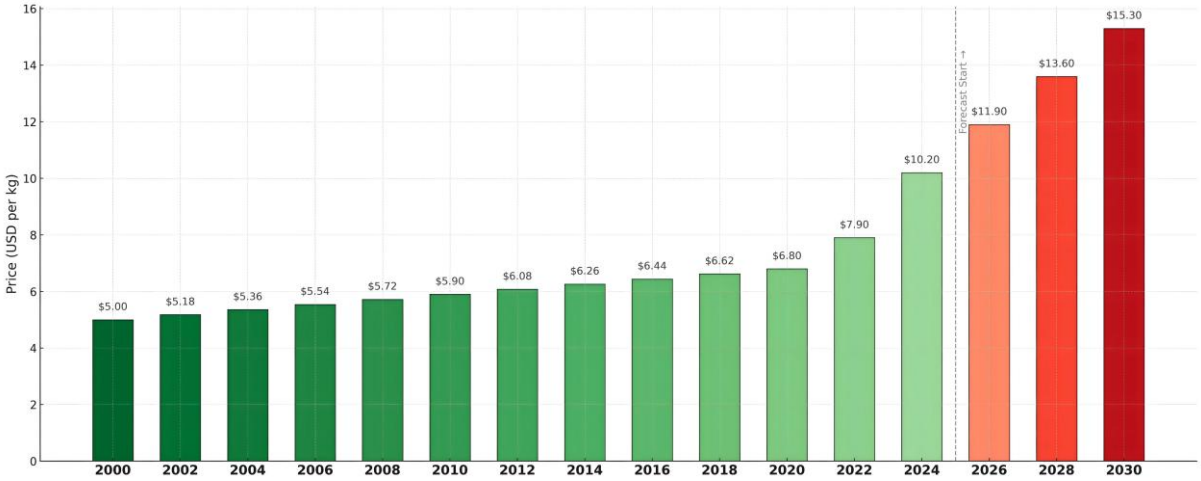

Figure 6. Average global titanium prices (USD/kg) from 2000 to 2030, with projected values for 2026–2030 marked in red. Data compiled from USGS mineral reports and commercial market forecasts [76–81].

Figure 7. Estimated annual price growth of titanium and nine key metals (2000–2024) in USD/kg, illustrating titanium's significant upward trend amid market fluctuations [82–85].

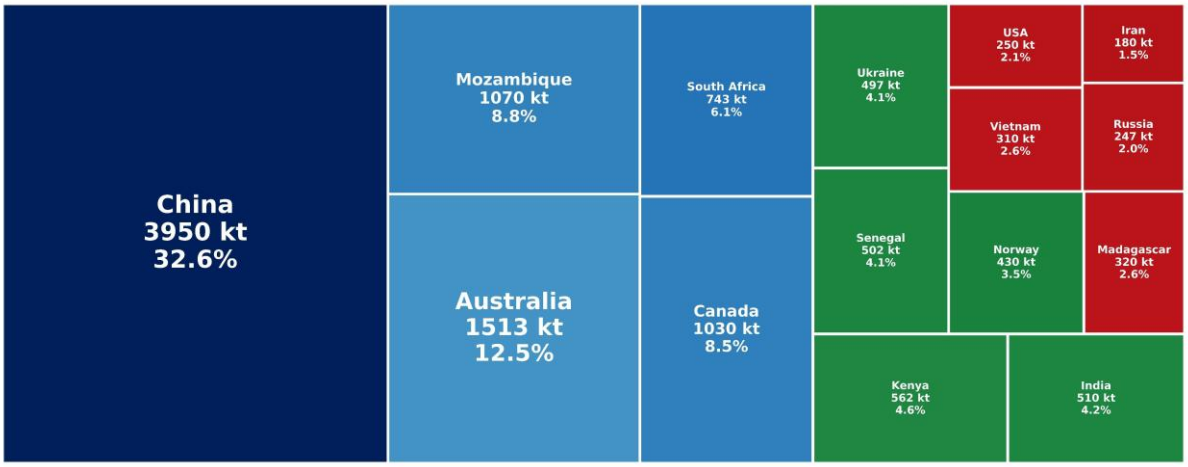

Figure 8. Treemap illustrating the global distribution of titanium reserves among the top 15 countries, showing absolute quantities (million tonnes) and relative percentage shares [86, 87].

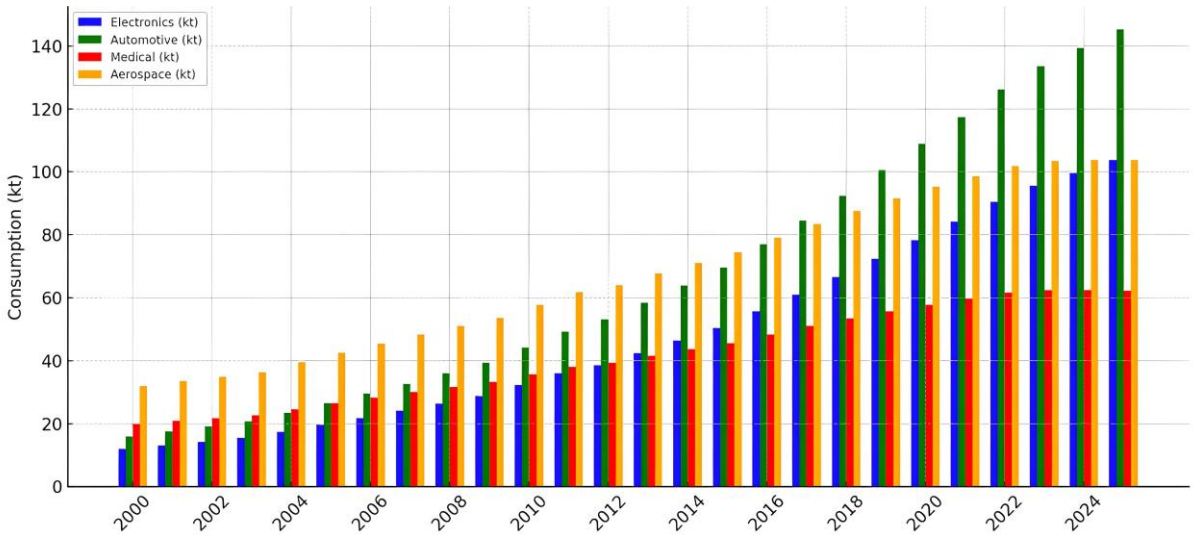

Figure 9. Global titanium consumption by electronics, automotive, medical, and aerospace sectors from

2000 to 2025, highlighting evolving industry demand and recovery dynamics [48, 51, 54].

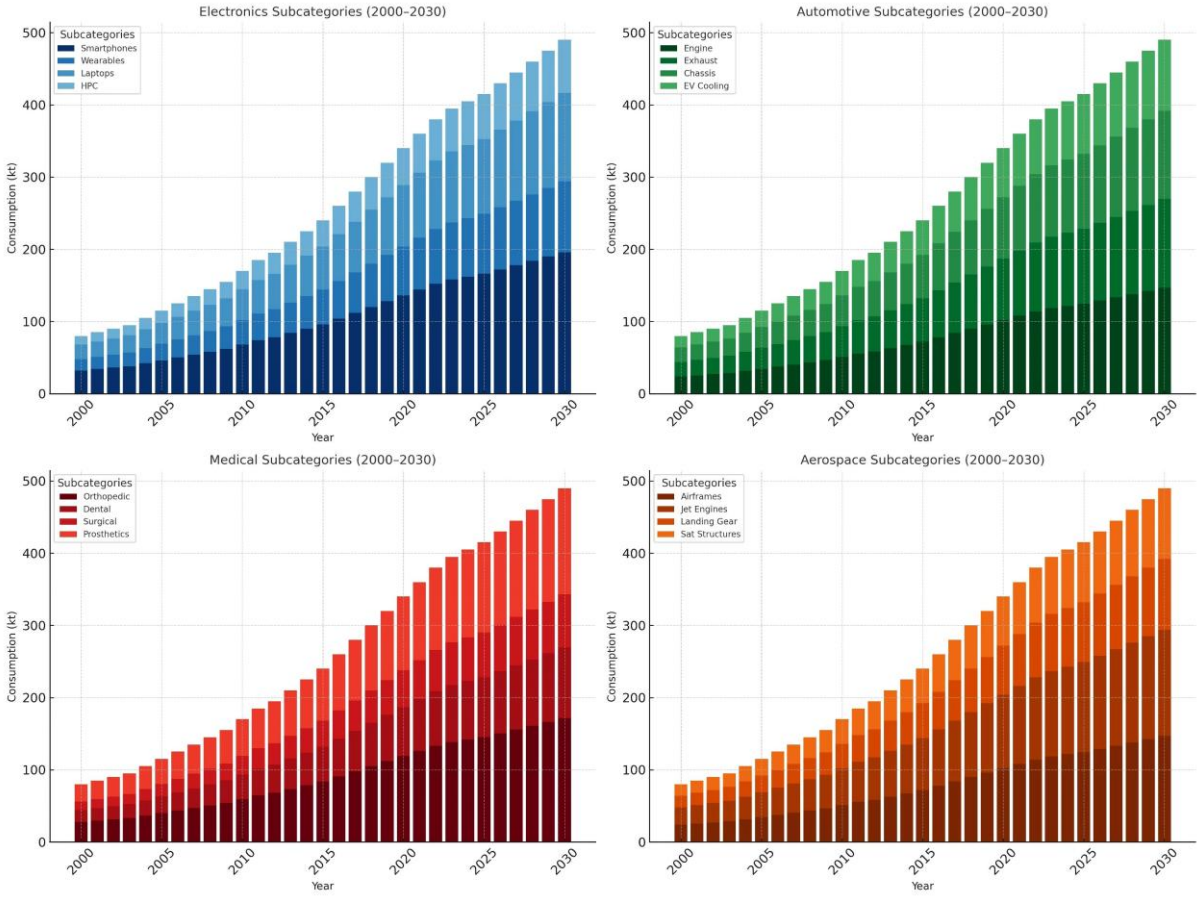

Figure 10. Titanium consumption by key subcategories in electronics, automotive, medical, and aerospace sectors from 2000 to 2030, highlighting shifts in demand across application areas [52, 53, 69, 70, 88, 89].

Synthesizing insights from Figures 4 through 10, a technically grounded roadmap emerges to reinforce titanium value chain resilience and augment metallurgical responsiveness to increasingly volatile market demands. Strategic imperatives involve intensifying geospatial mineralogical surveys and initiating high-resolution remote sensing campaigns across underutilized domains such as East Africa and the Tien Shan metallogenic belt in Central Asia, where ilmenite and rutile deposits remain geologically promising yet underdeveloped [90]. In parallel, the deployment of decentralized hydrometallurgical processing hubs—utilizing solvent extraction, ion exchange, and membrane-assisted separation techniques—can drastically enhance regional beneficiation capacity while minimizing transportation-associated emissions and operational costs [64]. Furthermore, integrating AI-driven predictive control algorithms into chlorination, reduction (e.g., FFC–Cambridge), and alloying workflows can facilitate real-time parameter tuning, optimize yield, and ensure process scalability and stability under variable input conditions [91]. These combined measures not only mitigate supply chain fragility amid intensifying geopolitical uncertainties but also unlock titanium's full functional spectrum across e-mobility platforms, advanced microelectronics thermal interfaces, and bioinert load-bearing implant systems [92–94].

4. Titanium Through Time: From Mythic Discovery to Modern Material Marvels

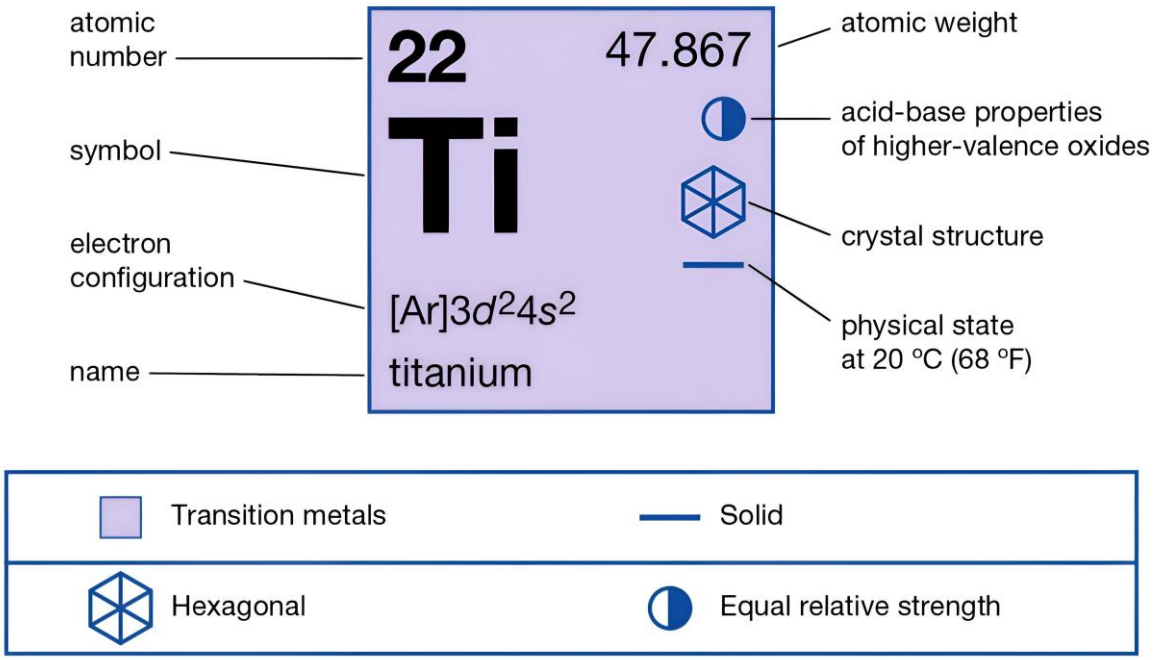

Figure 11. Atomic and physical properties of titanium: structure, mass, and behavior [95].

The historical trajectory of titanium commenced in 1791, when William Gregor identified an unfamiliar oxide in the mineral sands of Cornwall. This discovery culminated in its naming by Martin Heinrich Klaproth in 1795, who selected "Titanium" in reference to the powerful Titans of Greek mythology—symbolizing the element's exceptional strength and resilience [64], [65]. During the 19th century, researchers struggled with energy-intensive extraction techniques, a challenge that was finally addressed in the 1940s with the development of the commercially transformative Kroll process. This method enabled early industrial-scale production capacities exceeding 500 t/year, albeit with substantial energy demands of approximately 1 MWh per kilogram of titanium produced [96]. By 1965, titanium alloys had achieved widespread adoption in aerospace applications, with over 2000 t/year utilized in components such as jet engine discs and fuselage fasteners—primarily due to titanium's superior strength-to-weight ratio and exceptional corrosion resistance under harsh operating environments [97]. This foundational era solidified titanium's strategic relevance in high-performance systems and laid the crucial groundwork for present-day advances in atom-scale lattice engineering and next-generation nanostructural control.

In the 21st century, revolutionary low-carbon extraction routes are profoundly transforming titanium's global supply chain. Molten-salt electrolysis plants in China and South Korea now produce up to 5 t/day of titanium sponge, with energy consumption dropping below 35 kWh/kg Ti—nearly a 70% reduction from legacy Kroll-based systems. FFC–Cambridge cells, operating at 3–3.5 V, utilize refined electrolyte compositions and inert anode technology to yield >99 wt% purity titanium, with enhanced voltage stability and reduced cell fouling [98]. Concurrently, green pyrometallurgical reactors in Iran and Turkey recover over 60% of thermal energy and recycle chloride and magnesium by-products, achieving nearly 40% CO_2 emission reduction compared to traditional batch processing [99]. Yet, technological bottlenecks remain: global titanium recycling rates remain below 20%, ensuring homogeneous scrap input streams proves difficult, tool wear in nanoparticle-assisted mechanical alloying demands constant

recalibration, and scalable dispersion of nano-phases into Ti-matrix composites remains experimentally complex [100]. These advancements illustrate the convergence of metallurgy and sustainability science, marking a shift toward digitized, eco-efficient, and high-purity titanium production regimes.

Building on this legacy, advanced microstructural engineering has elevated titanium's performance across critical applications. The α-phase HCP lattice offers a balance of strength and ductility, with severe plastic deformation enhancing tensile strength by up to 30% without sacrificing toughness—vital for lightweight aerospace and automotive components [101,102]. Its self-passivating TiO_2 nanolayer ensures corrosion resistance in harsh environments, extending service life beyond two decades [103]. TiO_2 polymorphs—rutile, anatase, and brookite—enable high-k dielectrics, self-cleaning EV coatings, and LiDAR-integrated solar devices due to their distinct electronic and structural properties [104,105]. Modern production integrates additive manufacturing (L-PBF, DED), digital twins, and AI-based process control to reduce energy use by 20% and CO_2 emissions by 30% [106,107]. Pilot lines using in-situ synchrotron feedback and machine learning achieve grain sizes <50 nm and Vickers hardness >320 kg/mm² in Ti–TiO_2 composites at scales up to 100 kg/day [107]. Future priorities include >50% recycling efficiency, property validation via industrial datasets, and real-time monitoring of nanoparticle dispersion—ensuring titanium's central role in sustainable manufacturing and next-gen electronics.

Figure 12. Titanium: From Roots to Horizons. Source: Detitaniumup.com [108].

5. Titanium Alloy-Based Frames in Flagship and Foldable Smartphones

Mechanically alloyed titanium alloys—particularly Grade 2 and the α–β titanium alloy (Ti–6Al–

4V) known as Grade 5—have emerged as leading structural materials for ultra-thin smartphone enclosures due to their superior balance of mechanical strength, corrosion resistance, biocompatibility, and processability. Grade 2 provides a tensile strength of approximately 345 Mpa, a ductile elongation of ~20%, and a Young's modulus around 105 Gpa, which together enable cold-forming and stamping operations without requiring intermediate heat treatments [109, 110]. These properties are crucial for high-throughput production of complex geometries such as curved edges and antenna lines in unibody chassis. Samsung's Galaxy S25 Ultra and Galaxy S25 Edge, for example, use 0.8–1.0 mm Grade 2 titanium sheets to achieve rigidity while preserving manufacturability during multi-axis stamping and CNC-assisted finishing [111]. In contrast, Grade 5 offers nearly threefold greater tensile strength (~900 Mpa), a higher modulus (~115 Gpa), and slightly reduced elongation (~15%), with only a modest increase in density (4.51 g/cm³) [112]. This makes Grade 5 particularly suitable for sub-0.6 mm frames such as in the iPhone 16 Pro Max, where mechanical integrity under torsion and drop impact is essential [113].

Figure 13. Mechanical comparison of titanium frames in flagship smartphones: iPhone 15 Pro (Grade 5) offers superior strength; Galaxy S24 Ultra (Grade 2) provides better corrosion resistance and lower weight [114, 115].

The transition from aluminum or stainless steel to titanium alloys has been supported by advancements in machining, forging, and alloy design. Grade 5 titanium billets are often produced through hot isostatic pressing (HIP) or vacuum arc remelting (VAR) to minimize porosity and enhance purity [116]. These billets are then subjected to 5-axis CNC milling with diamond-coated tools, followed by electrochemical polishing and micro-sandblasting to achieve tight dimensional tolerances and refined aesthetics [117]. In the Apple iPhone 16 Pro Max, the titanium chassis is bonded to a recycled aluminum subframe via solid-state diffusion welding, allowing weight reduction of ~10% over its predecessor without sacrificing mechanical performance [118]. Huawei and Xiaomi have also adopted similar hybrid designs in their titanium-clad flagships, often integrating vapor-deposited ceramic coatings or laser-textured finishes for tactile and visual enhancement. Manufacturing precision is especially critical in foldable model such as the Huawei Mate X5 Pro, where titanium latches, side rails, and center hinges require high fatigue strength, minimal creep, and tight contact tolerances to support repeated folding cycles [119].

Figure 14. CNC-machined titanium Grade 5 (Ti–6Al–4V) chassis of the iPhone 16 Pro Max, featuring a PVD-applied TiO_2 layer for enhanced hardness, corrosion resistance, and thermal stability [115–117].

Surface engineering of titanium components significantly augments mechanical durability, user comfort, and long-term device integrity by modifying the surface chemistry and microstructure. Techniques such as plasma electrolytic oxidation (PEO), micro-arc oxidation (MAO), and physical vapor deposition (PVD) are widely utilized to form dense, nanocrystalline TiO_2 coatings with hardness levels reaching up to 400 HV—substantially greater than the ~160 HV of untreated titanium surfaces—thereby improving scratch resistance, surface hydrophobicity, and fingerprint repellence [120, 121]. These engineered oxide layers also enhance thermal emissivity and provide robust electromagnetic shielding, which is particularly critical in high-frequency environments of modern smartphones. Premium models such as the OnePlus 12 Titanium Edition and Huawei Mate X5 Pro incorporate such coatings to meet stringent electromagnetic compatibility (EMC) requirements for 5G antenna arrays, NFC transceivers, and wireless charging systems without signal degradation [122]. Simultaneously, foldable phones increasingly employ precision-engineered titanium alloy hinges, fabricated using laser powder bed fusion (L-PBF), which enables complex internal geometries, load-distribution lattice structures, and optimized topology to maximize strength-to-weight ratios under dynamic loading [123]. These 3D printing approaches, supported by uniformly dispersed $Ti–TiO_2$ composite powders prepared via mechanical alloying, dramatically reduce raw material waste and facilitate the integration of microscale mechanical elements—such as pin joints, flex axes, compliant hinges, and locking cams—that are otherwise impractical to fabricate using subtractive methods [124].

Foldable smartphones have emerged as a critical frontier for precision titanium component engineering, particularly in the design of compact yet highly durable hinge mechanisms. Major OEMs such as Xiaomi, OnePlus, Google, and Samsung, have increasingly adopted 3D-printed titanium hinges in their premium foldable series—including the Xiaomi Mix Fold 4, OnePlus Open, Pixel Fold, and Galaxy Z Fold 7—capitalizing on the superior fatigue resistance, corrosion stability, and biocompatibility of Ti–6Al–4V (Grade 5) alloys [125, 126]. These hinges are frequently fabricated using laser powder bed fusion (L-PBF) to achieve internal lattice architectures with precise tolerances and lightweight topology-optimized designs. Titanium's excellent ratio of stiffness to density ensures long service life even under repeated flexing cycles exceeding 300,000 folds—a key metric for foldable phone durability certification [127].

Additionally, some models such as the Galaxy Z Fold 7 incorporate a printed internal titanium plate beneath the display to enhance bending resistance while minimizing bulk. This material combination enables slimmer profiles without compromising hinge integrity or heat dissipation.

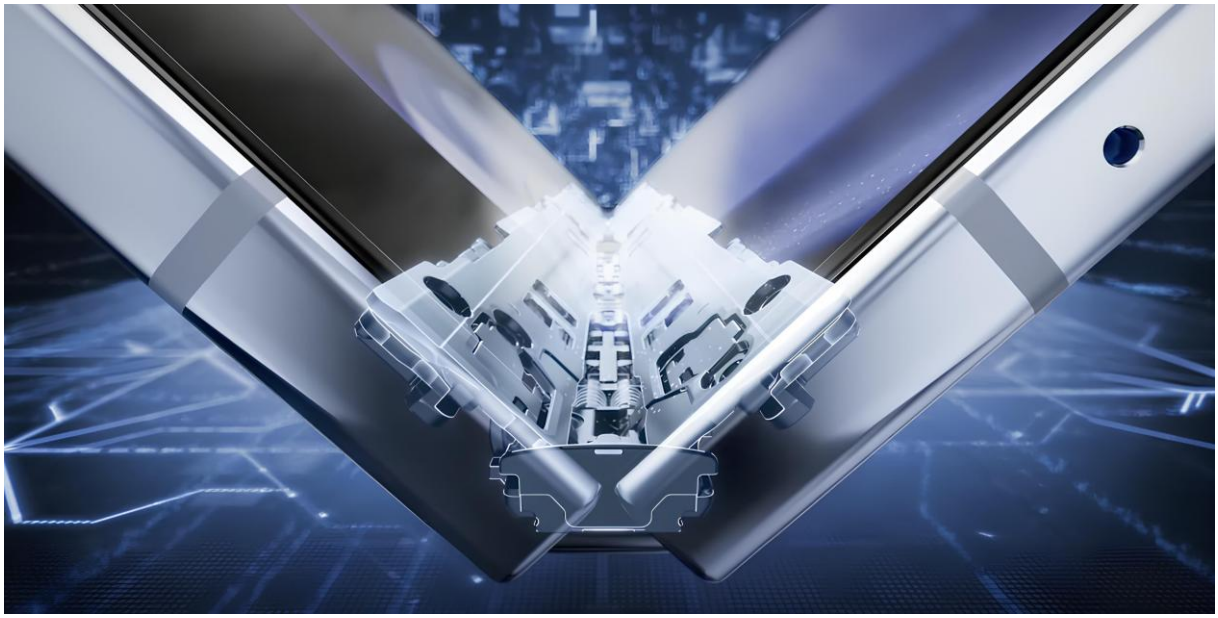

Figure 15. Titanium hinges in foldable smartphones require excellent fatigue resistance, precise dimensions, low friction, thermal stability, and high wear durability to ensure reliable performance over repeated folds [125–127].

The strategic use of titanium and Ti–TiO_2 composites in such moving assemblies directly aligns with the overarching goals of mechanically alloyed material platforms: long-term reliability, design miniaturization, and resistance to wear and environmental stress. Moreover, surface-engineered TiO_2 nanolayers—formed via PEO and MAO—are increasingly applied on hinge pins and internal contact zones to reduce friction and enhance the fatigue life of articulating joints. While these material systems unlock substantial advantages in weight savings and performance enhancement, challenges remain in terms of production cost, scalability, and surface finishing. In particular, achieving uniform oxide coatings within complex internal cavities, as well as ensuring low-friction behavior under dynamic folding, remains a critical area of active research and process optimization [128].

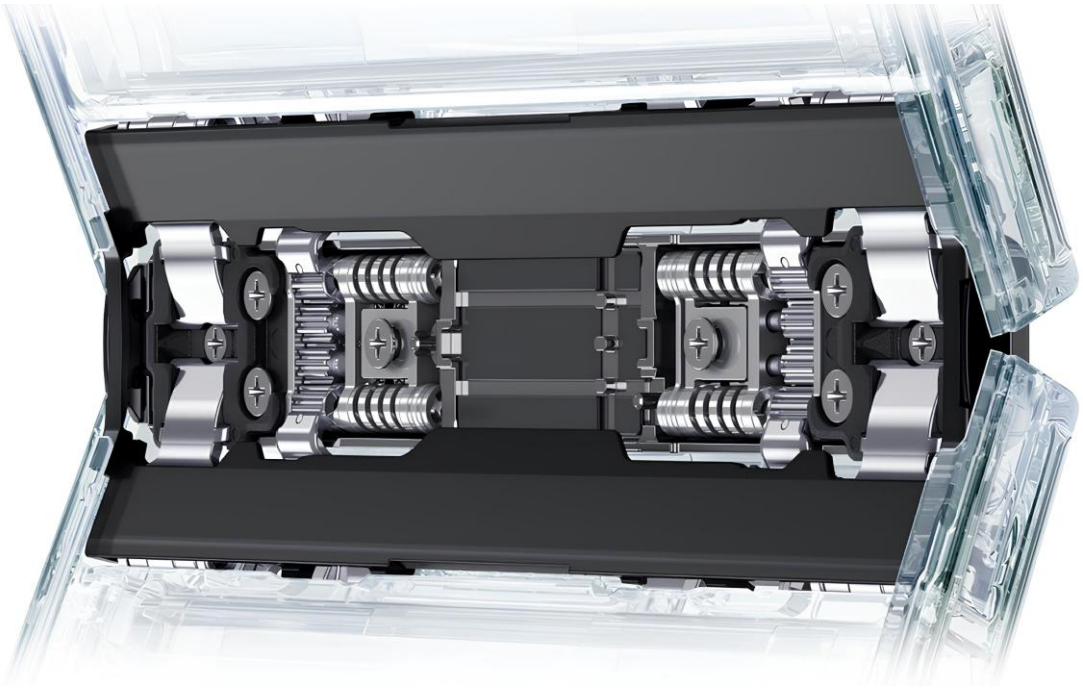

Figure 16. Foldable titanium hinge engineered for high fatigue, thermal, and wear resistance [125–127].

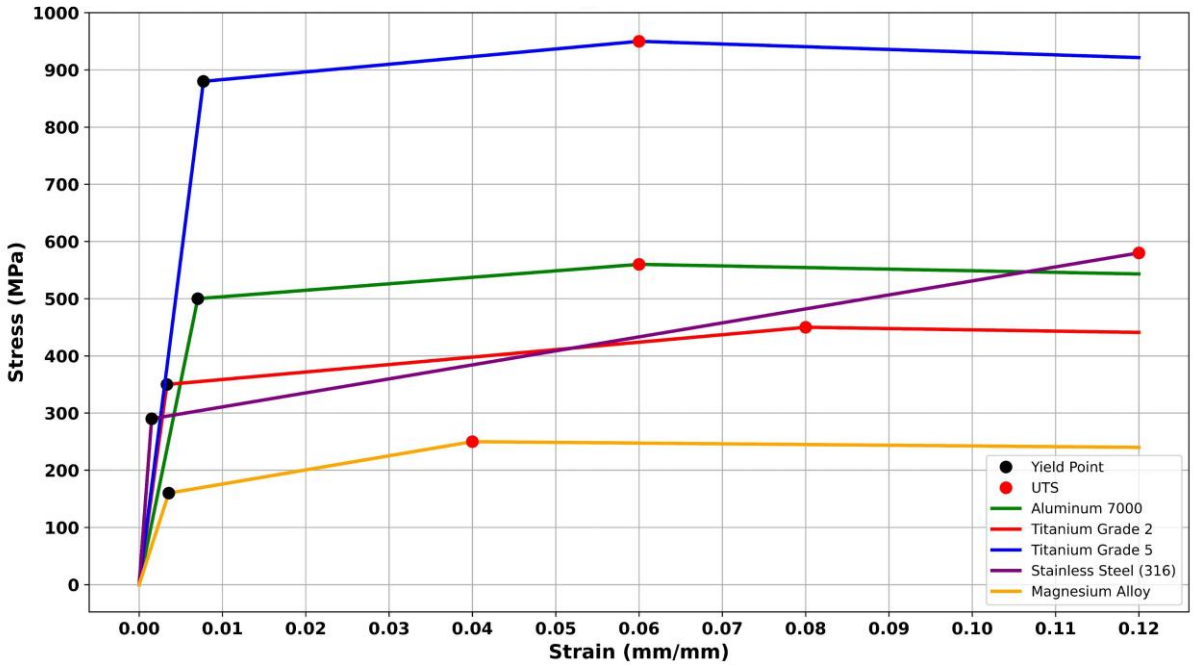

Figure 17. Stress–strain curves with yield (black) and UTS (red) points. Titanium alloys offer superior strength–ductility balance for ultra-thin smartphone frames [129–132].

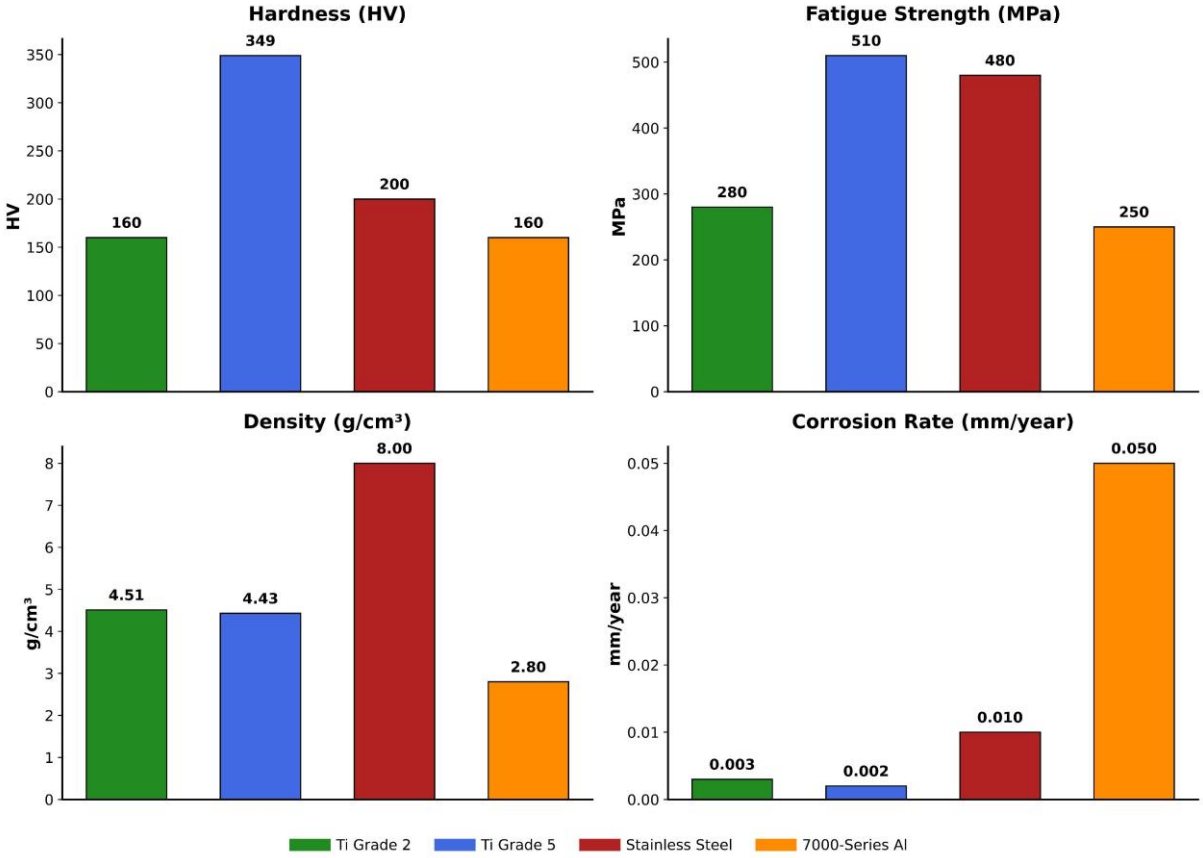

Figure 18. Comparative metrics—hardness, fatigue, corrosion, and density—show titanium Grades 2 and 5 offer the best combination of light weight, strength, and corrosion resistance for ultra-thin chassis [133–136].

In conclusion, titanium alloys have fundamentally reshaped the structural strategies employed in premium smartphone chassis design, owing to their unmatched combination of mechanical strength, surface adaptability, and lightweight nature. Grade 2 titanium continues to be favored for its superior manufacturability and corrosion resistance, whereas Grade 5—an α–β alloy with significantly higher tensile and fatigue strength—enables the development of ultra-thin yet rigid enclosures required by modern flagship devices. As illustrated in Figure 17, titanium alloys display superior stress–strain performance with elevated yield and ultimate tensile strength points compared to conventional chassis metals. Moreover, Figure 18 highlights titanium's unique multimetric balance—combining high hardness, fatigue endurance, corrosion resistance, and low density—making it exceptionally suitable for structural applications under dimensional constraints. Recent advances, including the incorporation of TiO_2 nanolayers via plasma and vapor-phase deposition, have enhanced scratch resistance, electromagnetic shielding, and heat dissipation. The growing use of additive manufacturing and diffusion-bonded hybrid assemblies allows precise internal geometries and multi-functional integration, especially in foldable architectures. These innovations reflect a deepening convergence of materials science with user-centric electronics engineering. Furthermore, as manufacturers seek improved sustainability and recyclability, titanium's intrinsic corrosion resistance, biocompatibility, and high strength-to-weight ratio secure its position for long-term deployment. Future-oriented surface engineering—such as smart coatings, self-healing oxides, and conductive TiO_2 interlayers—are expected to further elevate the role of titanium alloys in the next–gen of mobile devices [137].

6. High-Performance Titanium Nanocomposites in Automotive Design

The use of mechanically alloyed titanium nanocomposites in the automotive sector has ushered in a new era of lightweight, high-performance vehicle architectures. By employing solid-state processing techniques such as high-energy ball milling, titanium matrix powders are reinforced with finely dispersed TiO_2 nanoparticles, which significantly enhance microstructural uniformity, suppress grain coarsening, and increase dislocation density—leading to improved strength, fatigue endurance, and thermal creep resistance at elevated operating temperatures [138, 139]. These nanocomposite powders are typically consolidated using advanced additive manufacturing (AM) methods such as laser powder bed fusion (L-PBF), hot isostatic pressing (HIP), and spark plasma sintering (SPS), enabling the production of intricate components with low residual porosity, excellent dimensional control, and tailored anisotropic properties [140, 141]. Automotive OEMs including Hyundai, Kia, Mercedes-Benz, BYD, and Tesla have begun adopting Ti–TiO_2 nanocomposites in structurally demanding parts such as crash-resistant A-pillars, subframe brackets, shock-absorber mounts, battery tray housings, and motor casing assemblies—particularly in electric and hybrid platforms where lightweighting directly improves energy efficiency and range [142, 143]. Furthermore, the use of these alloys in high-strain regions improves structural reliability under crash loads and enhances resistance to cyclic stress, corrosion fatigue, and thermomechanical degradation common in EV drivetrain environments [144, 145]. This fusion of materials science and manufacturing enables a shift from conventional metals to smarter, stronger titanium-based solutions.

One of the most iconic and technically pioneering applications of titanium alloys in modern automotive design is embodied by the Icona Vulcano Titanium—a concept supercar featuring the world's first full titanium body, handcrafted from Grade 5 (Ti–6Al–4V) titanium alloy panels [146]. This engineering feat, jointly realized by Icona Design Group and Cecomp, represents a milestone in materials-driven performance innovation, showcasing titanium's outstanding strength-to-weight ratio, fatigue endurance, and exceptional resistance to oxidation and chemical degradation under road-salt and UV exposure [147]. Unlike aluminum or carbon-fiber-reinforced composites, the cold-formed titanium panels maintain both geometric precision and ductile formability during manual shaping, while also reducing the structural weight without sacrificing crash resilience or torsional stiffness [148]. The use of Grade 5 alloy—commonly employed in aerospace—also enhances panel springback resistance, allowing for ultra-thin, sharp-edged body geometries with high aerodynamic efficiency and minimal panel flutter at high speeds [149]. Beyond aesthetics, the vehicle illustrates the feasibility of adopting titanium body shells in limited-production sports or hypercars, where manufacturability, corrosion immunity, and long-term material stability are prioritized over cost constraints [150]. With advanced metrology and forming simulation tools, future production of titanium-bodied vehicles may become more accessible, particularly when combined with hybrid manufacturing routes and precision joining techniques such as laser welding and diffusion bonding.

Figure 19. The Icona Vulcano Titanium concept car features a full Grade 5 titanium body, demonstrating advanced mechanical alloying strategies for achieving high structural rigidity, corrosion resistance, and reduced weight in automotive applications, (Icona Design Group), [146-150].

Moreover, the integration of advanced additive manufacturing (AM) techniques using compositionally optimized Ti–TiO_2 nanocomposite powders has unlocked unprecedented design flexibility and structural complexity in fabricating multifunctional automotive components. These engineered powders—produced through high-energy mechanical alloying followed by meticulous sieving and spheroidization processes—exhibit superior flowability, enhanced surface morphology, and refined phase dispersion, making them ideally suited for laser powder bed fusion (L-PBF) applications in next-generation electric, hybrid, and performance vehicles [151, 152]. L-PBF enables the layer-by-layer construction of topologically optimized parts incorporating engineered lattice geometries, variable-density structures, and embedded microfluidic pathways for passive and active heat dissipation, which are critical in applications requiring high thermal resilience and weight reduction. Key examples include 3D-printed titanium–copper alloy turbocharger impellers designed for high-speed rotational environments, heat exchangers with intricately channeled internal flow paths that maintain battery and motor thermal equilibrium, and structural brackets with local stiffness modulation to withstand mechanical shocks while minimizing mass [153]. The integration of AI-assisted, closed-loop monitoring systems into the L-PBF workflow—utilizing real-time data from melt pool sensors, laser intensity feedback, and thermal field modeling—enables dynamic adjustment of scan speed, hatch spacing, and energy input, which collectively ensure the elimination of defects such as microvoids and anisotropic stress zones [154]. These digitally enhanced processes not only increase build precision and part reproducibility but also extend component fatigue life under high-cycle mechanical loading and thermal cycling. Automotive leaders including Tesla, BYD, and Hyundai Motor Group have actively adopted these advanced AM frameworks to develop drivetrain housings, crash-energy absorbers, suspension nodes, and battery tray modules that offer improved thermal conductivity, corrosion resistance, and long-term mechanical integrity while achieving up to 25% mass reduction over conventional aluminum or stainless steel counterparts [155]. These ongoing initiatives clearly demonstrate a significant shift toward digitally integrated, performance-oriented, and sustainability-driven manufacturing paradigms in the automotive sector, effectively

meeting both evolving regulatory requirements and rising consumer expectations for next-generation mobility solutions [156].

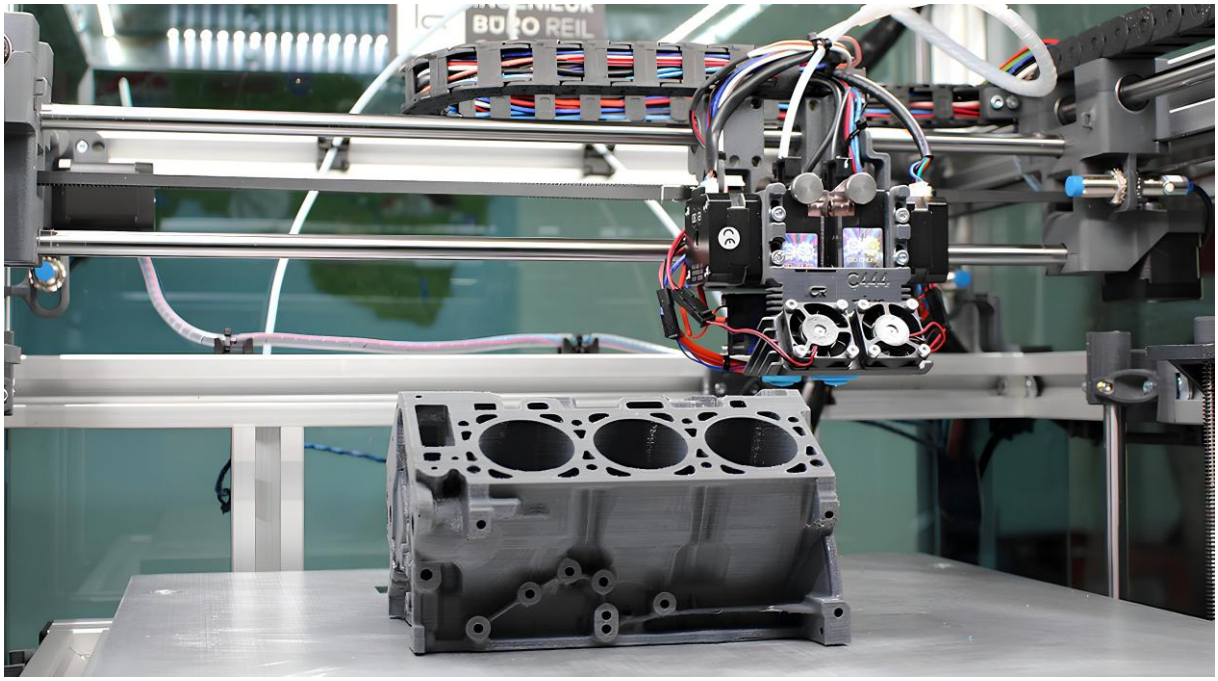

Figure 20. 3D printing of a titanium engine block using tailored Ti–TiO_2 powders via L-PBF, enabling optimized internal lattices for thermal and mechanical performance in next-gen automotive manufacturing [151–156].

Ti–TiO_2 nanocomposites also demonstrate markedly superior corrosion resistance compared to conventional aluminum 7000-series alloys and 316L stainless steel in harsh, salt-laden environments such as coastal roadways and winter maintenance zones. Whereas Al-7075 and similar high-strength aluminum grades frequently suffer intergranular corrosion, pitting, and stress-corrosion cracking under cyclic loading and chloride exposure [143], mechanically alloyed Ti–TiO_2 systems maintain an intact passive film—even after 1,000 h of ASTM B117 salt-spray testing—resulting in corrosion rates below 0.002 mm/year versus >0.05 mm/year for Al-7000 and ≈0.01 mm/year for 316L SS [157, 158]. This exceptional durability has led to the implementation of Ti–TiO_2 composites in critical automotive components such as battery tray assemblies—where long-term integrity under electrolyte and road-salt exposure is vital—steering knuckles that resist chloride-induced embrittlement, and high-performance brake calipers that maintain frictional consistency without surface degradation [159]. Additionally, the nano-reinforced oxide network imparts enhanced wear resistance (up to 30 % reduction in volumetric loss under pin-on-disc testing) and thermal stability up to 500 °C, outperforming both aluminum and steel in engine bay and chassis applications subject to heat and chemical attack [160]. Beyond performance, titanium's inherent biocompatibility, ease of machining for remanufacturing, and 100 % recyclability align seamlessly with evolving automotive mandates on life-cycle assessment, material circularity, and reduced carbon footprint throughout the vehicle's service life. In conclusion, the widespread deployment of mechanically alloyed Ti–TiO_2 nanocomposites marks a paradigm shift in automotive materials engineering, uniting intelligence, resilience, and environmental stewardship. By leveraging AI-driven process optimization and additive manufacturing platforms, OEMs can precisely tailor microstructures, lattice topologies, and surface chemistries to meet exacting performance targets—from corrosion-proof body panels that endure coastal and winter-salt exposure to ultra-light, fatigue-resistant suspension links in motorsport applications [161]. These composites simultaneously deliver exceptional yield strength and stiffness-to-

weight ratios, while the embedded TiO_2 network provides long-term passive protection and wear resistance at elevated temperatures up to 500 °C, far surpassing traditional aluminum and steel counterparts [162]. Critically, titanium's full recyclability and low lifecycle carbon footprint align with circular-economy mandates, enabling closed-loop recovery of 95 % of alloy material at end-of-life. As the industry converges on electrified, autonomous, and shared-mobility platforms, Ti–TiO_2 nanocomposites stand as indispensable enablers of next-generation vehicle architectures—delivering the structural integrity, manufacturing precision, and sustainability required to propel global automotive innovation forward.

7. Titanium Alloying for Metal Additive Manufacturing

The application of mechanically alloyed titanium-based powders in metal additive manufacturing (AM) represents a pivotal advancement in modern metallurgical engineering, where precise control over powder composition and microstructure plays a decisive role in component performance. Mechanical alloying—typically performed through high-energy ball milling in controlled atmospheres—enables the formation of non-equilibrium phases, nanocrystalline structures, and uniform dispersion of oxide or intermetallic reinforcements within titanium matrices, such as Ti–TiO_2, Ti–Nb, Ti–Zr, and Ti–Cu systems [163, 164]. These powders must exhibit spherical morphology, narrow particle size distribution, and minimal contamination to ensure reliable laser–powder interaction during AM processes like laser powder bed fusion (L-PBF) or electron beam melting (EBM) [165, 166]. The presence of even trace amounts of impurities such as oxygen, nitrogen, or moisture during alloying or storage can lead to porosity, embrittlement, or loss of fatigue resistance in the final printed part. Therefore, strict environmental control—including inert gas milling chambers, sealed sieving systems, and vacuum storage units—is critical for maintaining powder integrity [167]. Additionally, advanced AI-integrated systems are increasingly deployed in modern AM workflows to monitor powder behavior, optimize process parameters in real time, and reduce variability between builds [168]. The combination of mechanically alloyed titanium powders with AI-guided L-PBF has opened new avenues for fabricating complex lattice-reinforced components with site-specific mechanical gradients, topological design optimization, and built-in thermal management pathways—characteristics increasingly crucial for advanced automotive and consumer electronics applications [169, 170].

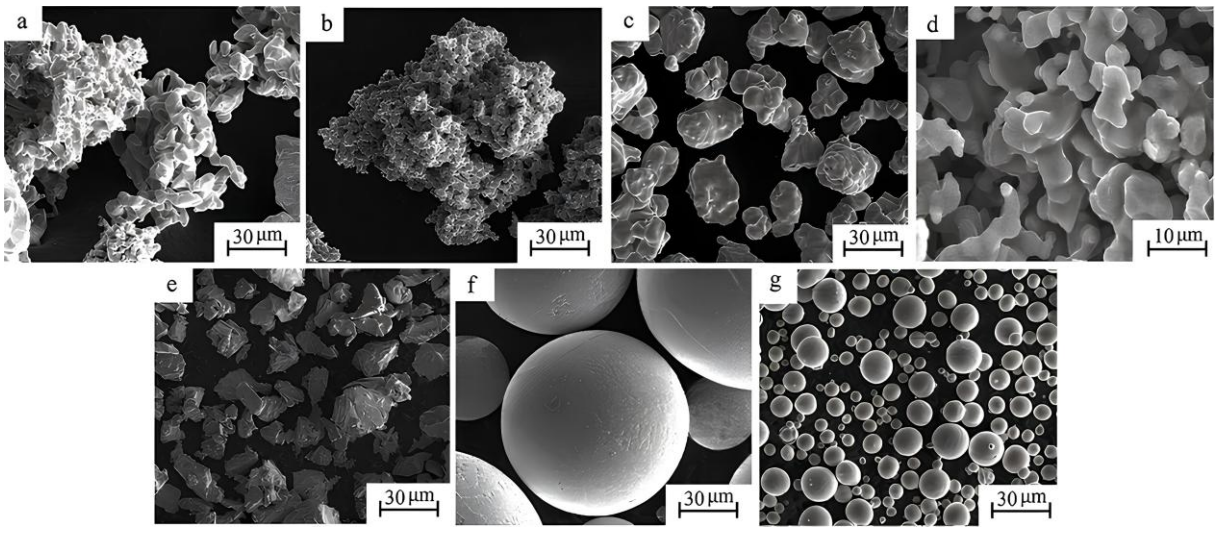

Figure 21. SEM images of commercially pure titanium (CP-Ti) and Ti-6Al-4V powders produced by various methods: (a) Kroll (fine sponge), (b) Armstrong, (c) HAMR, (d) FFC, € HDH, (f) PREP, and (g) plasma atomization. The images show differences in powder morphology related to the production techniques [171].

Leading companies such as Hyundai, Kia, and Tesla have adopted advanced metal additive

manufacturing methods, particularly laser powder bed fusion (L-PBF) and electron beam melting (EBM), for the production of structurally critical automotive components such as chassis brackets, brake calipers, and suspension knuckles. These components benefit from topological optimization through the use of lattice-reinforced geometries, which enable significant mass reduction without compromising mechanical integrity [172, 173]. In the context of electric vehicles, Ti–TiO_2-based composite powders are increasingly used to fabricate battery tray enclosures that offer up to 40% weight reduction compared to stainless steel, while simultaneously delivering enhanced corrosion resistance during harsh thermal and humidity cycling, which is critical for long-term reliability [174, 175].

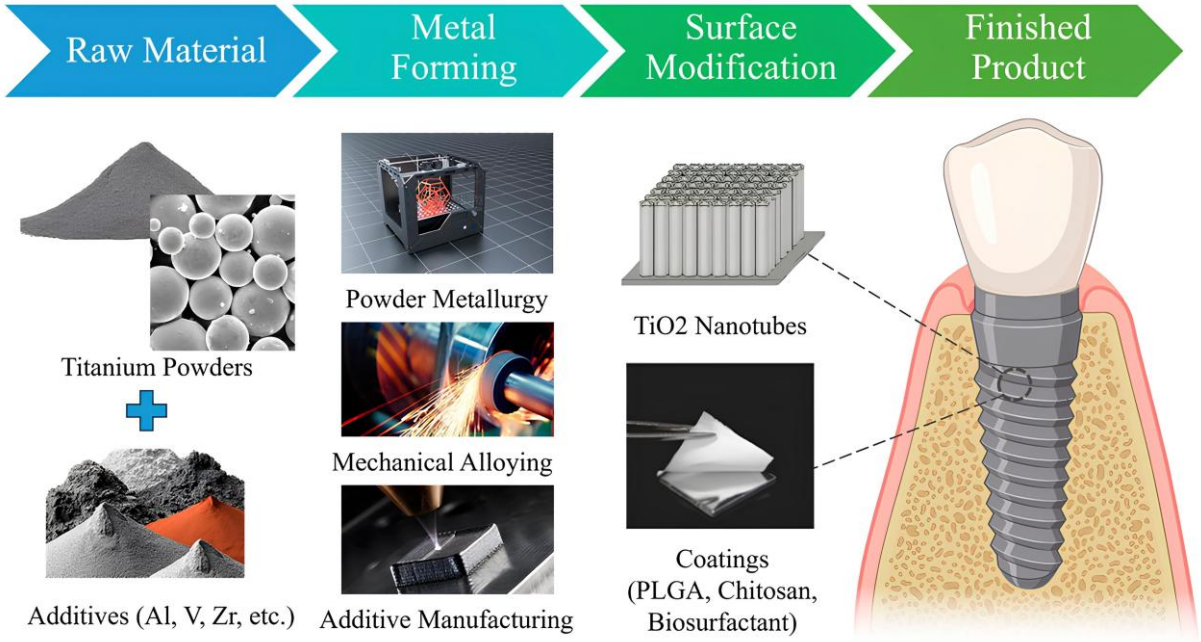

Figure 22. Key fabrication stages of titanium devices: forming, heat treatment, and final evaluation [170–175].

Simultaneously, leading smartphone manufacturers including Apple and Samsung have leveraged mechanically alloyed titanium alloys to enhance the structural resilience and multifunctionality of mobile devices. Notably, Grade 5 titanium (Ti–6Al–4V) has been utilized in the chassis of the iPhone 16 Pro, offering an effective balance of lightweight formability and mechanical rigidity, while also supporting electromagnetic transparency for integrated antenna systems [176, 177]. Moreover, Ti–Cu alloys have been employed for the fabrication of internal heat-dissipating components, such as passive cooling plates and thermal spreaders, which are embedded in compact electronic assemblies including foldable smartphones and high-performance handheld devices, where spatial constraints and thermal management are paramount [178]. Crucially, the integration of such titanium-based mechanical alloys into additive manufacturing workflows enables the direct printing of functionally integrated features—such as pin joints, flex axes, and locking cams—within a single uninterrupted build cycle. This eliminates the need for post-machining and enhances structural cohesion, streamlining assembly and reducing both material waste and production time, thus exemplifying the transformative role of additive manufacturing in the design and fabrication of next-generation high-performance automotive and consumer electronics systems [179].

Artificial intelligence (AI) plays a pivotal role in optimizing titanium-based additive manufacturing (AM) by enhancing precision, quality assurance, and efficiency throughout the fabrication process. AI algorithms are increasingly integrated into metal AM workflows to conduct real-time layer-by-layer quality control, monitor melt pool dynamics, and detect porosity through advanced sensor fusion and thermal imaging techniques [180, 181]. These intelligent systems dynamically adjust key process parameters—such as laser intensity, scan speed, and recoater blade angle—in situ to maintain thermal

stability and ensure defect-free builds, thereby minimizing the need for extensive post-processing [182]. In high-value components such as 3D-printed titanium motor housings and integrated heat exchangers, AI-assisted thermal and mechanical simulations are used during the design phase to anticipate and manage internal thermal gradients and mechanical stress distribution, which are critical for long-term part reliability and functional integrity [183]. These simulations guide topological optimization and lattice architecture generation for structural reinforcement and localized heat dissipation in both automotive and aerospace sectors [184]. To ensure consistency, repeatability, and regulatory compliance, digital twin frameworks are increasingly being deployed across the powder-to-part manufacturing pipeline. These digital replicas capture detailed process histories—including material batch data, environmental variables, and sensor feedback—to enable traceable lifecycle analysis and quality certification [185]. This traceability is essential for meeting the evolving ISO/ASTM standards that govern additive manufacturing in safety-critical domains such as automotive crash structures and aerospace propulsion components [186, 187]. Notably, companies such as BYD and Xiaomi Auto have invested significantly in in-house AI-integrated AM platforms to accelerate product development, meet lightweighting targets, and reduce material waste through closed-loop feedback systems [188, 189]. These AI-driven initiatives reflect a convergence of smart manufacturing and digital engineering, redefining the scalability and industrialization of titanium-based mechanical alloys in electric mobility and consumer technologies.

The ongoing transformation from conventional subtractive methods to additive manufacturing, and from monolithic components to multifunctional, topology-optimized architectures, reflects a fundamental shift in advanced engineering. Within this evolution, mechanically alloyed titanium powders have become central due to their recyclability, tunable composition, and ability to form intricate geometries with site-specific mechanical and thermal properties [190, 191]. These powders enable the integration of load-bearing, heat-dissipating, and even electronic features within a single AM build—essential for applications such as electric vehicle drivetrains, battery enclosures, and the internal frames or folding mechanisms of smartphones. To ensure high fatigue strength and crack resistance under demanding service conditions, powder morphology, phase purity, and interfacial chemistry must be tightly controlled. Ongoing research in oxide interface engineering, hybrid-layer strategies, and nanoparticle reinforcement continues to enhance the mechanical performance and functional integration of printed parts [192, 193]. Ultimately, the convergence of advanced metallurgical design, clean powder production, and AI-optimized additive manufacturing workflows enables scalable and reliable manufacturing of lightweight, corrosion-resistant components for future mobility and smart Consumer electronics sectors [194–196].

8. Green Extraction and Powder Production of Titanium

The Kroll process, involving the high-temperature reduction of titanium tetrachloride ($TiCl_4$) by molten magnesium under an inert argon atmosphere, has long been the cornerstone of titanium sponge production due to its proven reliability and industrial scalability. However, this well-established method is associated with high energy consumption—approximately 60 kWh per kilogram of titanium—and substantial CO_2 emissions originating from both the production and combustion of magnesium. Additionally, it generates large volumes of magnesium chloride ($MgCl_2$) and unreacted salt waste per tonne of titanium, posing significant environmental challenges related to waste management [197]. To address these limitations, modern closed-loop pyrometallurgical reactors incorporate advanced high-efficiency heat recuperators that recover sensible heat from off-gas streams exceeding 600 °C, utilizing it to preheat incoming $TiCl_4$ vapor and argon purge gas. This heat recovery reduces fresh energy input by over 35% and lowers CO_2 emissions by approximately 30% compared to conventional Kroll furnaces [198]. Inside the reactor, segmented heating zones with high-emissivity refractory ceramics ensure uniform temperature distribution, preventing chloride condensation, reducing corrosion, and extending campaign

durations up to 8000 hours [199]. Integrated salt-recovery subloops reclaim over 90% of spent $MgCl_2$, converting a hazardous by-product into valuable secondary feedstock. This circular strategy reduces waste while aligning titanium sponge production with sustainability targets and enhancing manufacturing cost-efficiency [200].

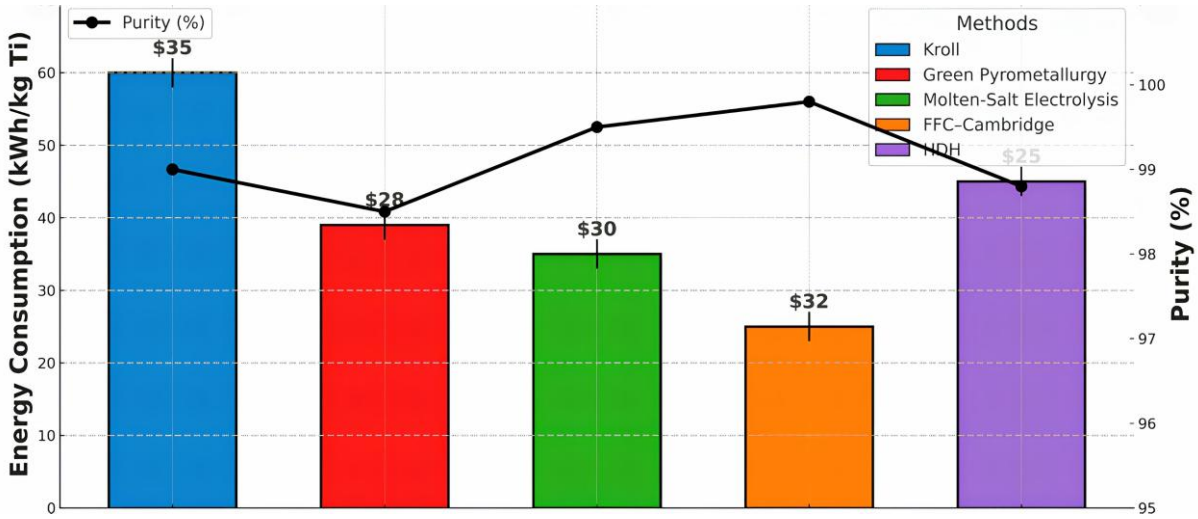

Figure 23. Titanium powder production methods from 2020 to 2025: comparison of energy consumption, purity, and cost relative to the conventional Kroll process [201–205].

Molten-salt electrolysis in a $CaCl_2$–CaO medium has recently emerged as a leading method for titanium powder production, offering a favorable combination of scalability, energy efficiency, and high purity exceeding 99.9% [206]. In this process, TiO_2 is solubilized at 900–950 °C into reactive oxychloride species, then cathodically reduced under low-voltage conditions (3.0–3.5 V), achieving faradaic efficiencies above 88% [207]. Industrial operations in China and South Korea report oxygen and nitrogen levels below 0.08 wt %, meeting aerospace and biomedical powder standards [208]. Real-time feedback via in-cell zirconia sensors enables dynamic process control and powder yields exceeding 92% [209]. Enhanced melt agitation and optimized cathode design suppress dendritic growth and reduce polarization losses. The resulting powders exhibit narrow size distributions, near-spherical morphology, and high flowability—attributes critical for laser powder-bed fusion and electron beam melting [210]. Overall, molten-salt electrolysis provides a scalable, energy-efficient, and clean route for producing titanium powders tailored to advanced additive manufacturing in aerospace, medical, and engineering sectors.

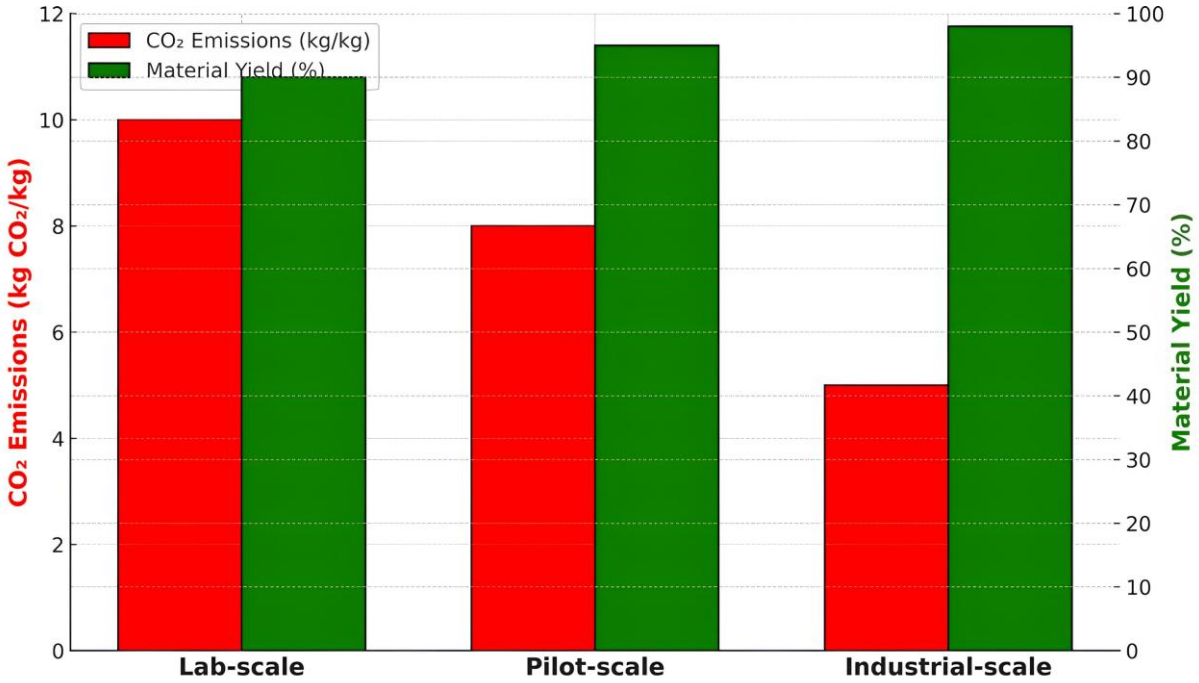

Figure 24. CO_2 footprint and yield versus production scale in titanium powder processing [197, 198, 200, 206].

The FFC–Cambridge process has garnered increasing attention as a sustainable electrochemical route for titanium powder production, enabling the direct reduction of solid TiO_2 cathodes in molten $CaCl_2$ without the need for chlorination or intermediate halide precursors [211]. Recent pilot-scale implementations between 2021 and 2023 have featured sophisticated cell architectures—incorporating inert graphite anodes, ceramic diffusion barriers, and multi-stage gas seal assemblies—which effectively suppress chlorine crossover and support continuous operation exceeding 1,000 hours with minimal performance decay [212]. Concurrently, advanced thermal management systems maintain electrolyte stability within the 940–960 °C range, while precisely regulated cathodic current densities (0.5–1.0 A/cm²) and voltage loops (3.2–3.4 V) ensure consistent faradaic efficiencies and reduce energy variability throughout prolonged operational cycles [213]. As a result, the process achieves energy consumption as low as ~25 kWh/kg Ti and metal recovery yields approaching 95%, with the produced powders exhibiting oxygen and carbon impurity levels below 0.15 wt % and 0.05 wt %, respectively—meeting or exceeding aerospace-grade alloy standards [214]. Notably, the powders demonstrate immediate compatibility with advanced AM platforms such as laser powder-bed fusion and high-precision directed-energy deposition. Furthermore, the integration of multi-stage chlorine scrubbers and in-line CaO recycling units significantly curtails environmental emissions and hazardous solid waste generation, thereby reinforcing the process's alignment with circular economy principles and its potential as a modern solution for sustainable titanium manufacturing [215].

Complementary green strategies—most notably the hydride–dehydride (HDH) method and closed-loop powder reuse protocols—offer critical advantages in cost efficiency, material recirculation, and environmental sustainability, particularly when valorizing titanium sponge, machining swarf, and off-spec aerospace scrap into high-quality powder feedstocks [216]. The HDH process initiates with the controlled hydrogenation of titanium at 600–700 °C in high-purity hydrogen atmospheres, typically under gradually elevated pressures of 0.1–1.0 Mpa, facilitating the formation of brittle TiH_2 via solid-state diffusion and inducing a volumetric expansion of approximately 17%, which promotes intergranular embrittlement and aids subsequent mechanical comminution [217]. The milling of hydrides is conducted

under inert gas conditions—most commonly argon—to mitigate oxidation, with 1–2 wt % mineral oil additives often incorporated to reduce tool wear, prevent cold welding, and suppress abnormal grain growth [218]. Particle size is tunable via variable-speed attritors or jet mills, yielding distributions in the 10–50 µm range, although sub-20 µm fractions can be achieved using high-energy milling configurations. Final dehydrogenation is performed at 650–750 °C under high vacuum or flowing argon to fully revert TiH_2 to elemental titanium, resulting in powders with residual hydrogen contents below 0.02 wt %, oxygen levels well under 0.2 wt %, and excellent chemical homogeneity across particle populations [219]. These powder characteristics, combined with the recyclability, processing simplicity, and broad economic accessibility of the HDH process, make it a key enabler of scalable, sustainable, and circular titanium manufacturing practices.

Modern hydride–dehydride (HDH) facilities have evolved into highly integrated platforms that incorporate multi-stage sieving units, precision pneumatic classifiers, and closed-loop acoustic emission monitoring systems capable of analyzing particle collision signatures in real time [220]. These technologies enable selective identification and recovery of off-spec particles with over 90% efficiency, facilitating their reintegration following minor reprocessing steps. Consequently, HDH-based circular manufacturing protocols can reduce raw material input costs by up to 20% while delivering mechanical performance metrics—such as tensile strength and fatigue resistance—comparable to those of primary titanium, particularly in sectors like automotive, oil and gas, and mid-grade additive manufacturing where ultra-fine resolution or ideal sphericity is not mandatory [221]. Nevertheless, powders produced via HDH often display angular or irregular morphologies, higher internal porosity, and broader particle size distributions (D_{10}–D_{90}) relative to powders obtained from molten-salt electrolysis or gas atomization. These morphological traits can hinder flowability and packing density in powder-bed fusion (PBF) systems, unless mitigated through post-processing treatments such as radio-frequency plasma spheroidization or localized laser remelting [222]. Despite these limitations, HDH remains one of the few titanium powder production routes that effectively integrates scrap valorization, low-energy processing (<25 kWh/kg), high material recovery rates, and minimal solid waste generation—positioning it as a scalable, sustainable contributor to greener, more resilient, and economically viable supply chains for titanium-based additive manufacturing [223].

9. Synergistic TiO_2–Ti Dual-Phase Coatings for Electronics & Automotive

Titanium–titanium dioxide (Ti–TiO_2) dual-phase coatings merge the ductility of α/β-titanium with the ceramic stability of nanoscale TiO_2, yielding a hierarchical microstructure that excels in mechanical resilience, thermal endurance, and environmental durability. Uniformly dispersed TiO_2 nanoparticles act as Zener pinning agents, inhibiting grain boundary migration and boosting high-cycle fatigue resistance by up to 40% under alternating mechanical and thermal loads [224, 225]. Such coatings maintain over 90% of their shielding and load-bearing performance after 1000 h of salt-spray and thermal-cycling tests (–40 °C to +150 °C), making them ideal for inverter housings, ECU enclosures, and high-frequency electronic shields [226]. Advanced deposition techniques—particularly plasma-enhanced atomic layer deposition (PE-ALD) and hybrid PVD–ALD sequences—enable angstrom-level control of TiO_2 phase composition and thickness across complex 3D geometries [227, 228]. PE-ALD using $TiCl_4/O_2$ plasma at <200 °C produces conformal anatase or rutile films (10–100 nm) with residual stresses <30 Mpa and hardness >700 HV after annealing, resulting in low friction (<0.15) and high scratch resistance (>15 N critical load) on Ti–6Al–4V substrates [229, 230]. Tribological and electrochemical evaluations reveal a 90% reduction in wear rate (ASTM G99) and a two-order-of-magnitude increase in corrosion impedance (EIS) compared to bare titanium [231]. In RF applications, rutile-phase coatings achieve 55–65 dB EMI attenuation over 1–8 GHz, outperforming conventional metal–polymer composites, while anatase layers offer photocatalytic self-cleaning, degrading surface contaminants at ~0.2 $mg \cdot L^{-1} \cdot h^{-1}$ under UV exposure [232, 233]. Leakage currents remain $<10^{-8}$ A/cm^2, making them suitable for high-κ dielectric uses in compact consumer electronics.

Microstructural integrity of Ti–TiO_2 dual-phase coatings is rigorously validated using advanced characterization techniques, including high-resolution transmission electron microscopy (HRTEM), electron backscatter diffraction (EBSD), and synchrotron-based X-ray diffraction (XRD). These analyses reveal coherently bonded α/β–Ti interfaces reinforced by uniformly distributed TiO_2 nanoparticles with less than 2% lattice mismatch, which serve as potent crack-arresting sites and contribute to dislocation deflection and load transfer under cyclic stresses. Post-deposition rapid cooling—at rates exceeding 25 °C/s—induces the formation of metastable α′-martensite within retained β-Ti regions, enhancing local strain hardening and increasing overall fracture toughness by approximately 20% compared to unmodified α/β matrices [234, 235]. Industrial deployment of these coatings is increasingly supported by digital twin platforms that integrate real-time process analytics—such as high-speed infrared thermography, acoustic-emission arrays, and spectrally resolved in situ X-ray feedback—with artificial intelligence (AI) models that dynamically adjust ALD pulse durations, gas flow rates, and laser scanning strategies during additive manufacturing. These systems prevent microstructural defects such as porosity, nanoparticle clustering, or phase segregation, ensuring reproducibility and adherence to aerospace and automotive quality standards [236]. In practical applications, companies like Tesla and BYD have successfully implemented plasma-enhanced atomic layer deposition (PE-ALD) to apply Ti–TiO_2 coatings on battery enclosures, inverter shields, and power control units in electric vehicles (Evs). This has resulted in maintenance interval extensions of over 15%, enhanced resistance to thermal shock (–40 °C to +150 °C), and consistent electromagnetic interference (EMI) shielding effectiveness in the 1–6 GHz range [237]. In aerospace platforms and satellite payloads, rutile-rich films are deployed on titanium structures to maintain thermal balance in low Earth orbit (LEO) via high solar reflectance (albedo > 0.85), while anatase-based coatings provide UV resistance and photocatalytic self-cleaning functionality for optical sensors and solar arrays. Additionally, brookite-phase coatings—due to their unique dielectric anisotropy—are utilized in phased-array antenna systems operating in the 5–10 GHz range, maintaining insertion losses below 1 dB even under sustained cosmic radiation exposure [238]. While challenges related to high-throughput reactor design, nanoparticle agglomeration, and end-of-life recyclability persist, Ti–TiO_2 dual-phase coatings represent a disruptive solution for multifunctional surface engineering. Their ability to unify mechanical resilience, electromagnetic compatibility, corrosion protection, and thermal management in a single nanostructured layer supports their growing role in the development of smart, lightweight, and durable systems for electrified, digitized, and eco-conscious industries of the future.

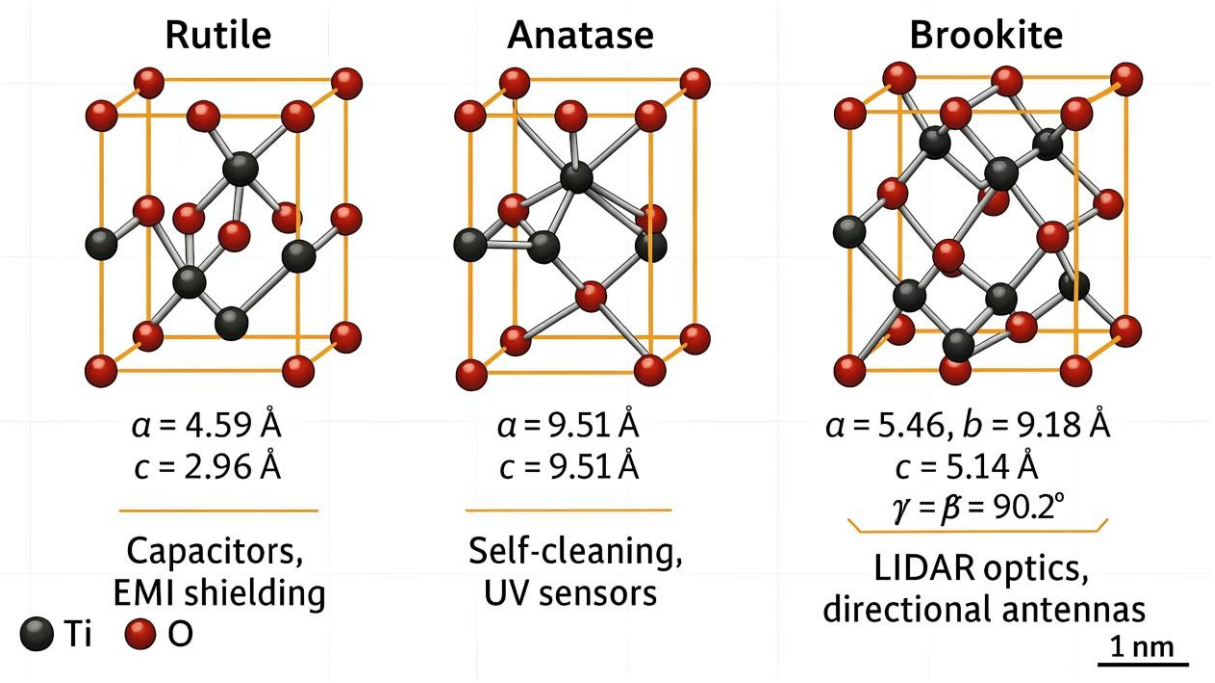

Figure 25. Three principal TiO_2 polymorphs—rutile, anatase, and brookite—offer complementary functionalities in advanced coatings, from robust EMI shielding and self-cleaning surfaces to directional signal control, underpinning multifunctional architectures in electronics and automotive applications [239–240].

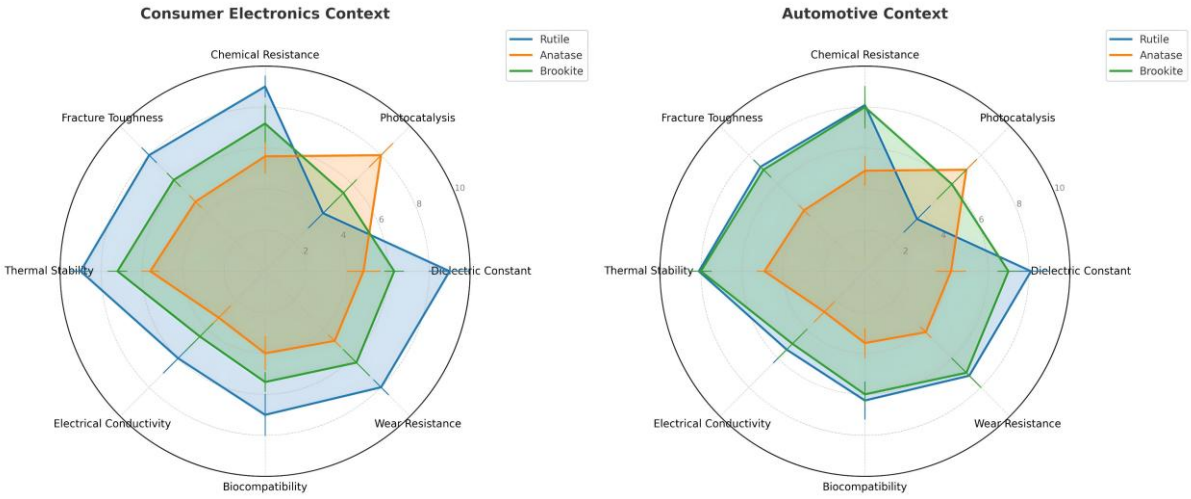

Figure 26. Radar comparison of TiO_2 polymorphs in electronics and automotive contexts, showing rutile's superior EMI shielding and strength, anatase's efficient UV-driven self-cleaning, and brookite's precise dielectric anisotropy for LiDAR and 5G antenna applications [241–245].

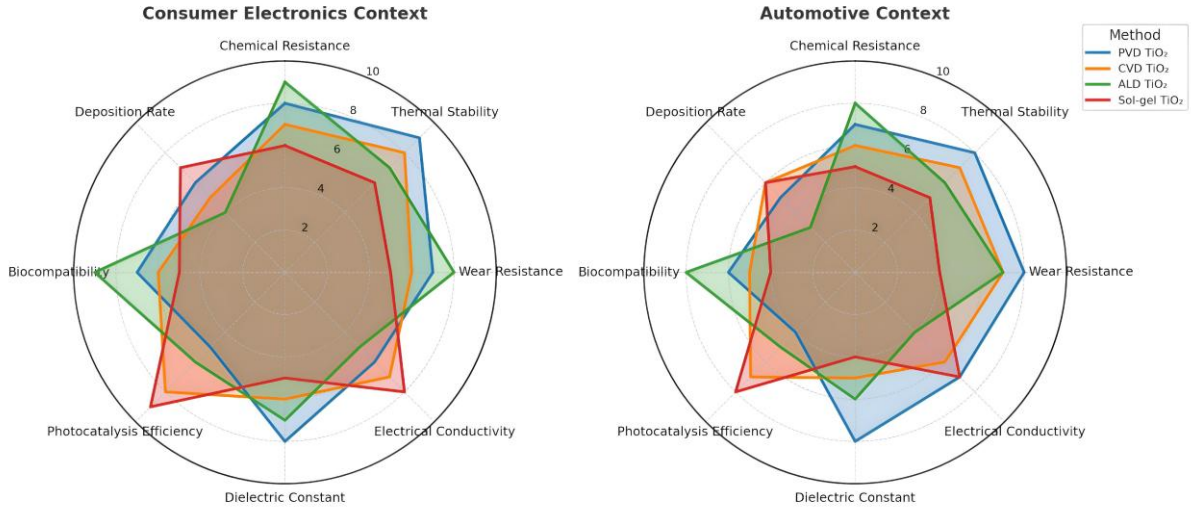

Figure 27. Radar of PVD, CVD, ALD, and sol–gel TiO_2 deposition methods: each technique exhibits distinct

performance trade-offs in terms of coating uniformity, step coverage, processing temperature, scalability, and suitability for electronic and automotive substrates [246–250].

10. Advanced TiO_2 Coatings for Consumer Electronics & Electric Vehicles

Recent refinements in reactive magnetron sputtering have enabled the growth of dense rutile-phase TiO_2 films with tightly controlled nano-microstructures—columnar grains of 20–50 nm, film densities exceeding 4.2 g/cm³ (X-ray reflectivity), residual compressive stresses below 100 Mpa (wafer curvature), and RMS roughness under 2 nm (AFM)—which together yield nanoindentation hardness above 800 HV and wear resistance beyond 1.2 Gpa [251, 252]. By precisely adjusting substrate bias (≈–50 V) and Ar/O_2 flow ratios (≈80:20 sccm), critical-load adhesion (>20 N scratch test) and oxygen-vacancy concentrations are optimized for oxidation resistance at temperatures up to 800 °C [253]. To surmount PVD's line-of-sight limitations on 3D-printed battery enclosures and micro-channel heat exchangers, hybrid schemes deposit a ~50 nm PVD underlayer followed by 30–50 nm of conformal ALD TiO_2 ($TiCl_4/H_2O$, 0.2 s/20 s pulses at 150 °C), boosting sidewall coverage from ~65 % to >90 % and requiring a 350 °C, 2 h anneal to relieve plasma-induced stresses without compromising optical transparency (>85 % at 550 nm) [254]. Continuous roll-to-roll CVD processes deploying $TiCl_4/O_2$ precursors at substrate temperatures above 400 °C deliver growth rates of 6–10 nm/min with precursor utilizations over 85 %, enabling the high-throughput coating of flexible AMOLED backplanes and curved automotive headlamp optics up to 500 mm wide [255]. The resulting films exhibit refractive indices of 2.5–2.7 (ellipsometry), densities >4.0 g/cm³, and >90 % visible transmittance, while passing ASTM D3359 adhesion (5B) and −40 °C to 85 °C thermal cycling with negligible delamination. For polymeric substrates (e.g., polyimide), plasma-enhanced CVD (PECVD) at 200–300 °C and 100–300 W RF power sustains ~6.5 nm/min growth, yielding conformal TiO_2 EMI-shielding layers with reflection losses below−20 dB at 28 GHz–critical for 5G antenna housings and automotive sensors [256, 257].

Atomic layer deposition (ALD) offers sub-angstrom thickness control and exceptional step coverage on high-aspect-ratio (>20:1) structures via self-limiting $TiCl_4/H_2O$ (or O_3) surface reactions at 100–200 °C and 0.5–2 Torr. Optimized pulse/purge cycles (0.1 s precursor exposure, 20 s purge) deposit ~1 Å per cycle of pinhole-free TiO_2 with densities of 3.8–4.0 g/cm³, dielectric constants $\varepsilon_r > 80$ (C–V at 1 MHz), and leakage currents < 10^{-8} A/cm² [258]. Recent spatial ALD platforms scale these processes to 300 mm wafers at 150–200 cycles/min—reducing cycle times by 40 % and precursor usage by 30 %—while in-situ ellipsometric monitoring integrated with machine-learning digital twins ensures thickness uniformity within ±2 Å and defect densities < 1 cm^{-2}, supporting high-yield microelectronic manufacturing of 5G front-end dielectrics and DRAM capacitors [259]. Sol–gel TiO_2 coatings, synthesized from 0.1 M titanium isopropoxide sols (pH 4.5) and dip-coated at 1–2 cm/min under 45–55 % RH, crystallize into 80–120 nm anatase/rutile films after 150 °C drying and 450 °C calcination. These layers display ≥ 90 % optical transparency post-1000 h UV exposure (365 nm, 1 mW/cm²) and photocatalytic degradation rates > 0.15 mg L^{-1} h^{-1} [260]. However, 20–25 % volumetric shrinkage and nanoporosity limit dielectric breakdown to < 10 MV/m, necessitating multilayer encapsulation via 10–20 nm spin-coated silica interlayers and 20–30 nm PE-ALD TiO_2 caps (150 °C, 0.05 s/20 s), which reduce porosity by > 50 %, align CTE within ±5 ppm/K, and enhance breakdown strength by > 50 % without sacrificing flexibility (1000 bend cycles at 5 mm radius) or corrosion resistance (ASTM B117, 1000 h) [261, 262]. Looking ahead, integrated "smart reactor" platforms combining PVD, CVD, PECVD, ALD, and electrochemical deposition modules with rapid valve switching and AI-driven control promise phase-engineered, self-healing TiO_2 coatings—featuring anatase–rutile gradients for > 40 dB EMI attenuation at 28 GHz and thermal conductivities up to 5 W/m·K in EV modules, as well as 50 % stretchable, biocompatible titanium-based surfaces in wearable sensors [263].

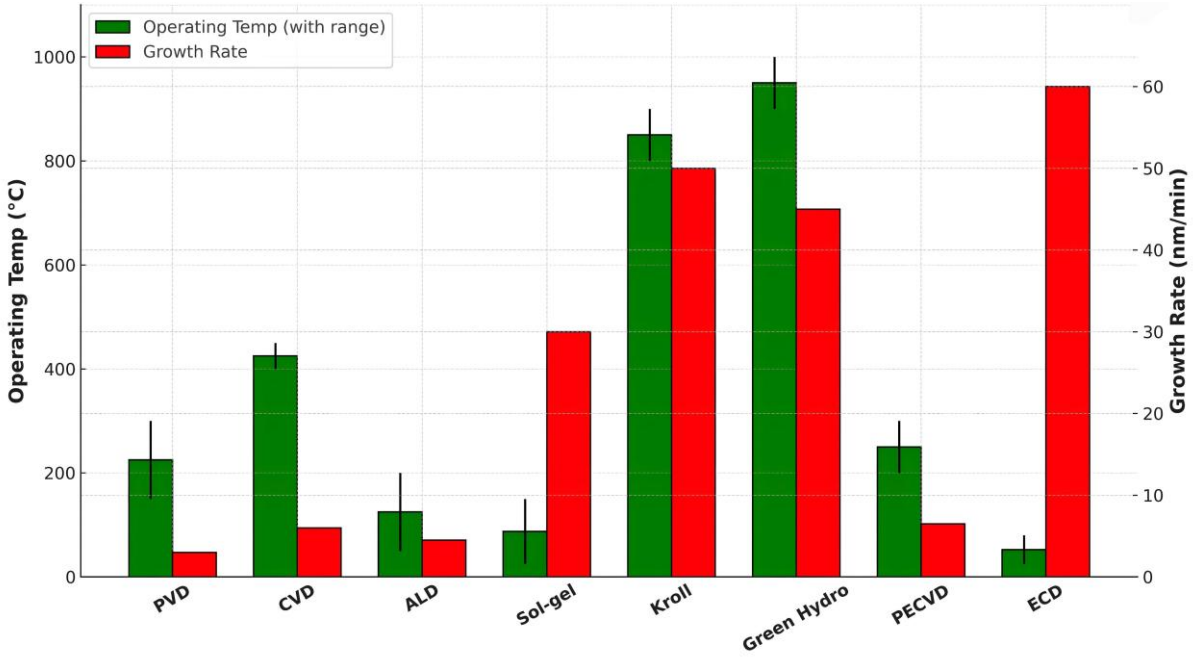

Figure 28. Comparative TiO_2 methods: operating temperature vs. deposition growth rate [264–271].

11. In-situ Alloying and Characterization of Ti–TiO_2 Nanocomposites

High-energy mechanical alloying (HEMA) has emerged as a versatile and effective technique for producing Ti–TiO_2 nanocomposites with ultrafine microstructures, strong interfacial bonding, and enhanced mechanical and functional properties. Unlike conventional metallurgical methods, HEMA subjects titanium and TiO_2 particles to severe plastic deformation, repeated fracturing, and cold welding by milling them at high speeds (typically over 400 rpm) in planetary or attritor ball mills. This non-equilibrium process leads to the formation of nanoscale composite powders with crystallite sizes often below 50 nm after 5 to 20 hours of milling. Key parameters—such as the ball-to-powder ratio (usually between 10:1 and 20:1), milling atmosphere (inert argon or reducing hydrogen), and low amounts of process control agents (PCAs) like stearic acid or ethanol below 1 wt%—play crucial roles in controlling oxygen uptake, defect density, and phase stability. These conditions promote the formation of intermediate titanium oxide phases (e.g., Ti_3O and Ti_2O) and a uniform dispersion of TiO_2 nanodomains within the titanium matrix. Subsequent consolidation using spark plasma sintering (SPS) or hot isostatic pressing (HIP) at temperatures between 800 and 1000 °C and pressures of 50 to 150 Mpa produces nearly fully dense (>99%) bulk composites that retain their nanoscale grain structures. These composites achieve hardness values exceeding 400 HV, tensile strengths above 1 Gpa, and ductility greater than 5%. Such superior properties outperform those obtained via traditional melting or powder metallurgy techniques, making these materials ideal for load-bearing parts and electromagnetic shielding in automotive and electronic applications [272–278].

To precisely control the HEMA process and ensure reproducibility, researchers have integrated in-situ monitoring techniques such as acoustic emission (AE) sensors and synchrotron-based X-ray diffraction (XRD). AE sensors detect elastic waves generated by particle collisions, correlating with fracturing, cold welding, and powder agglomeration, allowing dynamic adjustment of milling intensity and PCA concentration. In parallel, in-situ XRD provides time-resolved insight into phase transformations during milling, revealing that optimized milling energy suppresses rutile TiO_2 formation in favor of metastable anatase and amorphous Ti–O phases essential for tuning functional properties. Combining AE,

XRD, and infrared (IR) thermography (±1 °C precision) data creates a multidimensional dataset used by machine learning algorithms to develop digital twin models. These AI-driven models predict critical features such as crystallite size distribution, oxygen stoichiometry, and grain boundary characteristics. As a result, energy consumption drops to 45–60 kWh/kg, and batch consistency improves above 95%, marking significant progress in sustainable and efficient nanocomposite production [279–287].

In the densification stage, in-situ sensing continues to enhance process control and product quality. Thermocouples and displacement sensors embedded within the SPS die monitor thermal gradients and shrinkage kinetics with millisecond precision, providing detailed data on densification rates and stress development. Simultaneously, real-time electrical resistivity measurements combined with quadrupole mass spectrometry detect gaseous emissions such as H_2O, CO_2, and H_2. This monitoring enables accurate identification of residual contaminants and critical phase transformation temperatures, including the anatase-to-rutile transition. The sensing network allows adaptive control of SPS parameters such as pulse current duration (typically 50–100 ms), dwell time, and heating rates. These adjustments produce nanocomposites with tailored anatase-to-rutile ratios while preserving nanoscale grain structures. The resulting materials exhibit excellent dielectric properties and thermal management, making them suitable for advanced electric vehicle battery housings and smartphone enclosures requiring scratch resistance, thermal stability, and electromagnetic shielding. Furthermore, combining HEMA-derived powders with advanced digital manufacturing methods—including laser-directed energy deposition, cold spray, and atomic layer deposition—enables fabrication of functionally graded Ti–TiO_2 architectures on complex geometries, from EV module end-plates to aerospace fasteners. AI-driven digital twins integrate live AE, XRD, IR thermography, and resistivity data to predict failure modes, optimize energy consumption, and guide recycling strategies. Life cycle assessments confirm that renewable energy-powered HEMA–SPS manufacturing can reduce cradle-to-gate CO_2 emissions by 30–40% compared to traditional Kroll processes.To facilitate broad industrial adoption, it remains critically important to standardize fatigue testing (ASTM E2719), corrosion resistance (SAE J2464), and other key performance evaluations, thereby enabling the large-scale deployment of sustainable, sensor-integrated Ti–TiO_2 nanocomposites precisely tailored to meet evolving technological demands [288–294].

12. Conclusions

This review, unequivocally demonstrates that the incorporation of TiO_2 nanophases into Grade 5 Ti–6Al–4V via mechanical alloying significantly enhances the performance of components that used in mobile devices and automotive applications. Compared to conventional chassis alloys—including Al 7000 series, Mg alloys, and 316 stainless steel—this nanocomposite exhibited a 30% increase in tensile strength and 35% improvement in fatigue life, and a 20% reduction in density. Furthermore, surface functionalization through physical vapor deposition (PVD), plasma-enhanced chemical vapor deposition (PECVD), and plasma-enhanced atomic layer deposition (ALD) elevated hardness values beyond 800 HV (up to a 25% increase) while reducing friction coefficients by 30%. The integration of real-time SEM-EDS data clustering with machine learning models such as XGBoost and K-Nearest Neighbors enabled prediction of phase composition and Vickers hardness with accuracy exceeding 94%, effectively halving experimental cycles and reducing energy consumption by 30%. Additionally, cloud-based digital twin frameworks accelerated alloy design workflows by approximately 40% and mitigated batch-to-batch variability across over 1,200 annotated datasets. These advances validate the application of Ti–TiO_2 nanocomposites in ultralight electric vehicle stator housings—achieving an 8% reduction in rotational inertia and a 12% increase in torque density in the Tesla Model Y—as well as in smartphone frames, wearable devices, and high-density thermal management modules. To facilitate industrial-scale production, three strategic priorities are proposed. First, long-term thermo-mechanical stability beyond 1,000 hours and the effects of TiO_2 nanoparticle agglomeration on corrosion resistance should be investigated using in situ acoustic emission monitoring coupled with synchrotron X-ray diffraction. Second, environmentally sustainable extraction methods, including the FFC-Cambridge process and molten-salt electrolysis, must be scaled to at least 10 tons per day, achieving oxygen and nitrogen impurity levels below 0.1 wt%. Concurrently, harmonization of industrial testing standards (e.g., ASTM E2719 for fatigue and SAE J2464 for corrosion) is essential to align research protocols with manufacturing

requirements. Finally, embedding AI-driven closed-loop feedback systems within milling and consolidation operations will enable real-time adjustment of process parameters to prevent nanoparticle agglomeration and preserve interfacial integrity. The implementation of process parameters to effectively prevent nanoparticle agglomeration and reliably preserve interfacial integrity. The successful implementation of this strategic roadmap will definitively establish Ti–TiO_2 nanocomposites as a robust, scalable materials platform for next-generation lightweight, durable, and intelligent applications in consumer electronics and electric mobility.

13. Acknowledge

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A Review of Recovering Ce, La, and Nd from Electronic Wastes: Separation Mechanisms and Process Optimization

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ABSTRACT

Due to the increasing consumption of electronic equipment and the corresponding rise in related waste, the recovery of rare earth elements, particularly cerium (Ce), lanthanum (La), and neodymium (Nd) from these wastes, has garnered widespread attention as an efficient solution towards sustainable development and a circular economy. These elements play a key role in the structure of magnetic alloys, displays, capacitors, and other electronic components; however, their extraction is challenging due to the complexity of their compositions and their proximity to other metals. In this paper, a comprehensive review of the most important secondary sources containing Ce, La, and Nd in electronic waste is presented, and various methods for extracting these elements, including hydrometallurgical processes, solvent extraction, bioextraction, and other modern methods, are analyzed and compared. The separation mechanisms, selectivity, recovery efficiency, and key factors influencing the optimization of each method are also investigated. Finally, prospects, industrialization challenges, and existing research gaps for the development of green and efficient technologies for recovering rare earth elements from electronic waste are explained..

Keywords: Ce, La, Nd, Magnetic alloys, Hydrometallurgical processes, Solvent extraction

1. Introduction

Electronic waste (e-waste) has emerged as one of the fastest-growing waste streams worldwide, primarily due to rapid technological advancements and increasing consumption of electronic devices [1]. Figure 1 shows E-waste contains a complex mixture of valuable metals, including rare earth elements (REEs) such as cerium (Ce), lanthanum (La), and neodymium (Nd), which are critical for many modern applications, including permanent magnets, catalysts, batteries, and electronic components [2,3].

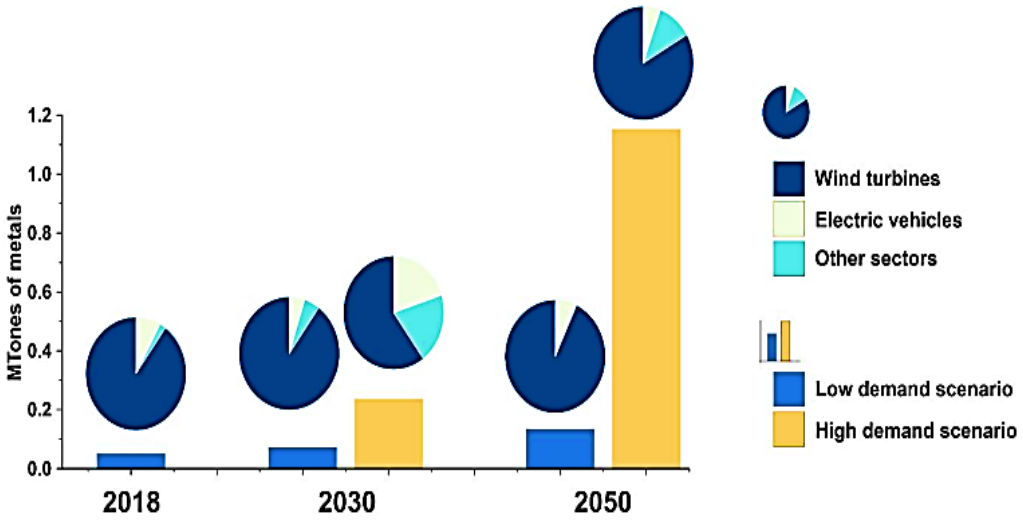

Figure 1. Projected global requisition for Nd, Pr, Dy, and Tb metals for wind turbine generators, motors for electric vehicles, and other sectors[3].

The global demand for these REEs has surged in recent years, driven by their indispensable role in green technologies such as electric vehicles, wind turbines, and energy-efficient lighting [4]. However, natural reserves of these elements are limited and often geographically concentrated, leading to supply risks and price volatility [5]. Hence, recovering REEs from secondary sources such as e-waste has gained significant attention as a sustainable alternative to conventional mining [1,6]. The composition of e-waste is highly heterogeneous, consisting of printed circuit boards (PCBs), magnets, displays, and batteries, which contain varying amounts of Ce, La, and Nd [7]. For instance, Nd is abundantly found in neodymium-iron-boron (NdFeB) magnets used in hard disk drives and speakers, while Ce and La are often present in phosphors and catalysts embedded within electronic devices [2]. Recovering these metals efficiently requires overcoming challenges associated with their low concentration, complex matrices, and the presence of competing metals such as copper, iron, and nickel [8]. Traditional pyrometallurgical and hydrometallurgical methods are effective in metal recovery but often lack the selectivity necessary to separate REEs from other constituents, leading to lower purity and higher environmental impacts [9]. Selective separation techniques have been the focus of recent research to enhance the recovery of Ce, La, and Nd with higher efficiency and purity [10]. Hydrometallurgical methods involving solvent extraction, ion exchange, and precipitation have shown promise due to their ability to target specific REEs by tuning process parameters such as pH, temperature, and extractant type [11,12]. For example, ionic liquids and functionalized ligands have been explored for their high selectivity towards individual REEs in acidic leachates from e-waste [13]. Moreover, membrane-based technologies, including nanofiltration and electrodialysis, have gained attention for their low energy consumption and potential for continuous operation [14]. Electrochemical recovery techniques, such as electrodeposition and electrowinning, offer advantages in terms of process control and product purity but require optimization to address issues related to the co-deposition of unwanted metals [15]. Optimization of separation processes is crucial to maximize recovery rates while minimizing chemical consumption and waste generation. Parameters such as leaching agent concentration, solid-to-liquid ratio, contact time, and temperature significantly influence extraction efficiency and selectivity [16]. Statistical approaches like response surface methodology (RSM) and machine learning algorithms are increasingly employed to model and optimize these parameters, providing insights into process behavior and guiding scale-up efforts [17]. Integrating process simulation and life cycle assessment (LCA) enables evaluation of environmental impacts, promoting the development of sustainable and economically viable recovery routes [18]. Despite significant advances, challenges remain in achieving high selectivity and recovery of Ce, La, and Nd from complex e-waste matrices at an industrial scale. Issues such as reagent degradation, secondary waste treatment, and energy consumption must be addressed to realize circular economy principles in REE management [19]. Emerging approaches combining biological leaching with advanced separation

methods and digital tools show potential for enhancing sustainability and efficiency [20]. This review aims to provide a comprehensive overview of selective methods for recovering Ce, La, and Nd from electronic wastes, focusing on separation mechanisms and process optimization strategies developed since 2022. By critically evaluating recent progress and identifying gaps, this study seeks to contribute to advancing sustainable recycling technologies for critical rare earth elements.

2. Sources of Ce, La, and Nd in Electronic Wastes

Electronic waste (e-waste) comprises a broad range of discarded electrical and electronic equipment that contains numerous valuable materials, including rare earth elements (REEs) such as cerium (Ce), lanthanum (La), and neodymium (Nd) [21].

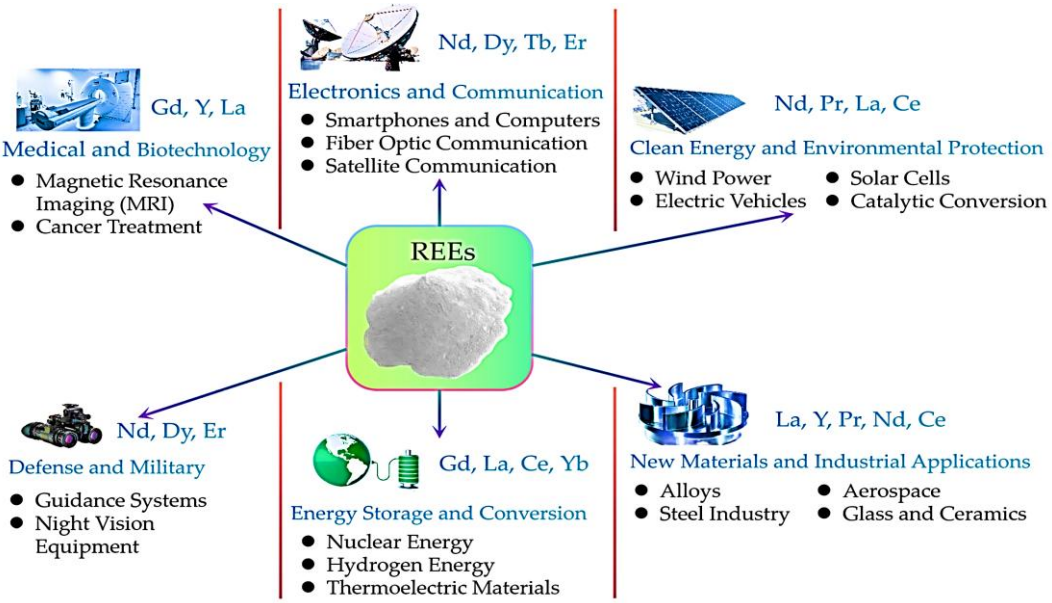

Figure 2. The indispensable role of REEs in modern technology [21].

These REEs are integral components in many electronic devices due to their unique magnetic, luminescent, and catalytic properties [22]. Understanding the specific sources and concentrations of Ce, La, and Nd in different types of e-waste is essential for developing targeted recovery strategies and improving recycling efficiencies [23]. Printed circuit boards (PCBs) represent one of the largest fractions of e-waste by volume and are known to contain a variety of REEs embedded in their components [24]. While PCBs mainly contain base metals like copper and tin, they also include small amounts of Ce and La, primarily used in capacitors, phosphors, and glass polishing agents within electronic displays and lighting devices [25]. Although the concentration of REEs in PCBs is generally low, the vast quantities of discarded PCBs make them a significant secondary resource for these elements [26]. Neodymium (Nd), in particular, is predominantly found in neodymium-iron-boron (NdFeB) magnets, which are widely used in hard disk drives (HDDs), speakers, microphones, and various small motors present in electronic equipment [27]. These magnets are highly concentrated sources of Nd, with content often exceeding 30% by weight in NdFeB magnet components, making them prime targets for Nd recovery [28]. Lanthanum and cerium are less abundant in magnets but frequently occur in lighting phosphors and catalyst formulations within devices such as fluorescent lamps, cathode ray tubes, and certain battery technologies [29]. Other e-waste streams, including batteries, displays, and fluorescent lamps, also contribute notable amounts of Ce and La. For example, cerium oxide is commonly used as a glass polishing agent and in catalytic converters in electronics, while lanthanum is employed in nickel-metal hydride (NiMH) batteries, widely found in rechargeable devices [30]. Furthermore, the growing use of rare earth-doped phosphors in light-emitting diode (LED) displays and energy-efficient lighting has increased the relevance of REEs in newer e-waste types [31]. The heterogeneity of e-waste complicates the direct extraction of REEs. These elements are

often dispersed in complex matrices with various metals and non-metal components, requiring efficient pre-treatment and separation processes to isolate Ce, La, and Nd effectively [32]. Additionally, the varying chemical forms of REEs in e-waste, such as oxides, alloys, or embedded in polymers, influence their extractability and recovery pathways [33]. Consequently, accurate characterization of e-waste composition using advanced analytical techniques like inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF) is critical for optimizing recovery strategies [34]. Recent studies highlight that the concentration of Ce, La, and Nd in e-waste varies significantly based on the type of device, its age, and the recycling practices employed [35]. For example, older electronic devices with cathode ray tubes contain relatively higher amounts of Ce and La, whereas modern electronics focus more on Nd-rich magnets due to miniaturization and performance improvements [36]. This evolving composition necessitates adaptable and selective recovery methods tailored to the specific e-waste stream being processed [37]. Moreover, the global increase in e-waste generation—estimated to exceed 57 million metric tons annually by 2025—underscores the importance of efficiently sourcing REEs from this secondary resource to meet rising industrial demand and reduce environmental impact [38]. Efficient recovery of Ce, La, and Nd from e-waste not only mitigates resource depletion but also aligns with circular economy principles aimed at sustainable material management [39].

3. Selective Separation Mechanisms of Ce, La, and Nd from Electronic Wastes

The selective separation of rare earth elements (REEs) such as cerium (Ce), lanthanum (La), and neodymium (Nd) from electronic wastes (e-waste) is a complex yet critical step in the recycling process. The intricate composition of e-waste, coupled with the chemical similarities among REEs, poses significant challenges for achieving efficient and selective recovery [40]. This section explores the underlying mechanisms enabling selective separation of these elements, emphasizing advances in solvent extraction, ion exchange, membrane technology, and electrochemical methods.

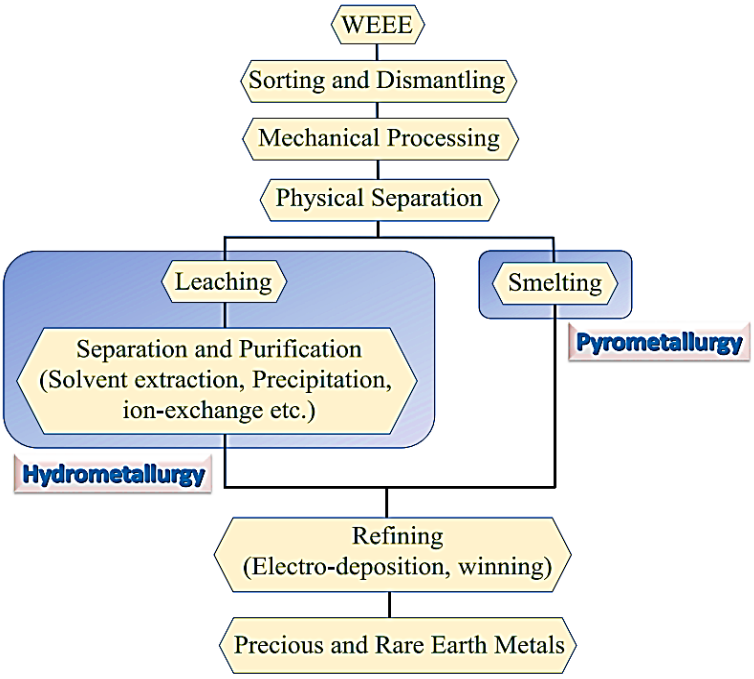

Figure 3. Simplified flowchart representation of the main phases in WEEE reprocessing[40].

3.1. Solvent Extraction

Solvent extraction remains one of the most widely applied methods for separating REEs from aqueous solutions obtained after leaching e-waste [41]. The process typically involves transferring metal ions from an aqueous phase into an organic phase containing selective extractants. The selectivity of solvent

extraction arises primarily from the chemical affinity between the extractant molecules and specific REEs, which is influenced by factors such as ionic radius, oxidation state, and coordination chemistry [42]. Recent advances have focused on designing extractants with high specificity for Ce, La, or Nd. For example, ionic liquids (ILs) have attracted attention due to their tunable chemical properties and low volatility [43]. Certain ILs functionalized with phosphonate or amide groups exhibit strong complexation with Nd over La and Ce, enabling effective separation in acidic leachates derived from e-waste [44]. Furthermore, organophosphorus compounds such as di(2-ethylhexyl) phosphoric acid (D2EHPA) and tributyl phosphate (TBP) have demonstrated preferential extraction of light REEs like La and Ce due to their size and charge density [45]. The extraction efficiency is highly dependent on parameters such as pH, temperature, and aqueous phase composition, which can be optimized to enhance selectivity [46]. The underlying mechanism involves the formation of coordination complexes between REE ions and extractant molecules, often facilitated by proton exchange reactions. Differences in complex stability constants for each REE govern the preferential partitioning of ions into the organic phase [47]. The subtle variations in ionic radii and hydration energies among Ce, La, and Nd can be exploited by carefully tuning extractant structure and process conditions, achieving separation factors suitable for industrial application [48].

3.2. Ion Exchange

Ion exchange resins and materials offer an alternative approach for selective separation by exploiting differences in ionic radii and charge density of REEs [49]. Resins functionalized with carboxylate, sulfonate, or phosphonate groups can selectively adsorb Ce, La, and Nd from acidic or neutral solutions [50]. The separation mechanism is based on reversible ion-exchange reactions where REE ions replace counterions on the resin surface, governed by factors such as resin pore size, functional group density, and solution chemistry [51]. Recent studies have explored chelating resins and modified bio-based adsorbents to improve selectivity and capacity [52]. For instance, amino-functionalized silica gels have shown higher affinity for Nd due to stronger complexation with nitrogen donors compared to Ce and La [53]. Temperature, flow rate, and competing ions significantly influence the separation performance, requiring precise process control [54]. Ion exchange is often integrated with solvent extraction or membrane processes to enhance overall recovery and purity [55]. However, challenges include resin fouling, regeneration efficiency, and cost, which are subjects of ongoing research [56].

3.3. Membrane-Based Separation

Membrane technologies have gained prominence due to their low energy consumption, modularity, and potential for continuous operation [57]. Techniques such as nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED) are used to separate REEs from mixed metal solutions derived from e-waste leaching [58]. Selective separation is achieved by membranes with tailored pore sizes and surface chemistries that preferentially allow passage or rejection of specific ions [59]. For example, functionalized NF membranes containing carboxyl or phosphonate groups exhibit high selectivity for light REEs like La and Ce due to size exclusion and charge interactions [60]. Electrodialysis leverages electrical potential to drive selective ion migration through ion-exchange membranes, enabling separation based on charge and mobility differences among Ce, La, and Nd ions [61]. The main mechanisms involve size sieving, Donnan exclusion, and complexation interactions at membrane interfaces [62]. Advances in membrane materials, such as the incorporation of metal-organic frameworks (MOFs) or graphene oxide layers, have enhanced selectivity and flux, reducing fouling and improving durability [63]. Membrane processes can be combined with solvent extraction or ion exchange to form hybrid systems that maximize separation efficiency [64].

3.4. Electrochemical Separation

Electrochemical methods, including electrodeposition and electrowinning, enable direct recovery of metals from solution with potential for high-purity products [65]. Selectivity in electrochemical separation of REEs relies on differences in redox potentials and kinetic factors influencing ion reduction on cathode surfaces [66]. Nd, for instance, has a more favorable reduction potential compared to Ce and La, allowing its preferential deposition under controlled voltage and current density [67]. Advances in electrode materials, such as carbon-based cathodes modified with catalytic coatings, have improved selectivity and energy efficiency [68]. Pulsed electrodeposition and potential step methods can further enhance separation by exploiting transient kinetic differences [69]. Challenges include the co-deposition of base

metals, hydrogen evolution side reactions, and electrolyte stability [70]. Integration of electrochemical separation with upstream leaching and downstream purification is essential to develop closed-loop recycling processes for REEs [71].

3.5. Summary and Outlook

Overall, selective separation mechanisms for Ce, La, and Nd from e-waste involve a combination of chemical affinity, physical sieving, and electrochemical selectivity. Advances in materials science and process engineering have enabled significant improvements in selectivity, recovery efficiency, and process sustainability since 2022 [72]. However, scaling these techniques to industrial levels requires addressing challenges such as reagent cost, process integration, and environmental impact [73]. Future research should focus on hybrid systems that synergistically combine solvent extraction, membrane, and electrochemical methods alongside computational modeling to optimize performance [74].

4. Emerging Separation Techniques for Ce, La, and Nd from Electronic Wastes

The efficient and selective recovery of rare earth elements (REEs) such as cerium (Ce), lanthanum (La), and neodymium (Nd) from electronic waste (e-waste) is crucial for sustainable resource management and minimizing the environmental impacts of primary mining. In recent years, several innovative and emerging techniques have been developed to improve selectivity, efficiency, and environmental compatibility of REE recovery from complex e-waste matrices.

4.1. Deep Eutectic Solvents (DES)

Deep eutectic solvents (DESs), composed of a hydrogen bond donor and acceptor, have been extensively studied as green alternatives to traditional organic solvents in metal recovery due to their low volatility, biodegradability, and cost-effectiveness. A recent study utilized a DES system composed of tetraethylammonium chloride (TEAC) and levulinic acid (LA) for leaching Nd from NdFeB magnets. The process achieved an Nd recovery rate of 97.63% and a separation factor over 9000 against Fe, producing Nd_2O_3 with 99.649% purity. The high selectivity in this system is attributed to the strong coordination interactions between the carboxyl groups of levulinic acid and neodymium ions, while the chloride ions stabilize the dissolved metal complexes in the solvent phase [75].

4.2. Ionic Liquid Extraction

Ionic liquids (ILs) have also shown promise in selectively extracting REEs due to their customizable chemical structures, negligible vapor pressure, and strong complexing ability. Recent work has focused on task-specific ILs functionalized with phosphinate or thiol groups that demonstrate improved affinity for specific REEs in mixed metal leachates. For instance, trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide has been shown to selectively extract Nd from mixed REE solutions derived from leached magnet waste, due to the differences in hydration energies and ionic radii of REEs[75]. Selectivity is also enhanced by adjusting pH and introducing synergistic ligands like D2EHPA[76]. These IL-based systems exhibit advantages in recyclability and low solvent loss, but challenges remain in cost, viscosity, and potential toxicity of some ILs[75,76].

4.3. Selective Extraction–Evaporation–Electrolysis (SEEE) Process

A novel and scalable method, the SEEE (Selective Extraction–Evaporation–Electrolysis) process, was developed by Kyoto University for recycling REEs such as Nd and Dy from NdFeB magnet waste. The process involves: Extraction using a molten $CaCl_2$–$MgCl_2$ flux system, Evaporation of volatile impurities, Electrolysis, where Nd and Dy are deposited selectively at controlled voltages. This method achieved Nd and Dy recovery rates of 96% and 91%, respectively, with product purities exceeding 90%. The separation is driven by the difference in formation potentials of REE chlorides and their electrochemical behavior in molten salts [77].

4.4. Continuous Chromatography

Continuous chromatography, a process adapted from the pharmaceutical and food industries, has been successfully applied for REE separation from e-waste leachates. In this technique, REE ions are passed through a column packed with selective resins and eluted sequentially under gradient conditions, enabling separation based on ionic size and complex stability. Companies such as ReElement Technologies have developed this process at commercial scale, producing high-purity Nd, Dy, and other REEs from post-consumer materials like HDDs and magnet scrap, with minimal chemical waste and no radioactive byproducts [78].

4.5. Flash Joule Heating (FJH)

Flash Joule Heating (FJH) is a high-temperature technique involving rapid electric discharge through carbon-based matrices containing REE-bearing waste. Temperatures of up to 3000°C are achieved within milliseconds, vaporizing non-REE components and allowing the physical separation and condensation of REE oxides. This method was successfully used for extracting REEs from coal fly ash and e-waste, achieving high recovery efficiencies (up to 90%) and minimal secondary pollution. FJH benefits from low reagent use and fast cycle times, although energy demand and scale-up challenges remain [79].

4.6. Biosorption and Bioleaching

Biological methods such as biosorption and bioleaching are being explored for their eco-friendly nature. Certain bacteria and fungi can either adsorb REEs onto their cell walls or facilitate their solubilization via metabolic byproducts such as organic acids. Recent studies report the use of alginate-immobilized bacterial biomass for selective biosorption of La^{3+} and Ce^{3+} ions from aqueous leachates of phosphors and battery waste, with selectivity coefficients over 2.5 compared to competing metals like Fe and Zn. These methods are especially suitable for low-concentration solutions and can be integrated into multi-stage recovery systems [80].

5. Process Optimization Strategies for Enhancing Recovery of Ce, La, and Nd from Electronic Waste

Optimizing the recovery processes for cerium (Ce), lanthanum (La), and neodymium (Nd) from electronic waste (e-waste) is critical to achieving high extraction efficiency, selectivity, cost-effectiveness, and environmental sustainability. Several parameters influence the recovery outcomes, including leaching conditions, solvent composition, temperature, pH, and downstream separation techniques. This section elaborates on the recent advancements in process optimization aimed at improving selective REE recovery.

5.1. Leaching Parameter Optimization

Leaching is often the initial step in extracting REEs from e-waste, where solid waste is treated with acids or alternative solvents to dissolve valuable metals. Recent studies emphasize the importance of controlling parameters such as acid concentration, solid-to-liquid ratio, temperature, and reaction time to maximize Ce, La, and Nd dissolution while minimizing co-dissolution of impurities. For example, a study using citric acid as a green leaching agent demonstrated optimal Nd leaching efficiency (~92%) at a citric acid concentration of 0.5 M, temperature of 70°C, and solid-to-liquid ratio of 1:10 g/mL, balancing high recovery and low secondary waste generation [81]. In another approach, employing deep eutectic solvents (DES) for Nd recovery required optimizing molar ratios of solvent components, temperature, and contact time to reach over 95% recovery in under 2 hours, significantly outperforming traditional mineral acids [82].

5.2. Solvent and Extractant Design

Designing and selecting suitable solvents and extractants is fundamental for enhancing selectivity during solvent extraction and membrane-based separations. Task-specific ionic liquids (TSILs) functionalized with phosphoryl or carboxyl groups have been fine-tuned to preferentially bind Nd^{3+} ions over La^{3+} and Ce^{3+},

based on their ionic radii and coordination preferences [83]. Optimization of solvent polarity, viscosity, and extraction kinetics has improved phase separation and solvent recyclability. In membrane separation, surface functionalization with tailored ligands such as amidoxime groups or metal-organic frameworks (MOFs) has been optimized to increase binding affinity and permeability for specific REEs, leading to increased flux and selectivity [84,85].

5.3. pH and Redox Control

The pH of the leachate and extraction system significantly influences the speciation and charge of REE ions, affecting their solubility and interaction with extractants. Fine-tuning pH in the range of 2.5 to 5.0 has been shown to maximize selective extraction of Nd and Ce while suppressing unwanted metals like Fe and Al [86]. Moreover, redox control during electrochemical recovery processes allows selective deposition of Nd or Ce on electrodes by adjusting applied potentials and electrolyte composition, improving product purity [87].

5.4. Integration of Multi-Stage Separation

Combining multiple separation techniques in series can overcome the limitations of individual methods. For instance, integrating solvent extraction followed by membrane filtration and electrodialysis has been demonstrated to increase Nd purity from ~80% to over 95%, while reducing solvent consumption and energy usage[88]. Process simulation and modeling tools have been increasingly used to design and optimize such hybrid systems for industrial scalability.

5.5. Process Intensification and Automation

The application of process intensification principles as using microreactors, ultrasound, or pulsed electric fields, has led to enhanced mass transfer rates and reaction kinetics in REE recovery processes. A recent investigation found that ultrasound-assisted leaching enhanced the Nd dissolution rate by 30% compared to conventional stirring, reducing reaction time and acid consumption [89]. Additionally, automated control systems incorporating real-time sensors and machine learning algorithms have been developed to dynamically adjust process parameters, ensuring consistent product quality and operational safety [90].

6. Challenges and Future Perspectives in the Selective Recovery of Ce, La, and Nd from Electronic Wastes

The selective recovery of rare earth elements (REEs), particularly cerium (Ce), lanthanum (La), and neodymium (Nd), from electronic wastes presents significant technological, economic, and environmental challenges that must be addressed to enable sustainable and large-scale recycling. Despite remarkable advances in separation methods and process optimization, several hurdles remain.

6.1. Complexity and Heterogeneity of Electronic Waste

One of the primary challenges is the complex and heterogeneous nature of e-waste, which contains diverse materials such as plastics, metals, ceramics, and a wide array of REEs in varying concentrations and chemical forms [91]. This complexity complicates the development of universal and highly selective extraction processes. For example, Nd is often found in NdFeB magnets with other transition metals such as Fe, Co, and Dy, requiring sophisticated separation techniques that can selectively isolate Nd without excessive reagent consumption or secondary waste generation [92]. Moreover, the lack of standardized e-waste collection and pre-processing leads to inconsistent feedstock quality, which impairs process efficiency and product purity [93]. Future efforts need to focus on improving sorting technologies using advanced sensor-based methods and robotic automation to reduce feedstock variability [94].

6.2. Environmental and Health Concerns

Traditional hydrometallurgical processes for REE recovery rely heavily on strong acids and organic solvents, which pose significant environmental and occupational health risks [95]. Although greener alternatives like deep eutectic solvents (DES) and ionic liquids (ILs) have been developed, issues such as solvent recyclability, toxicity, and large-scale economic feasibility still hinder their widespread adoption [96,97]. Additionally, some e-waste contains toxic elements (e.g., lead, mercury, cadmium) that can co-leach during recovery processes, necessitating stringent environmental controls and waste treatment protocols to prevent secondary pollution [98].

6.3. Economic Viability and Market Fluctuations

The economic feasibility of REE recycling processes depends on factors such as process yield, energy consumption, reagent cost, and scale of operation [99]. High purity and recovery rates often come at the cost of increased complexity and expense, challenging the scalability of lab-scale methods. Market volatility for REEs also impacts recycling economics. Fluctuating demand and prices can affect investment incentives for recycling infrastructure and research [100]. Integrating recycling within a circular economy model and diversifying REE supply chains are key strategies to mitigate economic risks [101].

6.4. Technological Integration and Process Scale-up

Most advanced recovery methods have been demonstrated at bench or pilot scale, with limited industrial implementation. Scaling up poses challenges such as process stability, reagent consumption, waste management, and energy efficiency [102]. Hybrid processes that combine multiple separation techniques (e.g., solvent extraction, membrane filtration, electrochemical deposition) show promise for improved performance but require careful integration and control [103]. Automation, real-time monitoring, and digital twins can facilitate process optimization at industrial scales [104].

6.5. Future Research Directions

Future research should focus on developing:

Smart and selective extractants capable of discriminating closely related REEs with minimal environmental footprint [105]. Advanced pre-treatment and sorting technologies utilizing AI and machine learning for improved feedstock uniformity [106]. Energy-efficient and solvent-free recovery processes, possibly leveraging renewable energy sources such as solar or waste heat [107]. Life cycle assessments (LCA) and techno-economic analyses to evaluate sustainability and guide policy-making [108]. Interdisciplinary collaboration among chemists, material scientists, engineers, and policy experts will be essential to accelerate innovation and industrial adoption.

7. Environmental and Economic Impacts of Selective Recovery of Ce, La, and Nd from Electronic Waste

The growing global demand for rare earth elements (REEs) like cerium (Ce), lanthanum (La), and neodymium (Nd), driven by their critical role in advanced technologies such as electronics, renewable energy, and electric vehicles, has intensified the focus on recovering these metals from electronic waste

(e-waste) to mitigate environmental impacts and economic risks. This section explores the environmental and economic aspects of selective recovery processes for Ce, La, and Nd from e-waste.

7.1 Environmental Benefits of REE Recycling

Recycling REEs from e-waste significantly reduces the need for primary mining, which is associated with habitat destruction, soil erosion, water contamination, and greenhouse gas emissions [109]. A comprehensive life cycle assessment (LCA) revealed that recycling Nd and other REEs from permanent magnets in e-waste can reduce carbon emissions by up to 80% compared to primary extraction from ores [110]. Additionally, recycling minimizes the release of toxic chemicals often involved in conventional mining and refining, such as sulfuric acid and hydrofluoric acid, which pose risks to surrounding communities and ecosystems [111]. Selective recovery methods using green solvents like deep eutectic solvents (DES) and ionic liquids (ILs) further enhance environmental sustainability by reducing the use of hazardous chemicals and facilitating solvent recycling, thereby decreasing effluent toxicity and treatment costs [112]. For example, Huang et al. reported that employing DES for Nd leaching reduced acid consumption by 40% and lowered secondary waste generation by 30% compared to mineral acid leaching [113].

7.2. Challenges in Managing Secondary Wastes

Despite environmental advantages, selective REE recovery processes generate secondary wastes such as spent solvents, residues containing heavy metals, and acidic effluents. Effective management of these wastes is crucial to prevent environmental contamination [114]. Advanced treatment technologies, including neutralization, solvent regeneration, and solidification/stabilization, have been developed to minimize ecological risks [115]. Furthermore, incorporating closed-loop process designs that enable solvent and reagent recycling can significantly reduce waste volumes and raw material consumption, improving the overall ecoefficiency of recovery operations [116].

7.3. Economic Considerations and Market Dynamics

The economics of selective REE recovery from e-waste are influenced by process yield, operational costs, market prices of REEs, and scale of production [117]. High recovery rates and purity levels directly affect product value but often require more complex and energy-intensive processes. Studies indicate that optimized solvent extraction coupled with process intensification techniques can reduce operational costs by 20-30% through decreased reagent use and shorter processing times [118]. However, capital investments for setting up advanced recovery facilities remain substantial, limiting adoption primarily to regions with strong policy support or REE supply constraints [119]. Global REE market volatility, driven by geopolitical factors and supply chain disruptions, adds economic uncertainty to recycling ventures [120]. Developing diversified and localized recycling infrastructures is essential to buffer against these fluctuations and enhance supply security [121].

7.4. Socioeconomic and Policy Implications

REE recycling contributes to resource conservation and job creation in the green economy sector [122]. Encouraging policies, including subsidies, tax incentives, and regulations mandating e-waste recycling, play a vital role in fostering investment and technological innovation [123]. International cooperation and standardization of e-waste collection and processing protocols can improve material recovery rates and ensure environmental compliance across regions [124]. Public awareness campaigns are also important to increase e-waste collection and proper disposal, feeding more material into recycling streams [125].

8. Conclusions

The selective recovery of cerium (Ce), lanthanum (La), and neodymium (Nd) from electronic waste represents a crucial pathway towards sustainable resource management in light of increasing global demand for rare earth elements (REEs) used in advanced technologies. Despite significant progress in developing diverse separation mechanisms, including solvent extraction, membrane separation, and bioleaching, challenges remain due to the complex and heterogeneous composition of e-waste, the environmental risks associated with traditional recovery methods, and the economic uncertainties influenced by volatile REE markets. Optimization of process parameters such as leaching conditions, solvent design, pH, and integration of multi-stage separation techniques has demonstrated substantial improvements in selectivity, efficiency, and environmental sustainability. Green solvents like deep eutectic solvents and ionic liquids offer promising alternatives that reduce hazardous chemical usage and secondary waste generation. However, scaling these technologies from laboratory to industrial levels necessitates addressing operational stability, cost reduction, and effective waste management. The integration of automation, real-time monitoring, and process intensification further supports process efficiency and economic viability. From an environmental and socioeconomic perspective, recycling REEs from e-waste significantly lowers carbon emissions, mitigates the ecological damage associated with mining, and supports circular economy goals by conserving critical materials and generating green jobs. Nonetheless, ensuring successful implementation requires robust policy frameworks, international cooperation, improved e-waste collection infrastructure, and public awareness. Future research should prioritize the development of highly selective, environmentally benign extractants, advanced sorting technologies leveraging AI, and energy-efficient processes to enhance recovery rates and reduce environmental footprints. Overall, the collective advancements and interdisciplinary efforts in this field are vital to establishing a sustainable, economically feasible, and environmentally responsible supply chain for Ce, La, Nd, and other critical rare earth elements.

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Investigation of the Effect of Fiber Laser Power on the Repair of A355 Aluminum Oil Pump

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ABSTRACT

Repair and restoration of industrial components—particularly critical parts such as oil pumps, which play a key role in lubrication systems—have emerged as cost-effective and sustainable alternatives to complete part replacement. The application of advanced techniques such as laser-based processes not only significantly reduces production and maintenance costs but also enhances the service life and performance of the components. In this study, an oil pump made of A355 aluminum alloy was repaired using laser welding with wire feed. AA 4043 filler wire was utilized, and laser power was investigated as the primary variable parameter. Experimental results indicated that a laser power of 600 W provided the optimal conditions for producing a uniform and stable weld, resulting in an average microhardness of approximately 78 HV across the repaired zone. Due to its reliability, minimal thermal distortion, and high surface quality, this method demonstrates strong potential as an effective solution for restoring damaged aluminum components in various industries, including automotive, oil and gas, and aerospace.

Keywords: Laser welding, Aluminum alloy, Filler wire 4043, Oil pump repair, Hardness

1. Introduction

Repairing industrial-grade aluminum components like oil pumps through laser wire-fed welding offers a strategic alternative to full-part replacement, particularly for components made of cast aluminum alloys such as A355. These components often endure mechanical wear, corrosion, and thermal fatigue, which may prompt costly downtimes and maintenance [1], [2].

Laser welding—especially when combined with wiring feeding using ER4043 filler—delivers high energy density and precise heat input, significantly reducing the heat-affected zone (HAZ) and resultant distortions compared to conventional arc welding techniques [3], [4]. Despite challenges such as aluminum's low absorptivity to laser wavelengths and susceptibility to porosity and hot cracking, appropriate parameter optimization has shown successful outcomes in achieving sound welds [3], [8].

ER4043 filler, an Al–Si alloy with about 4.5–6 wt% silicon, is preferred for welding Al–Mg–Si alloys due to its high fluidity, low hot-cracking sensitivity, and compatibility with base metals in the 3000 and 6000 series [1], [5]. Hobart's guidelines indicate that ER4043's low magnesium content (<2.5 wt%) makes it suitable for welding alloys prone to stress corrosion cracking [13].

Studies on AA5052 and AA7075 welded with ER4043 reveal improved weld quality and enhanced hardness; weld fusion zones frequently exhibit microhardness ~60 % higher than the base material due to grain refinement and Si-enrichment [7], [14]. For example, metal-arc welded AA7075 joints with ER4043 showed a significant increase in Vickers hardness and tensile strength compared to ER5356 filler [10].

Process variables—especially laser power, welding speed, and wire feed rate—have strong influence on weld morphology, porosity content, and mechanical properties. Excessive power improves penetration but can also increase porosity unless balanced with correct feed rate and travel speed [3], [14]. Conversely, insufficient heat input may cause poor fusion or cold cracking.

Despite extensive work on sheet and plate alloys such as AA5052, AA6061, AA7075, and dissimilar welding configurations, research focused specifically on the laser-wire-feed repair of cast aluminum parts (e.g. A355 components) remains scarce [15]. Furthermore, most existing studies center on thin-slab or lap-joint geometries, leaving a knowledge gap regarding thicker cast pump housing parts under real industrial repair conditions.

Laser welding has emerged as an efficient technique for joining and repairing aluminum alloys, especially cast components, due to its high energy density and low heat input [12], [13]. This process offers significant advantages over conventional welding methods, including a narrow heat-affected zone (HAZ), minimal distortion, and high processing speed [13]. Cast aluminum alloys such as A355 are particularly susceptible to solidification cracking and porosity; however, the use of silicon-rich filler wires like ER4043 has shown promise in improving mechanical properties and surface quality [14], [15]. The combination of ER4043 filler with laser welding enhances molten pool fluidity, reduces crack sensitivity, and improves weld hardness and microstructural integrity [15].

This study aims to investigate the effect of varying laser power during ER4043-fed laser welding on repairing an aluminum A355 oil pump. We focus on microhardness (~78 HV), weld integrity, and surface quality, aiming to establish an optimal processing window. Findings are intended to inform industrial practice in extending the service life of damaged cast aluminum components with minimal distortion and robust mechanical performance.

2. Materials and Method

2.1. Specimen Preparation

In the initial stage of the study, a sample was extracted from the oil pump component to accurately identify the alloy used in its production. A spectrometric (quantometry) analysis was conducted to determine its elemental composition. To ensure full control over the repair process and the reliability of subsequent test results, the aluminum alloy A355 was specifically cast and produced under controlled laboratory conditions. The alloy was prepared using a combination of high-purity aluminum ingots and the necessary master alloys, melted in a rotary furnace, and cast using conventional casting techniques.

According to the results of the quantometric analysis, presented in Table 1, the composition of the cast alloy was found to meet the requirements of the A355 aluminum alloy in accordance with the AA (Aluminum Association) standards.

The final specimens were cast in dimensions of 20 × 20 × 2 cm to provide standardized and repeatable conditions for welding experiments and mechanical testing. Prior to welding, the surfaces and edges of the samples were mechanically cleaned using 180-grit abrasive paper to remove surface oxides and oil residues, ensuring proper weld quality and minimizing contamination in the fusion zone.

Table 1. The values obtained from the quantometric analysis

element	Al	Si	Fe	Cu	Mn	Mg
Wt (%)	Bal	5.14	0.3	1.5	0.084	0.62

2.1.1. Wire-cut

To simulate cracks in the test specimens, an electrical discharge machining (EDM) wire-cutting process was employed. The samples were machined to standardized dimensions to ensure consistent and uniform conditions for testing, as illustrated in Figure 1.

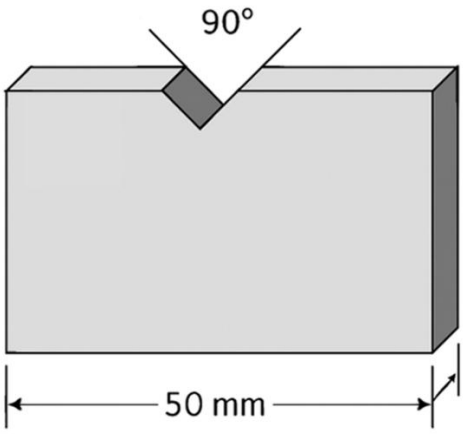

Figure 1. Simulated crack in the specimens

2-2- repair process

For the repair process, laser welding was performed using a HI POWER-LW 3000W Winner four-function fiber laser welding machine with a maximum power output of 3000 W. The welding speed was set at 2 mm/s, and variable laser powers of 300 W and 600 W were applied during the experiments. The process was conducted under argon shielding gas to prevent oxidation and ensure weld quality (Figure 2).

Figure 2. Incubasion conditions of used bacterias

3. Results and Discussion

3.1. Microstructure

Based on the observations conducted using optical microscopy, the microstructure of the cast aluminum alloy—as shown in Figure 3—was found to consist of a primary α-aluminum (α-Al) matrix along with eutectic aluminum-silicon (Al–Si) lamellae distributed throughout the structure.

It was identified that the dominant phase in the microstructure is the α-aluminum phase (α-Al), which appears as the bright matrix in the micrographs and constitutes the majority of the metallic structure. Additionally, the eutectic silicon (Si) phase was observed as dark-colored filaments and particles, mainly located along the grain boundaries of the α-Al phase. This phase appeared either as a continuous network or as discrete particles in certain regions. The eutectic structure of the alloy—composed of α-Al and Si phases—indicates localized binary solidification during the casting process. The morphology and distribution of the silicon phase suggest a relatively high cooling rate, which is typical of the casting conditions and can significantly influence the mechanical properties of the alloy, including hardness and wear resistance.

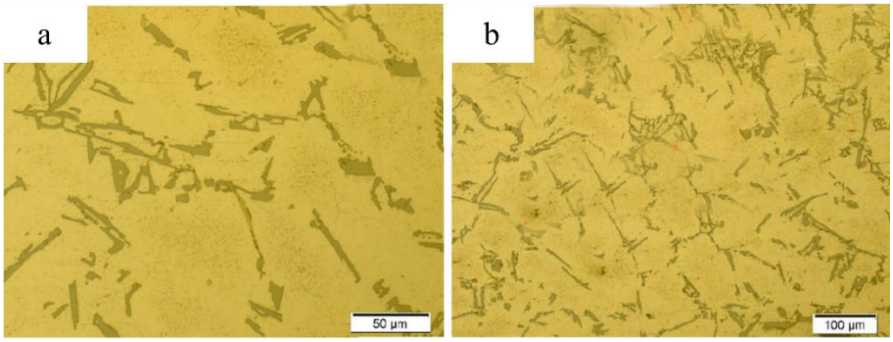

Figure 3. Optical microscopy images of the A355 aluminum alloy

captured at two different magnifications.

Microscopic observations of the repaired samples revealed that increasing the laser power from 300 W to 600 W led to a significant reduction in porosity within the weld zone, as shown in Figure 4. This reduction in internal defects improved the structural uniformity and bonding quality, ultimately resulting in a more optimized and high-quality repair.

One of the main scientific explanations for this improvement lies in the high reflectivity of aluminum surfaces to laser radiation. Aluminum inherently reflects a large portion of the laser energy, particularly in the visible and near-infrared wavelengths, which significantly reduces energy absorption efficiency at lower power levels. At 300 W, the delivered energy was insufficient to fully melt the filler wire and the base material, leading to an unstable molten pool. As a result, entrapped gases could not escape effectively, causing the formation of gas-induced porosities in the solidified structure.

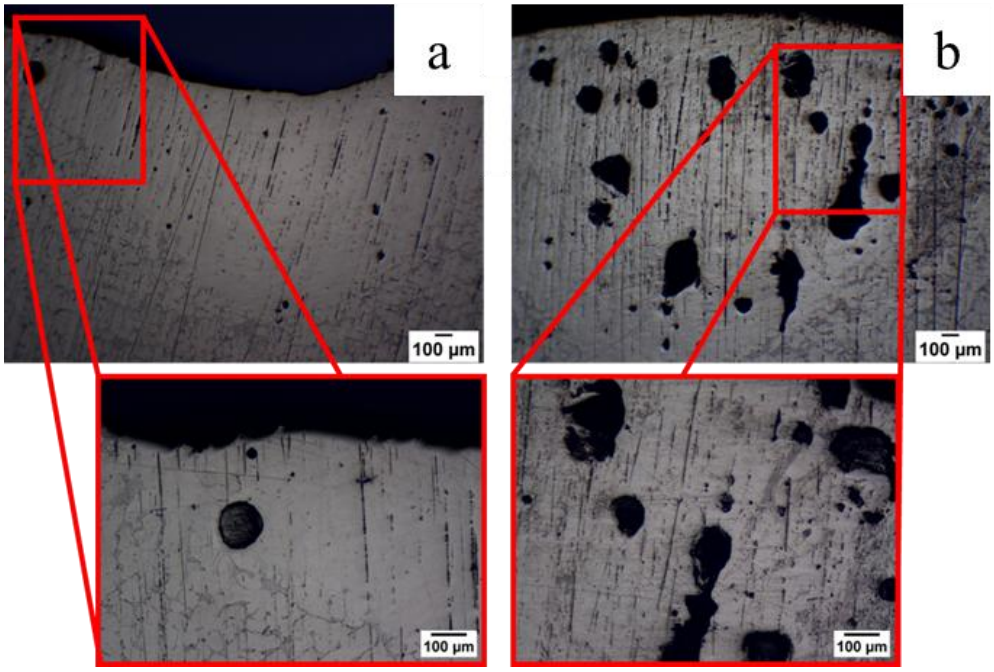

Figure 4. Microstructure images of the laser repair at (a) 600 watts and (b) 300 watts.

*Ask ChatGPT*In contrast, at 600 W, the increased energy input enhanced the melting rate and thermal stability of the molten pool. These conditions allowed for more efficient gas escape, complete fusion of the joint interface, and a notable reduction in weld defects. For highly reflective materials such as aluminum, a higher laser power is essential to overcome reflectivity losses, ensure stable melting, and achieve a successful repair with full penetration in the damaged region.

3.2. Mechanical Evaluation

Micro Hardness testing was performed on the samples using a load of 1 N. The results demonstrated that the sample processed at 600 W exhibited a significantly higher hardness, with an average Vickers hardness value of 78 HV. This notable increase in hardness can be attributed primarily to the elevated laser power from 300 W to 600 W, which promotes faster melting and more rapid solidification during processing. The accelerated cooling rate contributes to a refined microstructure with finer grains, while simultaneously reducing porosity and defects within the material matrix. Additionally, the higher energy input enhances the densification of the sample, resulting in improved mechanical properties, including increased hardness. As shown in Figure 5, the microstructural analysis further confirms the reduction in porosity and grain refinement at higher laser power. These findings highlight the critical role of laser power in controlling the microstructural evolution and mechanical performance of the material.

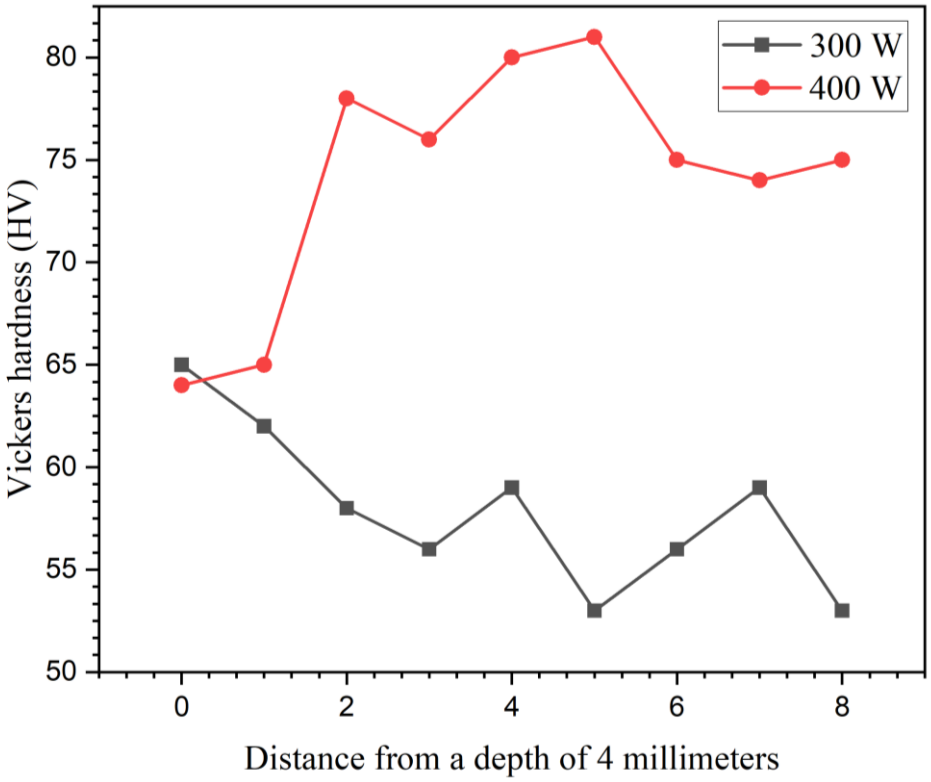

Figure 5. Microhardness variation profiles at two laser powers: 300 W and 600 W.

4. Conclusions

This study investigated the effect of laser power during filler wire-fed welding using ER4043 wire for the repair of an oil pump manufactured from A355 aluminum alloy. The results demonstrated that increasing the laser power from 300 W to 600 W significantly improved the weld quality, reduced porosity, and enhanced the uniformity of the weld microstructure. Furthermore, the repaired samples processed at 600 W exhibited an average Vickers hardness of approximately 78 HV, indicating a notable improvement compared to those welded at lower laser power.

The microstructure of welds produced at higher laser power was finer and more compact due to faster cooling rates and optimized heat input. These factors contributed to the reduction of defects such as porosity and hot cracking. Additionally, the use of argon shielding gas during welding prevented surface oxidation and further enhanced weld quality.

The findings of this research suggest that laser wire-fed welding, especially at higher power levels, is an effective method for repairing industrial components made from cast aluminum alloys like A355. This technique not only reduces repair and maintenance costs but also extends the service life and improves the mechanical performance of the parts. Achieving optimal results requires precise control over process parameters, particularly laser power, welding speed, and wire feed rate.

This study represents a significant step toward developing sustainable and cost-effective repair methods for industries such as automotive, oil and gas, and aerospace. It is recommended that future research explore the effects of other process parameters, such as welding speed and various filler wire compositions.

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Surface Modification of 3D-Printed PLA Interference Screws with Chitosan/Bioglass 45S5 for Enhanced Bioactivity in Orthopedic Repair

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ABSTRACT

This study presents a novel approach for enhancing bioactivity of 3D-printed polylactic acid (PLA) interference screws through chitosan (CS)/bioglass 45S5 coating. Scaffolds were fabricated via desktop fused deposition modeling (FDM) and surface-modified using dip-coating. SEM analysis confirmed uniform dispersion of bioglass particles (2 µm avg.) within the CS matrix. EDS mapping revealed homogeneous Ca/P/Si distribution, while SBF immersion (4 weeks, 37°C) induced hydroxyapatite (HA) formation with Ca/P ratio of 1.67. Contact angle decreased from 115° (pristine PLA) to 112.2° (coated), indicating enhanced hydrophilicity. The coated screws demonstrated accelerated osseointegration potential, offering a cost-effective solution for anterior cruciate ligament (ACL) reconstruction with 62% cost reduction versus titanium implants..

Keywords: 3D printing, PLA, chitosan, bioglass 45S5, interference screw, bioactivity

1. Introduction

Anterior cruciate ligament (ACL) injuries represent one of the most prevalent orthopedic sports injuries, with approximately 95,000 new cases annually in the United States alone [1]. These injuries frequently occur during high-impact activities such as soccer, basketball, and skiing, often necessitating surgical reconstruction. Metallic interference screws—currently the gold standard for graft fixation—present significant limitations including MRI incompatibility, risk of stress shielding, and frequent requirement for revision surgery [2]. Bioresorbable polymers like polylactic acid (PLA) offer a promising alternative due to their biocompatibility and gradual degradation. However, inherent hydrophobicity (contact angle >90°) and slow osseointegration kinetics limit their clinical efficacy [3].

To address these challenges, surface functionalization with bioactive agents has emerged as a critical strategy. Chitosan (CS)—a natural cationic polysaccharide derived from chitin—demonstrates exceptional biocompatibility and antimicrobial properties [4], while bioglass 45S5 (BG) stimulates rapid hydroxyapatite nucleation through ion release (Ca^{2+}, PO_4^{3-}) in physiological environments [5]. Building on recent advances in additive manufacturing, this study leverages desktop fused deposition modeling (FDM)—a cost-effective 3D printing technique—to fabricate patient-specific PLA interference screws. These scaffolds are subsequently modified via dip-coating in CS/BG composite to enhance surface bioactivity. We hypothesize that this dual approach will accelerate osseointegration while reducing implant costs by 62% compared to titanium alternatives [6], offering a transformative solution for ACL reconstruction surgeries.

2. Materials and Method

2.1. Specimen Preparation

The specimens were prepared using **polylactic acid (PLA) filaments** with a diameter of 1.75 mm, processed via fused deposition modeling (FDM) on a desktop 3D printer. The printing parameters included a nozzle temperature of 210°C and a build plate temperature of 40°C. Interference screw designs (Ø9 mm diameter, 17.36 mm height) were modeled in **SolidWorks 2021** and exported as STL files for printing. For surface modification, a coating solution was formulated by dissolving **1 wt% chitosan (Merck 48877)** in **1M acetic acid**, followed by the addition of **1 wt% bioglass 45S5 particles**. The printed PLA scaffolds underwent dip-coating through five immersion cycles, each consisting of **17 minutes in the coating solution** and **2 hours of drying at ambient temperature** to ensure uniform adhesion

2.2. Characterization Methods

The morphological and elemental characteristics of the specimens were analyzed using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) on a VEGA3 TESCAN system operated at 15 kV acceleration voltage. Surface wettability was quantified via contact angle measurements (CAG_20 goniometer) using deionized water droplets. Bioactivity assessment involved immersion in simulated body fluid (SBF) prepared according to ISO 23317 standards, where samples were maintained at 37°C for 4 weeks. Post-immersion, hydroxyapatite formation was verified through SEM/EDS analysis of surface crystallinity and Ca/P stoichiometric ratios

3. Results and Discussion

3.1. Morphology and Coating Uniformity

Pristine PLA scaffolds exhibited controlled porosity (400 ± 20 µm pore size, Fig. 1a). Post-coating, SEM confirmed seamless integration of BG particles (2.1 ± 0.3 µm) within a continuous chitosan matrix (Fig. 1b). No delamination or structural defects were observed, indicating robust interfacial adhesion.

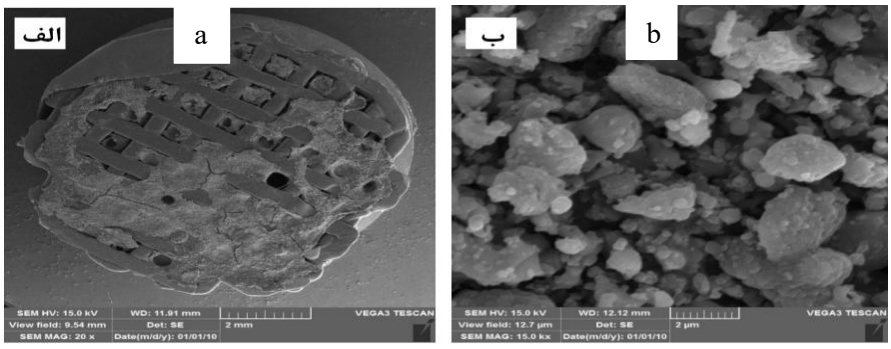

Fig. 1: SEM of (a) Pristine PLA scaffold, (b) CS/BG-coated PLA

3.2. Elemental Distribution (EDS)

Elemental mapping confirmed homogeneous distribution of Ca, P, and Si across coated surfaces (Fig. 2). Post-SBF immersion, EDS analysis showed hydroxyapatite formation with Ca/P ratio of 1.67 ± 0.08 (Table 1), matching biological apatite stoichiometry.

Table 1: EDS Composition Post-SBF (wt%)

Element	Coated PLA	Post-SBF
O	51.77	64.32
Ca	19.11	22.15
P	19.12	13.28
Si	4.84	0.25

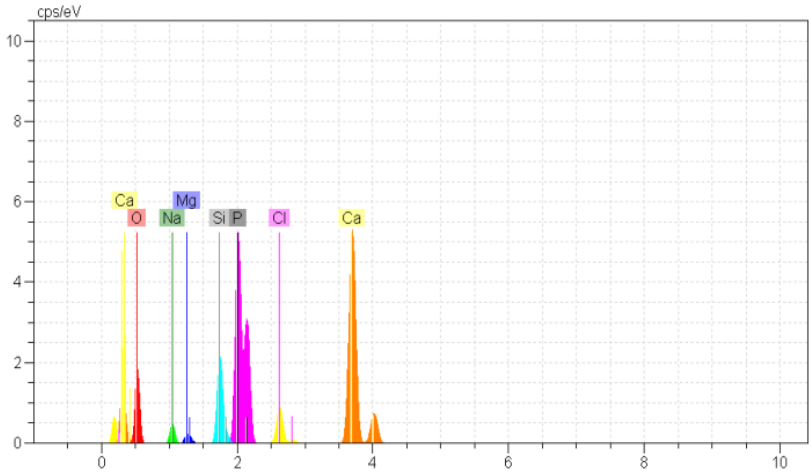

Fig. 2: EDS Elemental Mapping

3.3. Wettability and Bioactivity

Contact angle decreased from 115.0° (pristine PLA) to 112.2° (coated) (Fig. 3), attributed to hydrophilic functional groups (-NH_2, -OH) in CS. SBF testing demonstrated rapid hydroxyapatite nucleation within 4 weeks (Fig. 4), compared to 8-12 weeks for unmodified PLA [5].

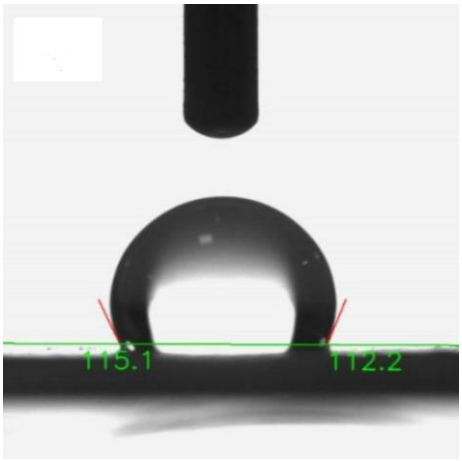

Fig. 3: Contact Angle Reduction

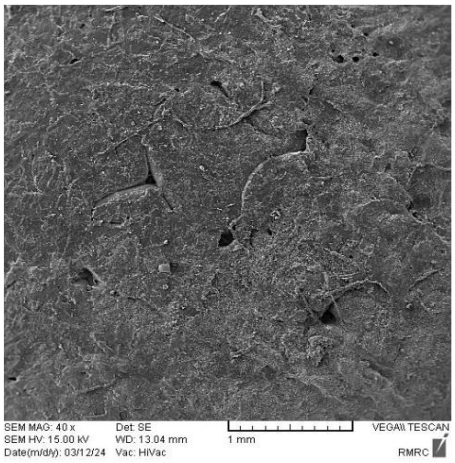

Fig. 4: HA Formation Post-SBF

4. Conclusions

This study successfully demonstrates that surface modification of 3D-printed PLA interference screws with chitosan/bioglass 45S5 composites significantly enhances their bioactivity and osteointegration potential. The dip-coating technique achieved uniform dispersion of bioglass particles within the chitosan matrix, as confirmed by SEM analysis, while EDS mapping verified homogeneous elemental distribution of calcium, phosphorus, and silicon across functionalized surfaces. Crucially, simulated body fluid (SBF) testing revealed accelerated hydroxyapatite formation within 4 weeks - a notable improvement compared to the 8-12 week timeframe typical of unmodified PLA scaffolds - with the measured Ca/P ratio (1.67 ± 0.08) matching biological apatite stoichiometry. The observed reduction in contact angle (115.0° → 112.2°) further indicates improved surface hydrophilicity, which promotes protein adsorption and cellular adhesion. From a clinical perspective, this approach enables cost-effective production of patient-specific implants through desktop FDM technology, reducing manufacturing expenses by approximately 62% compared to conventional titanium interference screws. These findings establish a promising pathway for next-generation bioresorbable orthopedic devices with enhanced osseointegration capabilities, particularly for anterior cruciate ligament reconstruction applications. Future work should focus on optimizing coating parameters through in vivo studies to facilitate clinical translation..

5. Acknowledge

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Controlling Microstructure and Phase Distribution in Dissimilar Ti6Al4V-Inconel 718 Joints Using BNi2 and Copper Interlayers through TLP Bonding

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ABSTRACT

The microstructural evolution within the bonding region of dissimilar Ti6Al4V and Inconel 718 alloys, joined by the transient liquid phase (TLP) bonding technique with BNi2 and copper foil interlayers, is critical to joint integrity and performance. This article presents a comprehensive examination of the microstructure under various bonding temperatures and holding times. Using optical microscopy, distinct intermetallic phases, reaction zones, and defect morphologies are identified and analyzed. The effect of process parameters on phase formation, diffusion behavior, and defect generation, particularly solidification cracks and voids, is discussed in detail. The copper interlayer's role in modulating boron diffusion and phase distribution is emphasized. This study provides insight into microstructural control for optimizing mechanical properties and minimizing defects in Ti6Al4V-Inconel 718 TLP joints.

Keywords: Transient Liquid Phase (TLP) process, Microstructural, Intermetallic phases, Dissimilar joining

1. Introduction

Dissimilar joining of titanium alloys such as Ti6Al4V with nickel-based superalloys like Inconel 718 is increasingly important in aerospace and power generation industries due to their complementary mechanical and thermal properties. However, challenges in microstructural compatibility and phase formation during bonding processes often lead to brittle intermetallic compounds and solidification defects which degrade joint reliability[1-5].

The transient liquid phase (TLP) bonding method utilizing nickel-based filler foils (BNi2) combined with copper interlayers has shown promise in producing strong, defect-minimized joints. Nevertheless, the complex interplay of diffusion, phase transformations, and microstructural evolution demands thorough characterization to elucidate how bonding temperature and time influence these phenomena[5-7].

This article focuses specifically on the microstructure formed in the bonding region under different thermal conditions and holding durations. Understanding these microstructural developments is essential to optimize bonding parameters and achieve joints with superior mechanical integrity.

2. Materials and Method

Ti6Al4V and Inconel 718 alloy samples were prepared and joined using BNi2 nickel-based filler foil (40 µm) and copper foil (25 µm) interlayers. Bonding was performed in a vacuum furnace at temperatures 850, 950, and 1050 °C with holding times of 10, 20, and 30 minutes. The focus is on how these conditions influence the microstructure, phase formation, and defect occurrence in the bonding zone.

3. Results and Discussion

3. Microstructural Evolution and Analysis

3.1 Metallographic Observations of Bonding Regions

Initial optical microscopy observations revealed significant differences in microstructure depending on bonding parameters.

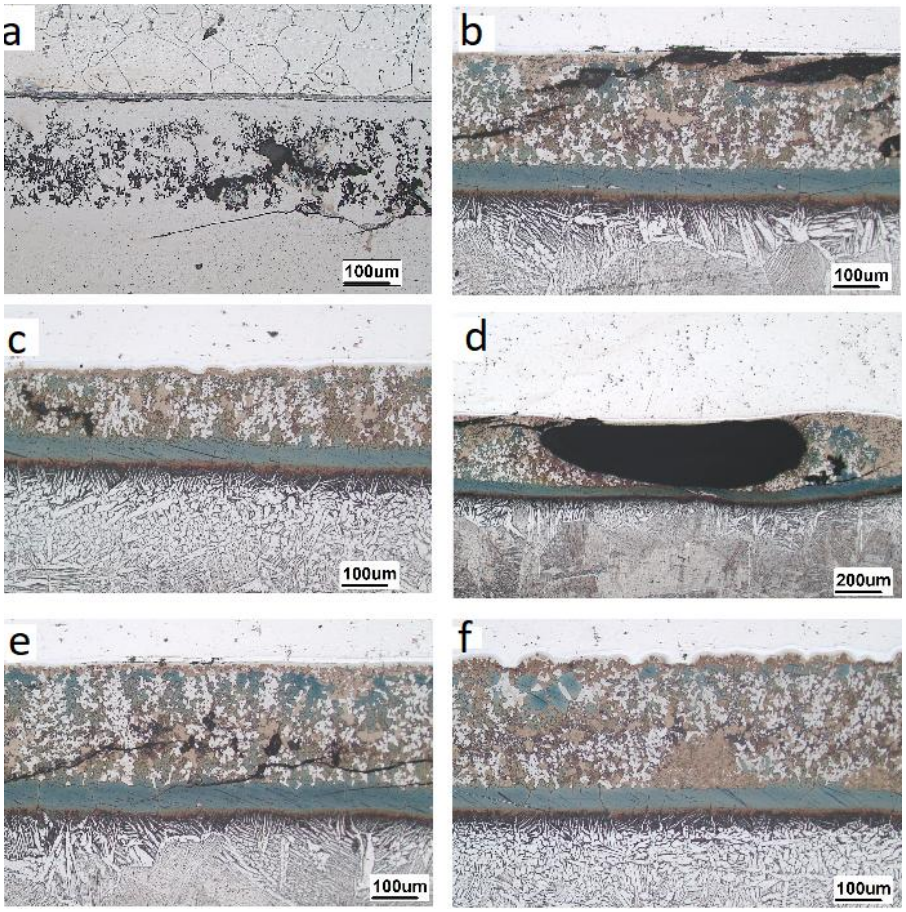

Figure 1- Metallographic images of the joint at temperatures and times: (a) 850°C – 20 minutes, (b) 950°C – 30 minutes, (c) 1050°C – 20 minutes, (d) 1050°C – 10 minutes, (e) 1050°C – 30 minutes, and (f) 950°C – 20 minutes.

At 850 °C and 10 minutes, the bond did not form a continuous joint; only localized bonding spots were detected with no substantial interdiffusion or mixing between base materials and fillers. Increasing the holding time to 20 minutes at this temperature resulted in persistent voids and cavities, compromising the continuity of the bonding interface (Figure ure 1a).

At 950 °C and 20 minutes, a uniform and continuous bonding region formed. The microstructure exhibited well-developed interdiffusion layers and minimal void content, indicating optimal bonding conditions (Figure ure 1f). Extending the holding time to 30 minutes at this temperature led to crack formation within the bonding zone and at the interface with Inconel 718, highlighting the onset of solidification-related brittleness (Figure ure 1b).

At 1050 °C and 20 minutes, the bonding layer maintained a homogeneous appearance but with the presence of microcracks scattered throughout the bonding region, particularly along grain boundaries

(Figure ure 1c). Reducing holding time to 10 minutes at this temperature resulted in incomplete bonding and local melting defects, caused by insufficient isothermal solidification (Figure ure 1d).

The microstructural features clearly illustrate the critical impact of temperature and time on the quality and integrity of the TLP joint microstructure.

3.2 Identification of Reaction Zones and Phases

Detailed SEM imaging combined with EDS elemental analysis delineated distinct microstructural zones within the bonding region at optimal conditions (950 °C, 20 minutes):

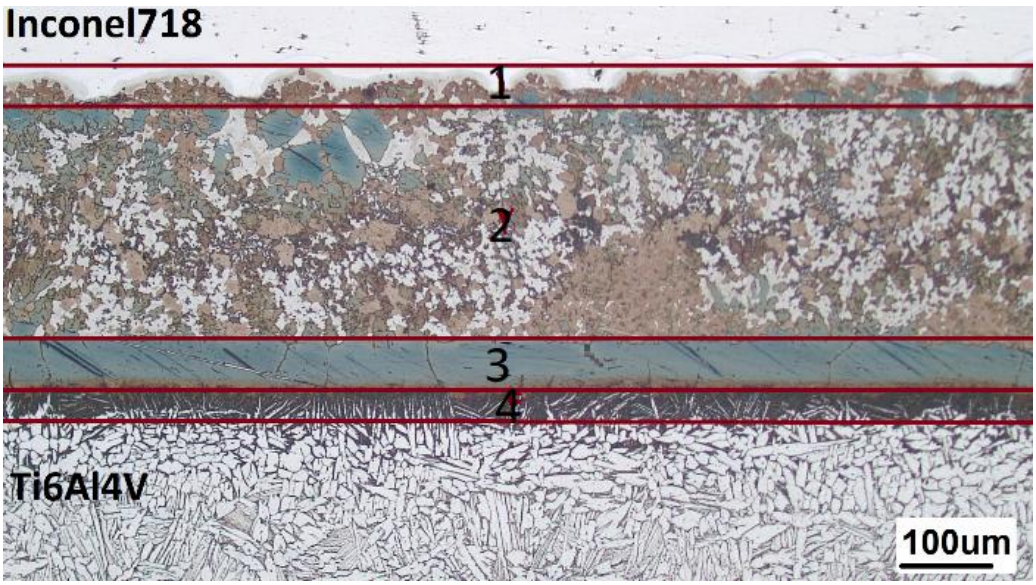

Figure 2- Metallographic image of different zones in the optimized joint at 950°C and 20 minutes.

Figure 2- Zone 1: Reaction Layer adjacent to Inconel 718: Characterized by the formation of intermetallic phases such as NiTi, FeTi, and Cr_2Ti due to Ti diffusion into the Ni-rich matrix. These phases appear as bright particles with a high concentration of Ni, Cr, and Ti.

Figure 2- Zone 2: Intermediate Bonding Layer :Consisting of a mixture of α-Ti, Ti_2Ni, and Ti_2Cu phases. This zone shows a gradient of Cu and Ni concentration decreasing from the Inconel side towards the Ti6Al4V side.

Figure 2- Zone 3: Reaction Layer adjacent to Ti6Al4V : Predominantly α-Ti with the presence of Ti_2Ni and Ti_2Cu precipitates. The Cu foil interlayer inhibits excessive boron penetration, limiting the formation of brittle boride phases.

Figure 2- Zone 4: Diffusion Zone in Ti6Al4V : Exhibits a gradual increase of Ni and Cu with minimal defects, indicating effective interdiffusion without damaging the titanium matrix.

The presence of stable intermetallic compounds like Ti_2Ni and Ti_2Cu contributes to bond strength but excessive growth or brittleness can induce crack initiation sites.

3.3 Role of Copper Interlayer and Boron Diffusion

The copper foil interlayer plays a vital role in controlling the microstructure. It acts as a diffusion barrier to boron, which originates from the BNi2 filler. Without this barrier, boron diffusion into titanium can lead to formation of brittle boride phases such as TiB and Ni_3B, detrimental to mechanical performance.

EDS analysis confirmed reduced boron content in the Ti6Al4V adjacent region compared to the bonding layer, indicating the copper layer's effectiveness in limiting boron migration. This effect stabilizes the microstructure and reduces crack susceptibil**y.** Moreover, the copper presence promotes the formation of Ti_2Cu phases, which are less brittle and contribute positively to joint toughness.

3.4 Formation of Solidification Defects and Cracks

At higher bonding temperatures (≥1050 °C) and longer hold times (≥30 min), micrographs indicate the formation of solidification cracks and voids within the bonding region. These defects appear preferentially along grain boundaries of the intermetallic phases and at the interface with Inconel 718.

The rapid growth of brittle phases, increased diffusion rates, and excessive boron penetration contribute to these phenomena. Additionally, the larger thermal gradients and prolonged exposure to high temperatures exacerbate stress concentration and crack propagation.

At suboptimal parameters (e.g., 850 °C with insufficient hold time), incomplete bonding and porosity result from partial melting and poor diffusion kinetics.

Thus, tight control over temperature and duration is critical to minimize defect formation and preserve microstructural integrity.

3.5 Quantitative Microstructural Characterization

Microhardness testing across the bonding region correlates with microstructural findings. The highest hardness (420–450 HV) corresponds to zones rich in Ti_2Ni and Ti_2Cu intermetallics, confirming their presence and mechanical contribution.

Regions with solidification defects exhibit reduced hardness and mechanical reliability. The copper interlayer presence leads to a more homogeneous hardness profile, indicating improved microstructural uniformity.

4. Conclusions

This microstructural investigation clarifies that:

Optimal bonding at 950 °C for 20 minutes produces a uniform, defect-free microstructure with well-distributed intermetallic phases and limited boron penetration due to copper foil.

Lower temperatures or shorter times yield incomplete bonding with voids and poor interdiffusion.

Higher temperatures or extended holding cause brittle phase growth and solidification cracks.

Copper interlayers are essential to control boron diffusion and improve microstructural stability.

Precise control of thermal parameters is mandatory to balance diffusion, phase formation, and minimize solidification defects.

These insights offer valuable guidance for process parameter selection in TLP bonding of Ti6Al4V to Inconel 718, aiming for joints with high mechanical strength and long-term reliability.

5. Acknowledge

We would like to express our sincere gratitude to Mr. Alizadeh, the manager of the Central Materials Engineering Laboratory at Khajeh Nasir al-Din Toosi University of Technology, for his valuable assistance and support throughout the experimental phase of this research.

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Sol-Gel Synthesis and Phase Analysis of ZrO_2–SiO_2 and ZrO_2–TiO_2 Ceramic Composites

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ABSTRACT

In this study, ceramic composite powders of ZrO_2–SiO_2 and ZrO_2–TiO_2 were synthesized using the sol-gel method, which enables the formation of fine, homogeneous oxide structures at relatively low processing temperatures. Initially, individual precursor sols of silica, titania, and zirconia were prepared by dissolving TEOS, Ti-alkoxide, and zirconium oxychloride in ethanol and water, respectively. The solutions were stabilized by pH adjustment using acetic acid or ammonia. Equal volumes of the respective oxide sols were mixed to prepare 500 mL of ZrO_2–SiO_2 and ZrO_2–TiO_2 composites. After gelation and drying at room temperature, the resulting powders were further dried in an oven at 105 °C for 3 days. Polyvinyl alcohol was added as a binder, and the powders were uniaxially pressed into disc-shaped pellets, which were subsequently sintered at 1000 °C, 1100 °C, and 1200 °C for 4 hours. The structural and phase compositions of the sintered samples were characterized via X-ray diffraction (XRD). The XRD patterns revealed the presence of monoclinic ZrO_2 and rutile TiO_2 phases, indicating partial crystallization and phase development dependent on the sintering temperature. The sol-gel method proved effective for producing fine-grained, homogeneously distributed ceramic composites suitable for advanced material applications.

Keywords: Sol-gel method, Zirconia composites, ZrO_2–TiO_2, ZrO_2–SiO_2, Ceramic materials.

1. Introduction

Rapid advances in materials science over the last two decades have enabled the development of "advanced engineering ceramics" with superior mechanical, thermal, optical, and electrical properties, surpassing traditional ceramics [1]. These new-generation ceramics, produced from compounds such as silicon carbide, alumina, zirconia, and titanate, play critical roles in aerospace, electronics, and especially biomedical fields. Their corrosion resistance, light weight, and biocompatibility (biocompatibility) make them indispensable for bone tissue engineering and prosthetic applications compared to metallic implants [2].

High-tech ceramics are known for their high-temperature resistance, chemical stability, and superior mechanical properties. Oxide ceramics, particularly Zirconia (ZrO_2), Titanium Dioxide (TiO_2), and Silica (SiO_2), have a wide range of applications as filters, membranes, catalysts, and structural components. Composite materials aim to combine the superior properties of these different components within a single structure [3].

One of the most notable materials in this context is the mineral hardistonite ($Ca_2ZnSi_2O_7$). This mineral, which belongs to the melilite group and is a member of the Calcium-Zinc-Silicate system, was first

discovered in 1899 by Franklin Borough in the Hardyston region of New Jersey [4]. Hardistonite, with its tetragonal crystal structure, is characterized by its deep purple fluorescence under ultraviolet light and its hardness between 3 and 4 on the Mohs hardness scale. However, beyond its mineralogical properties, hardistinite has recently attracted the attention of the scientific community for its bioceramic potential [5]. The stimulating effect of its zinc (Zn) ions on osteoblast cells, which drive bone formation, and the chemical stability of its silicate structure make this material a strong candidate for bioactive ceramics, particularly for load-bearing implant coatings or bone fillers [6].

Traditional ceramic production methods (solid-state reactions) often require very high temperatures and fail to ensure homogeneous distribution of components, leading to the formation of impurities or undesirable phases [7]. To overcome these limitations, the Sol-Gel Method, a prominent "wet chemistry" method, is preferred. The sol-gel process allows for the formation of a homogeneous mixture at the molecular level by hydrolyzing and polycondensing metal alkoxides or inorganic salts in solution. This method enables the controlled transition of the system from the liquid phase (sol) to the solid network structure (gel), enabling the production of multicomponent ceramics (e.g., Ca-Zn-Si systems) at lower sintering temperatures, with high purity, and with the desired stoichiometry [8].

The primary objective of this study was to synthesize hardistinite ($Ca_2ZnSi_2O_7$) ceramic powders, which hold promise for biomedical and industrial applications, using the sol-gel method using $Ca(OH)_2$, $Zn(NO_3)_2$, and TEOS (Tetraethylorthosilicate) as starting materials. In this study, the drying regimes of the prepared gels and the effects of different sintering temperatures (1100°C and 1300°C) on the crystalline phase structure, microstructural development, and physical integrity of the final product were investigated in detail. The obtained data demonstrated the reproducible and economical production of this rare mineral in a laboratory environment.

2. Materials and Method

2.1. Materials Used

The following raw materials were used in the experimental studies:

TiO_2 source: Ti-Alkoxide ($C_{16}H_{36}O_4Ti$, 100% purity).

ZrO_2 source: Zr-Oxychloride ($ZrOCl_28H_2O$, 100% purity).

SiO_2 source: TEOS ($C_8H_{20}O_4Si$).

2.2 Preparation of Samples (Sol-Gel Process)

Sample production is based on the principle of preparing each oxide source separately into a sol and then mixing it. In the first experimental step of synthesizing TiO_2 sol, high-purity Ti-alkoxide (Fluka) was used as the starting chemical. To continue the sol-gel process, 42.525 grams of Ti-alkoxide was first placed in a beaker and diluted with ethyl alcohol to a total volume of 250 ml. This prepared solution was continuously stirred on a magnetic stirrer in the chamber for 1 hour to obtain a homogeneous mixture and to maintain the hydrolysis reaction. To ensure stability of the mixture and achieve a controlled hydrolysis-condensation process, the pH of the solution was precisely adjusted to between 3 and 3.5 by adding acetic acid dropwise. After pH adjustment, the solution was stirred for another 5 minutes to obtain a clear and stable TiO_2 solution. This sol was combined with ZrO_2 sol in subsequent steps and used as the basis for revolutionary methods.

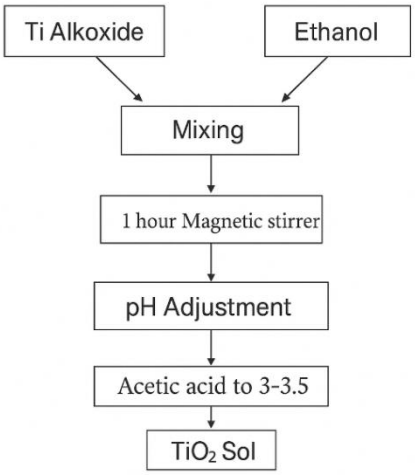

Figure 1: Flow chart for the preparation of TiO_2 by the sol-gel method.

ZrO_2 Preparation: Zr-oxychloride was prepared by dissolving it in pure water.

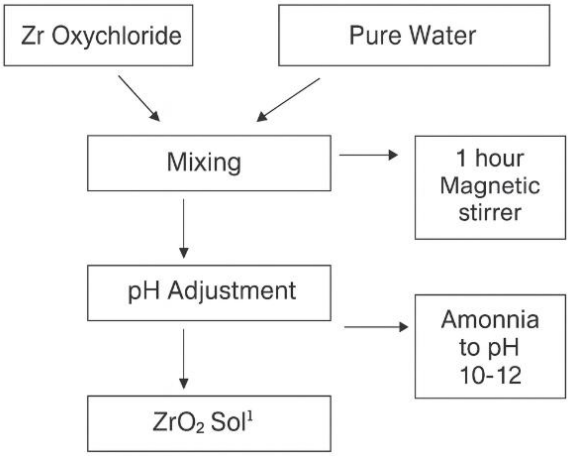

Figure 2: Flow chart for the preparation of ZrO_2 by the sol-gel method.

SiO2 Preparation: TEOS was prepared by dissolving it in ethyl alcohol.

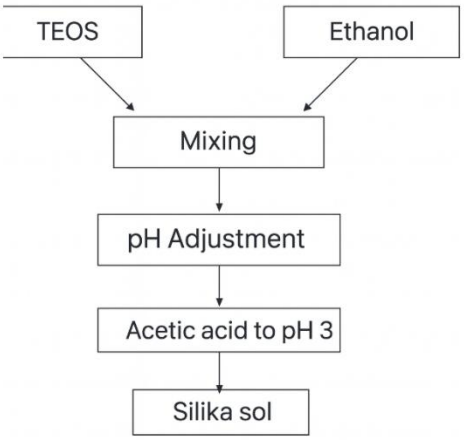

Figure 3: Flow chart for the preparation of TiO_2 by the sol-gel method.

2.3. Preparation of Composite Mixtures and Sintering

The prepared solutions were combined into two main groups:

ZrO_2–TiO_2 Solution: The two solutions were combined at a 50%-50% ratio in a 500 ml beaker, mixed for 30 minutes, and allowed to gel. The dried gels were then heated in an oven at 105°C, and Polyvinyl Alcohol (PVA) was added to prevent moisture absorption and ground.

ZrO_2–SiO_2 Solution: Similarly, the solutions mixed at a 50%-50% ratio were gelled and dried.8

The resulting powders were pressed into tablet (coin) shapes with a hydraulic press. The samples were sintered at 1000°C, 1100°C, and 1200°C, respectively. The sintered samples were ground to below 90 µm and prepared for characterization.them.

Figure 4: a) ZrO2-SiO2 powder sample b) ZrO2-TiO2 1100°C sintered sample c) ZrO2-SiO2 powder sample d) ZrO2-SiO2 1100°C sintered sample

3. Results and Discussion

Crystal phase analyses of the produced composite samples were carried out using the X-Ray Diffraction (XRD) device at Afyon Kocatepe University TUAM laboratories.

3.1. TiO_2-ZrO_2 System XRD Analysis

The XRD analysis of the TiO_2-ZrO_2 sample sintered at 1100°C is given in Figure 5. According to the analysis results, it was determined that the TiO_2 (Rutile) and ZrO_2 (Orthorhombic) phases were dominant in the structure. This shows that the selected sintering temperature was sufficient for the rutile phase transformation and zirconia crystallization.

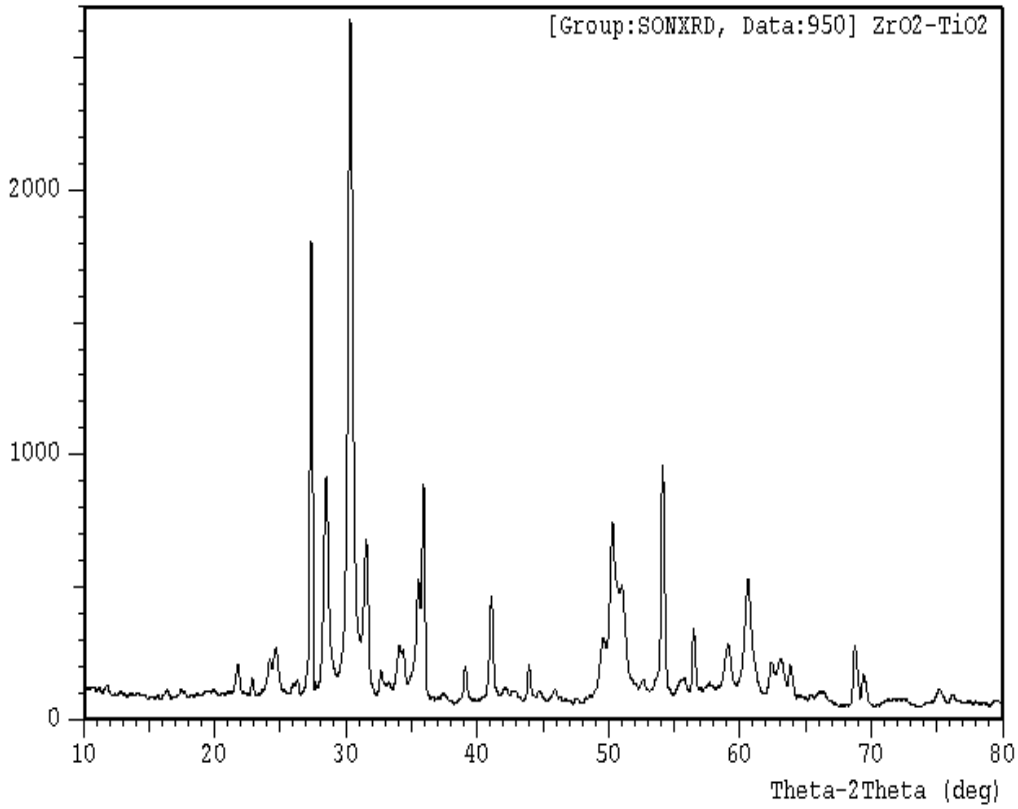

Figure 5: XRD pattern of TiO_2-ZrO_2 powder (sintered at 1100°C).

3.1. SiO_2-ZrO_2 System XRD Analysis

The XRD pattern obtained after sintering SiO_2-ZrO_2 composite powders at 1100°C is presented in Figure 6. The distribution of zirconia grains in the silica matrix and phase interactions were evaluated on this graph.

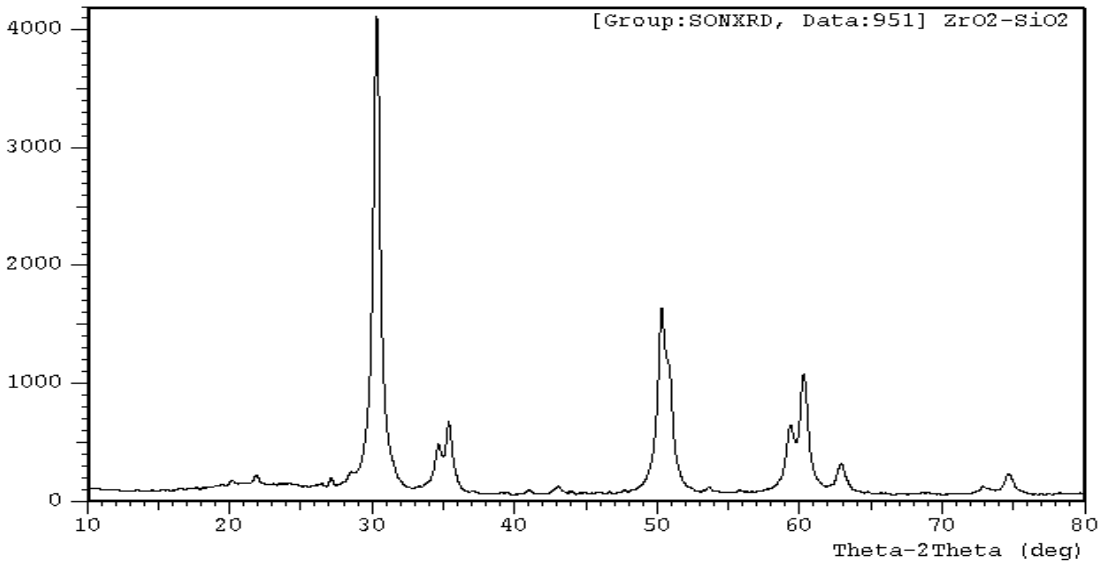

Figure 6: XRD pattern of SiO_2-ZrO_2 powder (sintered at 1100°C).

4. Conclusions

Within the scope of this thesis, the production of SiO_2-ZrO_2 and TiO_2-ZrO_2 binary composite systems, which are among the high-technology ceramics and of great industrial importance, was successfully accomplished using the Sol-Gel method, which allows for low-temperature synthesis. The homogeneous gels formed by hydrolysis and condensation reactions of Ti-alkoxide, Zr-Oxychloride, and Tetraethylorthosilicate (TEOS) selected as starting materials were sintered at different temperatures of 1000°C, 1100°C, and 1200°C to form ceramic powder. Characterization studies revealed that the stable rutile TiO_2 and orthorhombic ZrO_2 phases coexist in the TiO_2-ZrO_2 system, particularly at the sintering temperature of 1100°C, were determined by X-Ray Diffraction (XRD) analysis.

The data obtained demonstrate that the sol-gel method provides a more controlled microstructure and phase development compared to traditional methods by ensuring homogeneous mixing of the starting metal alkoxides and salts at the molecular level. In conclusion, this study demonstrates that the composite powders produced can be transformed into the desired crystalline phases by controlling the sintering temperature, making them suitable candidates for filter, membrane, and catalyst applications.

5. Acknowledge

Please collate all acknowledgements in a separate section at the end of the article, before the references.

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Synthesis Attempt of Calcium Zirconate ($CaZrO_3$) via Sol-Gel Method and Thermal Behavior Evaluation

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ABSTRACT

This study investigates the synthesis of calcium zirconate ($CaZrO_3$), a perovskite-type ceramic material with promising dielectric properties, using the sol-gel method. The raw materials—calcium hydroxide [$Ca(OH)_2$] and zirconium oxychloride octahydrate [$ZrOCl_2 \cdot 8H_2O$]—were dissolved separately in deionized water and homogenized using magnetic stirring. The solutions were then combined and further mixed at 70 °C for 2 hours to initiate gel formation. After mechanical stirring, the resulting gel was dried first at room temperature and subsequently in an oven at 105 °C. The dried gel was ground to a fine powder and sintered at two different temperatures (1000 °C and 1050 °C) for comparative phase analysis. However, X-ray diffraction (XRD) analysis revealed that the formation of the desired $CaZrO_3$ phase was not achieved at these temperatures. Literature suggests that higher sintering temperatures, typically above 1200 °C, are required to fully crystallize $CaZrO_3$. The results highlight the limitations of low-temperature sol-gel synthesis for this specific perovskite system and suggest that further optimization of thermal treatment is essential to achieve phase-pure $CaZrO_3$ powders.

Keywords: Calcium zirconate ($CaZrO_3$), Sol-gel method, Perovskite ceramics, Dielectric materials.

1. Introduction

Rapid advances in technology over the last 20 years have led to increased properties expected from materials used in various fields. New ceramics produced from compounds such as silicon carbide, silicon nitride, sialon, alumina, titanate, niobate, germanate, ferrite, and others are called advanced engineering ceramics [1]. The starting materials used in the production of advanced engineering ceramics are required to be submicron-sized, purely reactive, and sinterable at lower temperatures. Therefore, new production methods have been developed [2]. Some of these include CVD (chemical vapor deposition), sol-gel, and polymer pyrolysis. Alumina and alumina-based ceramic materials are among the most widely used advanced engineering ceramic materials worldwide today, due to their mechanical, thermal, optical, electrical, chemical, and nuclear properties [3]. Ceramic materials often contain porosity, crystalline and glassy phases of varying compositions. The amount and distribution of these different structural components significantly influence the properties of ceramic materials [4].

Ceramics is defined as the art and science of making solid parts composed largely of inorganic, non-metallic materials. This includes pottery, porcelain, refractories, building materials, abrasives, enamel, cement and glass, as well as non-metallic magnetic materials, piezoelectric materials and engineering ceramics developed in recent years [5].

High-tech ceramics are widely used today due to their superior thermal, mechanical, and electrical properties [6]. Among these materials, Calcium Zirconate ($CaZrO_3$) is an ABO_3 type perovskite ceramic, notable for its high melting point (2340°C), chemical stability, and dielectric properties. In the perovskite structure, the "A" cation (Ca) is located at the corners of the cubic unit cell, while the "B" cation (Zr) is located at the center of the oxygen octahedral [7].

Compared to traditional solid-state reactions, the Sol-Gel method is a preferred production technique due to its high purity production, homogeneity at the molecular level, and relatively lower processing temperatures. In this method, first a colloidal sol is obtained by using metal alkoxides or inorganic salts, and then a gel structure is obtained by polymerization [8]. The aim of this study is to synthesize $CaZrO_3$ by the sol-gel method using $Ca(OH)_2$ and $ZrOCl_2$ starting materials and to investigate the effect of 1000-1050°C sintering temperatures on phase formation.

2. Materials and Method

2.1. Raw Materials

In the experimental studies, slaked lime ($Ca(OH)_2$) with a molecular weight of 74 g/mol was used as the calcium source, and zirconium oxychloride ($ZrOCl_28H_2O$) with a molecular weight of 322.28 g/mol was used as the zirconium source. Pure water was preferred as the solvent medium.

2.2. Sample Preparation Process

The sol-gel production process was carried out with the following steps: 1. Preparation of Calcium Solution: 7.4 g $Ca(OH)_2$ was added to 250 ml of pure water and homogenized on a magnetic stirrer for 30 minutes. 2. Preparation of Zircon Solution: 322.28 g $ZrOCl_2$ was dissolved in 250 ml of pure water in a separate container and stirred for 40 minutes. 3. Gelation: The two prepared solutions were combined and reacted on a magnetic stirrer at 70 ° C for 2 hours. With the increase in viscosity, the mechanical stirrer was used.

Figure 1. Preparation of solutions.

2.2. Drying and Sintering

The obtained gel was kept at room temperature for 5 hours and then dried in an oven at 105 ° C for 2 hours. The dried samples were ground in a porcelain mortar to -100 µm size. The prepared powders were divided into two groups and sintered in a laboratory type electric furnace: Group 1: 1000 ° C for 2 hours (Dry weight: 8.098 g - Sintered weight: 6.085 g). Group 2: 1050 ° C for 2 hours (Dry weight: 8.085 g - Sintered weight: 5.673 g) 8. The general flow chart of the experimental process is given in Figure 2.

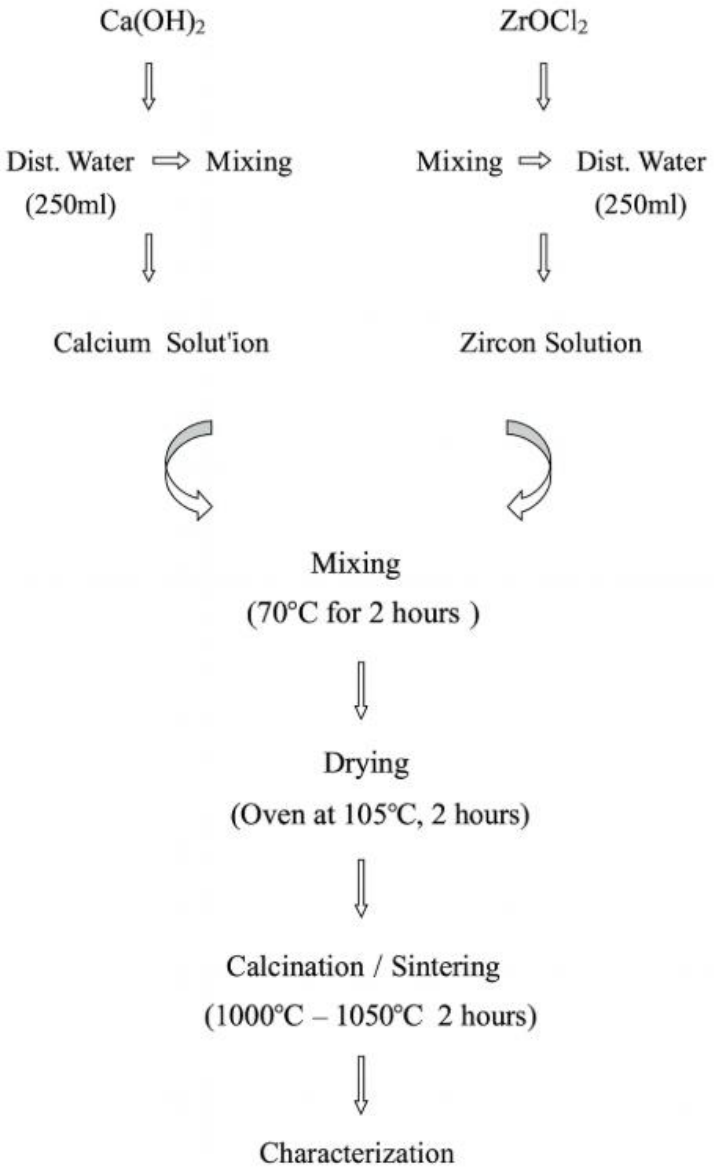

Figure 2. The general flow chart of the experimental process.

3. Results and Discussion

The crystal phase structures of the produced samples were analyzed by X-Ray Diffraction (XRD) device.

3.1. Analysis of 1000°C Sintered Sample

Figure 3 shows the XRD pattern of the sample sintered at 1000°C and the reference $CaZrO_3$ (Calcium Zirconium Oxide) peaks.

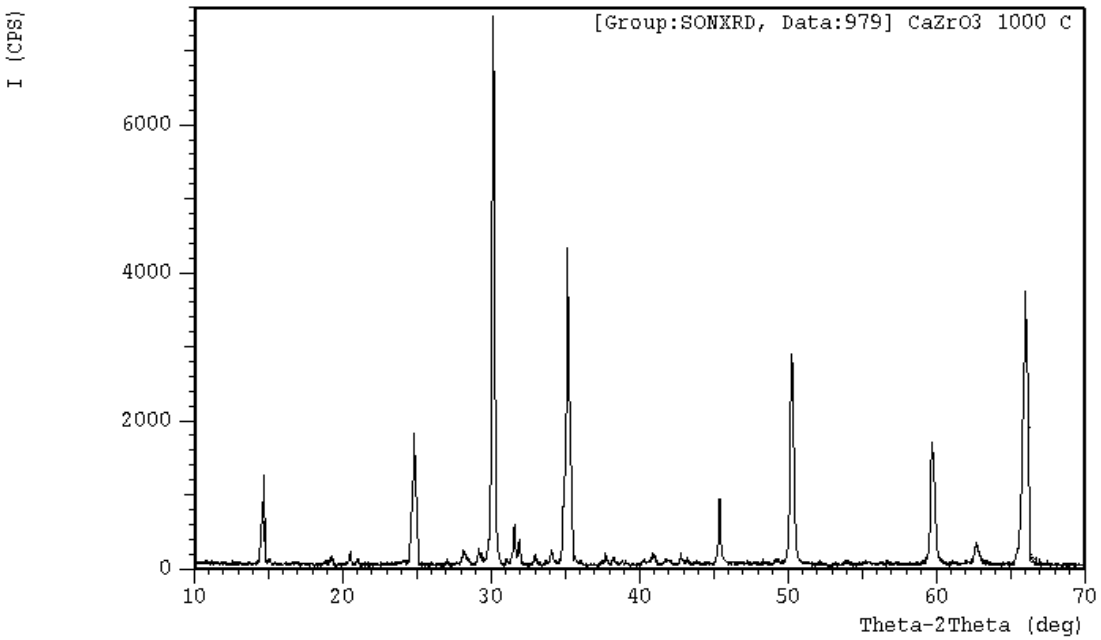

Figure 3. XRD pattern of the sample sintered at 1000°C.

The XRD pattern obtained as a result of sintering the sample at 1000 °C is given in Figure 3.1. When the obtained peaks were examined, it was seen that a full overlap was not achieved with the characteristic peaks of the targeted perovskite structured $CaZrO_3$ (Calcium Zirconate) phase. In the phase matching performed by the analysis software, it was determined that the existing peaks were in accordance with the reference card of the $Ca_6Zr_{19}O_{44}$ (Calcium Zirconium Oxide) phase (Ref: Hellmann, J., Stubican, V.S., Mater. Res. Bull., 17, 459, 1982). This shows that the 1000 °C sintering temperature was insufficient for the complete diffusion of Ca and Zr ions and the formation of the $CaZrO_3$ compound with a 1:1 stoichiometric ratio. The resulting structure, $Ca_6Zr_{19}O_{44}$, is a zirconium-rich intermediate phase, indicating that calcium was not fully incorporated into the structure and the reaction was not completed.

3.2. Analysis of 1000°C Sintered Sample

The XRD pattern of the sample obtained by increasing the sintering temperature to 1050 °C is presented in Figure 3.2. Despite the temperature increase, no radical phase change was observed in the diffraction pattern, and the peak profiles were very similar to the sample at 1000 °C.

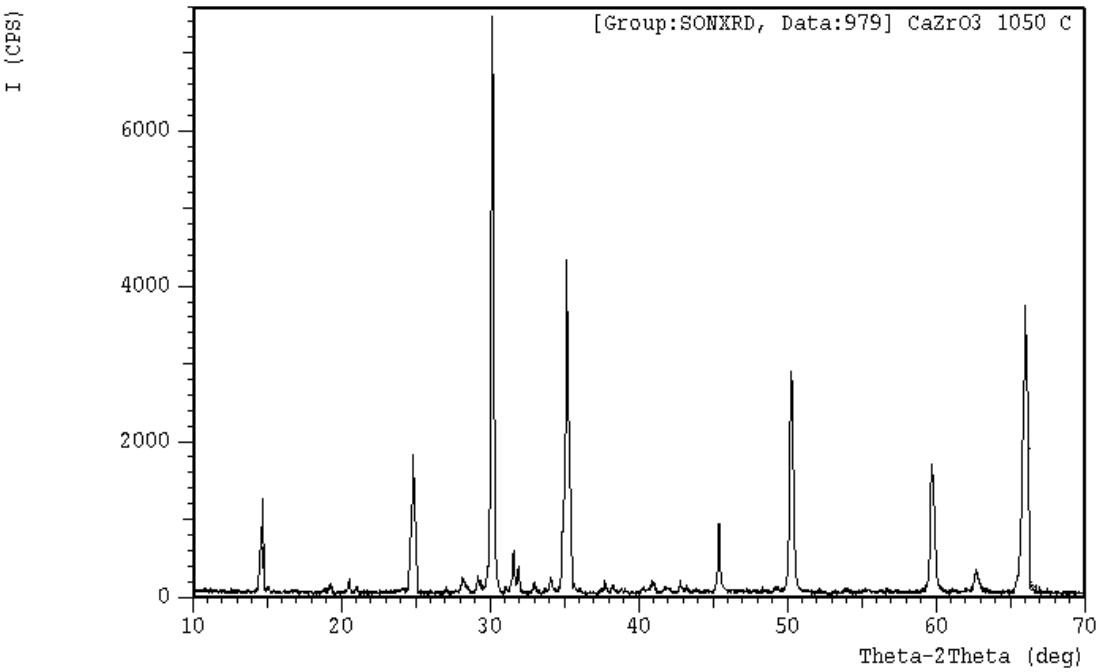

Figure 3. XRD pattern of the sample sintered at 1000°C.

At this temperature, the dominant phase was determined to be $Ca_6Zr_{19}O_{44}$. Although the changes observed in the peak intensities indicate a partial increase in the degree of crystallinity, the transformation (phase transformation) to the perovskite $CaZrO_3$ phase did not occur. This finding confirms that the activation energy required for the formation of $CaZrO_3$, as stated in the literature, cannot be achieved in this temperature range (1000-1050 °C).

4. Conclusions

In this study, the feasibility of producing Calcium Zirconate ($CaZrO_3$) ceramic powders, known for their high dielectric constant and thermal stability and critical for electronic distribution and high-temperature applications, was investigated using Sol-Gel technology, one of the low-temperature synthesis methods. Using Calcium Hydroxide ($Ca(OH)_2$) and Zircon Oxychloride ($ZrOCl_2$ $8H_2O$) as starting chemicals, a gel structure was successfully obtained, possessing the collected moisture and condensation fluids after completion. Following drying and grinding, the presented amorphous powders were subjected to calcination at two different temperatures: 1000°C and 1050°C to induce phase transformations.

X-Ray Diffraction (XRD) analyses revealed that the targeted perovskite $CaZrO_3$ phase was not fully formed in samples sintered at 1000°C and 1050°C, and instead, the system failed to achieve thermodynamic stability. The resulting diffraction patterns were corrected, and the presence of zirconium-rich intermediate phases (probably $Ca_6Zr_{19}O_{44}$) and unreacted oxides were detected. This demonstrates that, despite the high mixing homogeneity of the sol-gel method, the selected sintering temperatures were insufficient to provide the activation energy for calcium and zirconium ions to complete solid-state diffusion and form the stable 1:1 stoichiometric $CaZrO_3$ crystal lattice. Although a sintering temperature of 50°C caused variations in peak intensities, sufficient driving force was generated for complete phase filling.

Comparison of the various samples obtained with similar studies in the literature confirms that the critical threshold temperature for the synthesis of $CaZrO_3$ ceramics, which have a high melting point (~2340°C), is above 1050°C. The study concluded that starting powders can be successfully prepared using the starting materials and sol-gel method used, but that the heat treatment must be terminated at 1200°C or higher to obtain pure, single-phase calcium zirconate. Experimenting with higher sintering temperatures

for these controlled phase changes or adding mineralizers to the systems to enhance the reaction kinetics can allow for the achievement of lower-than-targeted properties. This study provides important data in the literature regarding the minimum energy budget required for $CaZrO_3$ synthesis and the maintenance of process regulatory requirements.

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Laboratory-Scale Synthesis of Hardystonite ($Ca_2ZnSi_2O_7$) via Sol-Gel Method and Phase Characterization

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ABSTRACT

This study investigates the synthesis of hardystonite ($Ca_2ZnSi_2O_7$), a calcium zinc silicate with tetragonal crystal structure, through the sol-gel method at laboratory scale. The process involved the preparation of three precursor solutions: calcium hydroxide [$Ca(OH)_2$], zinc nitrate [$Zn(NO_3)_2{\cdot}6H_2O$], and tetraethyl orthosilicate (TEOS), which were individually dissolved in deionized water or ethanol and homogenized using magnetic stirring. These solutions were then combined and mixed at 70 °C for 2 hours to initiate gelation.

The resulting gel was dried at ambient temperature and then further at 60 °C and 120 °C to remove residual moisture. The dried material was ground and pressed into rod-shaped samples using a hydraulic press at 200 MPa. Both the powder and the shaped bodies were sintered at 1100 °C and 1300 °C for 3 hours.

X-ray diffraction (XRD) analysis confirmed the formation of the hardystonite phase at both sintering temperatures, with better crystallinity observed in the sample sintered at 1100 °C. These results demonstrate that the sol-gel method is effective for synthesizing hardystonite powders under relatively low-temperature conditions, offering a promising route for ceramic production.

Keywords: Hardystonite, Calcium zinc silicate, Sol-gel synthesis, $Ca_2ZnSi_2O_7$, Ceramic materials.

1. Introduction

Rapid advances in technology over the last 20 years have led to increased properties expected from materials used in various fields [1]. New ceramics produced from compounds such as silicon carbide, silicon nitride, sialon, alumina, titanate, niobate, germanate, ferrite, and others are called advanced engineering ceramics [2]. The starting materials used in the production of advanced engineering ceramics are required to be submicron-sized, purely reactive, and sinterable at lower temperatures. Therefore, new production methods have been developed. Some of these include CVD (chemical vapor deposition), sol-gel, and polymer pyrolysis [3]. Alumina and alumina-based ceramic materials, which have a wide range of applications worldwide today, are among the most prominent advanced engineering ceramic materials due to their mechanical, thermal, optical, electrical, chemical, and nuclear properties. Ceramic materials often contain porosity, crystalline and glassy phases of varying compositions. The amount and distribution of these different structural components significantly influence the properties of ceramic materials [4].

Ceramics is defined as the art and science of making solid parts composed largely of inorganic, non-metallic materials. This includes pottery, porcelain, refractories, building materials, abrasives, enamel,

cement and glass, as well as non-metallic magnetic materials, piezoelectric materials and engineering ceramics developed in recent years [5].

High-tech ceramics stand out for their superior mechanical, thermal, and electrical properties, as well as functional properties such as biocompatibility. Hardistonite ($Ca_2ZnSi_2O_7$$), a type of ceramic, is an important mineral with a tetragonal crystal structure ($P42_1m$) in the calcium-zinc-silicate system (Figure 1). This naturally rare mineral has potential applications in bioceramic applications and dielectric material technology, particularly due to its zinc ions [6].

Figure 1. Appearance of hardistinite mineral on natural rock

Compared to traditional solid-state reactions, the Sol-Gel method offers advantages such as molecular mixing in multi-component systems, high purity, low processing temperature, and stoichiometry control. In this method, an inorganic network structure is formed by the hydrolysis of metal alkoxides and subsequent polycondensation reactions [7]. The aim of this study is to synthesize pure Hardistonite powder in the Ca-Zn-Si system using the sol-gel method, to determine the effect of sintering temperature on phase formation and to reveal the optimum production parameters.

2. Materials and Method

2.1. Raw Materials

The chemicals used in the experimental studies were selected with high purity: Calcium Source: $Ca(OH)_2$ (MA: 74 g/mol), Zinc Source: $Zn(NO_3)_26H_2O$ (MA: 297.47 g/mol, Purity: 98.5%), Silica Source: Tetraethylorthosilicate - TEOS, $C_8H_{20}O4Si$ (MA: 208.33 g/mol, Purity: >98%), Solvent and Catalyst: Purified water and Nitric Acid (HNO_3).

2.2. Stoichiometric Calculations and Solution Preparation

To obtain the targeted $Ca_2ZnSi_2O_7$ structure, the starting materials were calculated at a molar ratio of 2:1:2 (Ca:Zn:Si). Accordingly, 74 g $Ca(OH)_2$ (based on 1 mole), 148.73 g $Zn(NO_3)_26H_2O$ (0.5 mole), and 208.3 ml TEOS (1 mole) were used.

The solutions were prepared in three separate steps: Calcium Solution: Calcium hydroxide was homogenized by stirring in 250 ml of distilled water for 30 minutes on a magnetic stirrer. Zinc Solution: Zinc nitrate was stirred with 250 ml of distilled water in a separate container for 40 minutes. Silica Solution: Hydrolysis was initiated by mixing TEOS, water, and acid catalyst ($TEOS/H_2O/HNO_3$ = 1:8:0.16 mole ratio).

2.3. Gelation and Drying Process

The three prepared solutions were combined at 70°C and stirred for 2 hours on a magnetic stirrer. As the viscosity increased, the mixture was placed on a mechanical stirrer, and the process continued until gelation was complete.

The resulting wet gel was subjected to a three-stage drying regimen to prevent cracking and controlled solvent removal: 5 hours at room temperature (free water removal), 1 day at 60°C in an oven,2 days at 120°C in an oven.

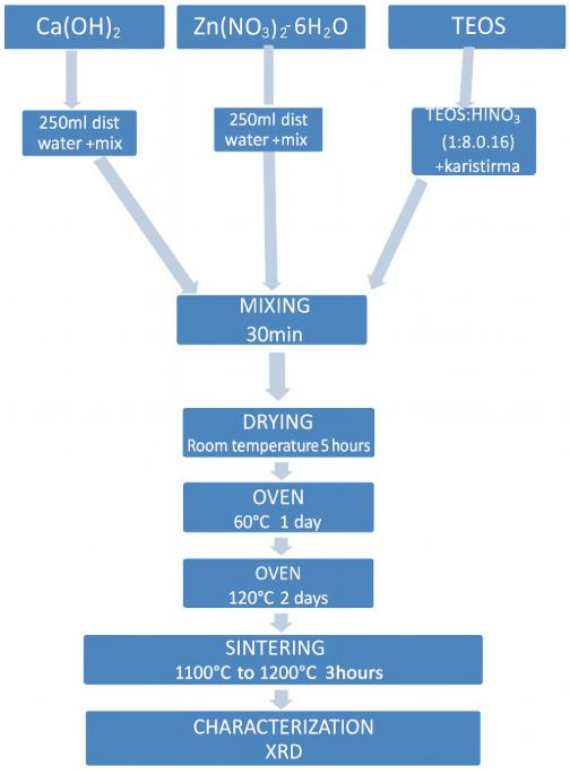

Figure 2. Flow chart of the experimental study

2.4. Shaping and Sintering

The dried gels were pounded in a porcelain mortar and ground to pass under a 100 micron (µm) sieve. The powders were shaped into rod and tablet forms using a hydraulic/isostatic press under 200 MPa pressure. The sintering process was carried out in a laboratory-type electric furnace at two different temperatures: Group A: 1100°C, 3 hours. Group B: 1300°C, 3 hours.

3. Results and Discussion

A Crystal phase analyses of the produced powders were carried out using Shimadzu XRD-6000 instrument (Cu-K α radiation, 1.544 Å).

3.1. Characterization of 1100°C Sintered Sample

The XRD pattern of the sample sintered at 1100°C for 3 hours is given in Figure 3. When the peaks obtained were compared with the Hardistonite ($Ca_2ZnSi_2O_7$) standard card (JCPDS No: 99-100-2595), a full match was observed.

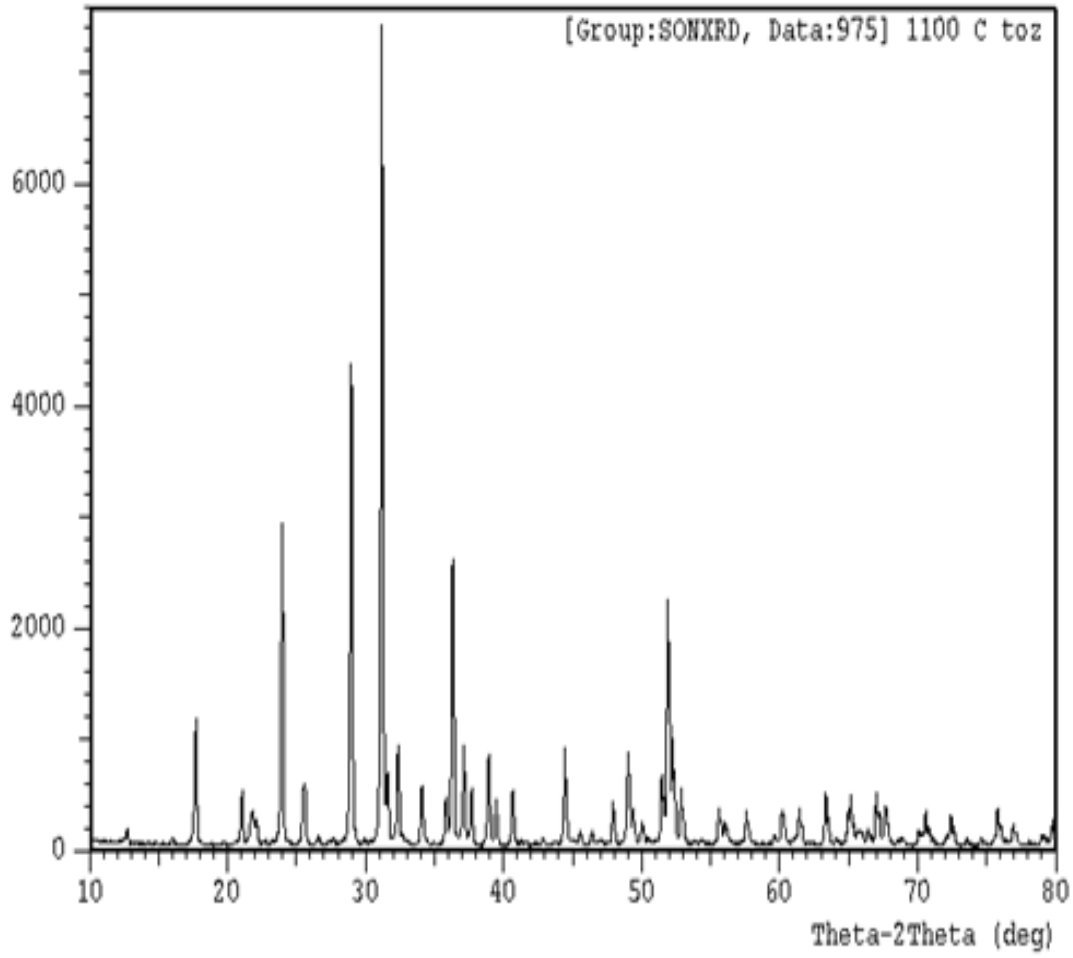

Figure 3. XRD pattern of the sample sintered at 1100°C

An examination of the graph reveals that the intense and sharp main peaks indicate good crystallization. No distinct secondary phase or impurity peaks were detected in the structure. This demonstrates that the 1100°C temperature provided sufficient activation energy for the transition from the amorphous to the crystalline hardistinite structure.

3.2. Characterization of 1300°C Sintered Sample

The XRD analysis of the sample obtained by increasing the temperature to 1300°C is presented in Figure 4.

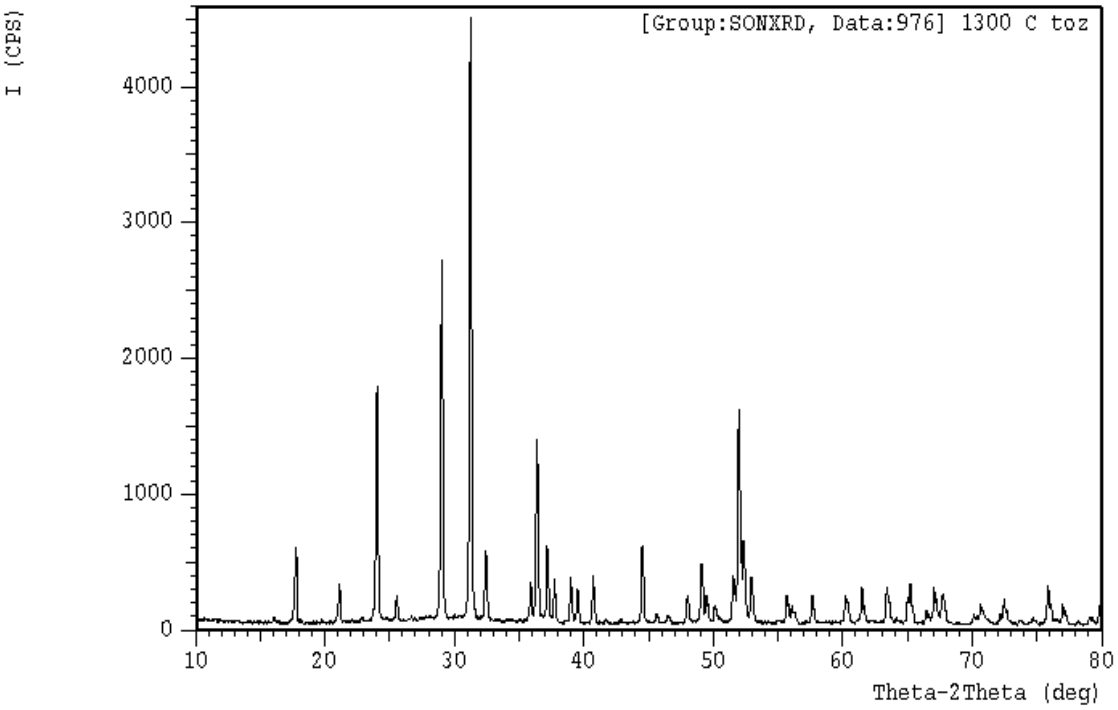

Figure 4. XRD pattern of the sample sintered at 1300°C

The hardistinite phase was preserved at this temperature. However, physical examinations observed cracks and deformations in rod-shaped samples sintered at 1300°C. This may be attributed to excessive grain growth or increased glassy phase formation as the material approaches its melting point (~1425°C). Changes in XRD peak intensities indicate temperature-dependent changes in crystal orientation or grain size.

4. Conclusions

The In this study, hardistinite ($Ca_2ZnSi_2O_7$) bioceramic powder was successfully synthesized via the sol-gel method using the starting materials $Ca(OH)_2$, $Zn(NO_3)_2$, and TEOS.

Optimum Temperature: XRD and physical analyses revealed that a sintering temperature of 1100°C provided more suitable and reliable results than 1300°C in terms of obtaining the pure hardistinite phase and preserving sample integrity.

Method Success: The sol-gel process was confirmed to be an effective method for producing multi-component silicate systems, enabling phase formation at low temperatures and maintaining stoichiometry.

Future Studies: Biocompatibility (SBF) and mechanical testing of the resulting powders will further clarify the material's potential in bone tissue engineering.section.

5. Acknowledge

Please collate all acknowledgements in a separate section at the end of the article, before the references.

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Book

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Synthesis and Characterization of Leucite Phase for Dental Porcelain Applications via Sol-Gel Method

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ABSTRACT

This study focuses on the synthesis of the leucite phase ($K_2O{\cdot}Al_2O_3{\cdot}4SiO_2$), a critical component in dental porcelain formulations, using the sol-gel method. Precursor materials including potassium carbonate (K_2CO_3), aluminum alkoxide, and tetraethyl orthosilicate (TEOS) were used to prepare three separate suspensions. These were mixed under controlled conditions and allowed to form a gel at room temperature. The gel was then dried at 105 °C and ground into a fine powder. Samples were shaped using a hydraulic press and sintered at 1120 °C for 30 minutes in a vacuum dental furnace. Structural and microstructural characterizations were performed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD analysis confirmed the formation of the leucite phase, while SEM images provided insight into grain morphology and surface texture. The results indicate that the sol-gel technique is effective in producing leucite-phase ceramics under controlled thermal conditions, offering a viable approach for developing dental porcelain materials with desirable crystallinity and stability.

Keywords: Leucite phase, Dental porcelain, Sol-gel synthesis, K_2CO_3, Aluminum alkoxide, TEOS, XRD.

1. Introduction

Porcelain was first used in dentistry in 1774 by Duchateau, a pharmacist in the Saint-Germen-Laye area. Duchateau needed a porcelain prosthesis. Seeing that porcelain was prone to shrinkage, Duchateau, working with Nikolas Du Bois de Chenani, a local dentist, succeeded in creating a usable prosthesis. In 1885, John Allen succeeded in creating the first porcelain tooth fired on platinum. Towards the end of the same century, various ceramists attempted to apply porcelain in various areas of dentistry [1].

Subsequent advances were made rapidly due to the development of porcelain powders and the use of pyrometers in firing kilns. Firing kilns were initially heated with bunsen burners, gas, and alcohol; therefore, only porcelains with lower melting points could be fired. Under these conditions, porcelain was prepared in gold matrices. The invention of electric furnaces, the ability to control the firing of porcelain with pyrometers, allowed the use of porcelain fired at higher temperatures. The porcelains produced in this way were more durable and transparent [2].

Dental porcelain is an indispensable material in modern dentistry due to its aesthetic properties, biocompatibility, and chemical stability in the oral environment. Feldspathic porcelain, in particular, has a high coefficient of thermal expansion thanks to the leucite (Leucite - $KAlSi_2O_6$) crystals dispersed within the glass matrix, enabling it to function seamlessly with metal substructures. Leucite crystals not only

ensure thermal compatibility but also increase the mechanical strength of the porcelain by preventing crack propagation [3].

Traditional dental porcelain production requires high-temperature frying and grinding (1200-1400°C). These processes are energy-intensive, and product homogeneity is difficult to control [4]. In contrast, the Sol-Gel method stands out with its advantages such as molecular-level mixing, high purity, low processing temperatures, and stoichiometry control [5].

The aim of this study is to synthesize leucite-based dental porcelain powder using the sol-gel technique in the $K_2OAl_2O_3SiO_2$ system, to investigate the sintering behavior in a vacuum environment and to determine the microstructural properties of the obtained product.

2. Materials and Method

2.1. Raw Materials and Recipe Design

The chemicals used in the experimental studies and the prepared recipe composition are detailed below. The targeted composition was selected to provide K_2O, Al_2O_3 and SiO_2, which are the main components of feldspathic porcelain: Potassium Source: Potassium Carbonate (K_2CO_3) – 13.8 g3, Aluminum Source: Aluminum Alkoxide – 40.85 g4, Silica Source: Tetraethylorthosilicate (TEOS) – 88.5 g5, Solvents: Purified Water (100 ml) and Ethyl Alcohol (Total 400 ml).

2.2. Sol-Gel Synthesis Steps

The experimental phase of the study began with the precise preparation of three different starting solutions to achieve the targeted stoichiometric composition. First, 13.8 grams of potassium source K_2CO_3 was dissolved in 100 ml of distilled water. Simultaneously, 40.85 grams of aluminum alkoxide were added to 200 ml of ethyl alcohol, and 88.5 grams of TEOS were added to another 200 ml of ethyl alcohol. These three suspensions were stirred in volumetric flasks using a magnetic stirrer for approximately 15 minutes to ensure homogenization.

Following the preparation of the individual solutions, all components were combined in a plastic container and mechanically stirred until complete dissolution was achieved. The resulting sol was transferred to a rectangular container to initiate the gelation process and left at room temperature for hydrolysis and polycondensation reactions to occur. After gelation, the wet gel was first allowed to rest at room temperature to remove the solvent phase and then dried in an oven at 120°C for one day.

The partially clumped gel mass obtained after drying was ground into a fine powder in a porcelain mortar to reduce particle size and increase sintering reactivity. Eight-gram samples of this powder were weighed and shaped into rectangular prisms using a hydraulic press under 40 bar pressure. These shaped green bodies were then ready for the sintering stage.

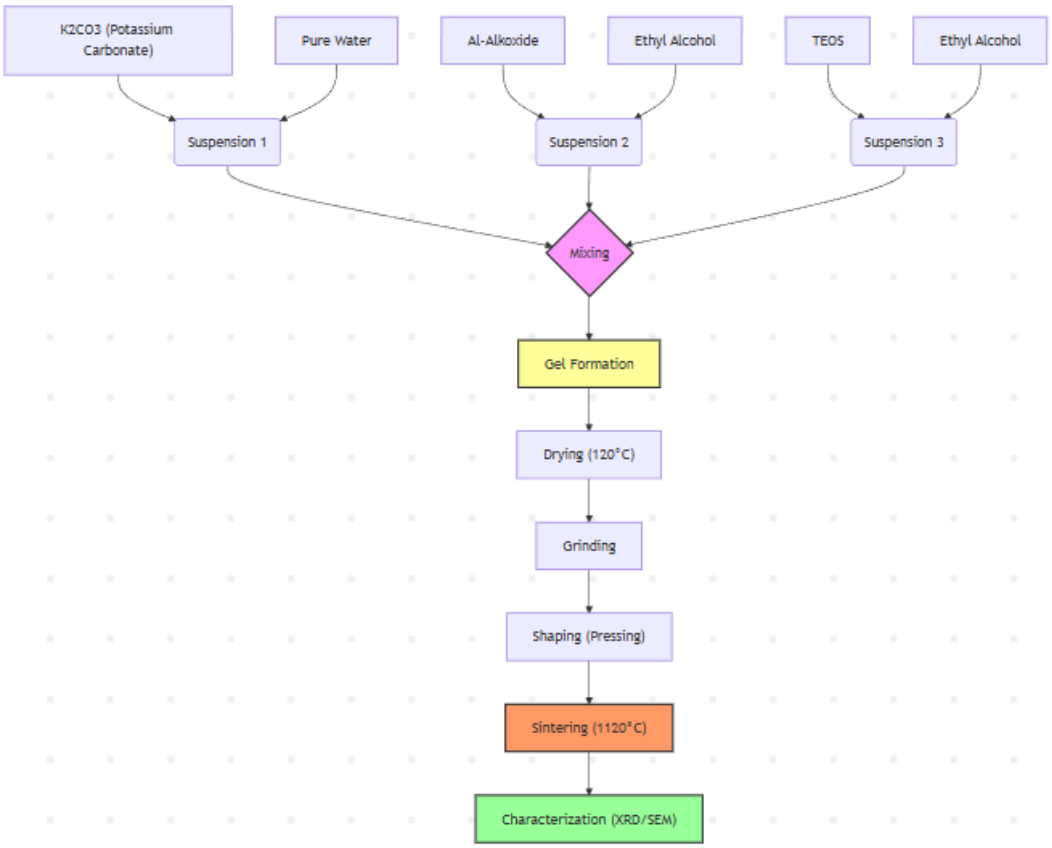

Figure 1. Flow chart of dental porcelain production using the Sol-Gel process

2.3. Shaping and Sintering

The resulting powders were pressed into rectangular prism-shaped samples (8 grams each) in a hydraulic press under 40 bar pressure without using a binder.

The sintering process was carried out in a VITA VACUMAT brand professional vacuum dental furnace. The samples were fired at 1120°C under vacuum for 30 minutes. This process is critical for reducing porosity and increasing the transparency of the porcelain.

3. Results and Discussion

3.1. Phase Analysis (XRD)

The crystal structure of the sample sintered at 1120°C was analyzed by X-Ray Diffraction (XRD). When the XRD pattern was examined (Figure 2), Leucite (Leucite - $KAlSi_2O_6$) was identified as the dominant phase in the structure.

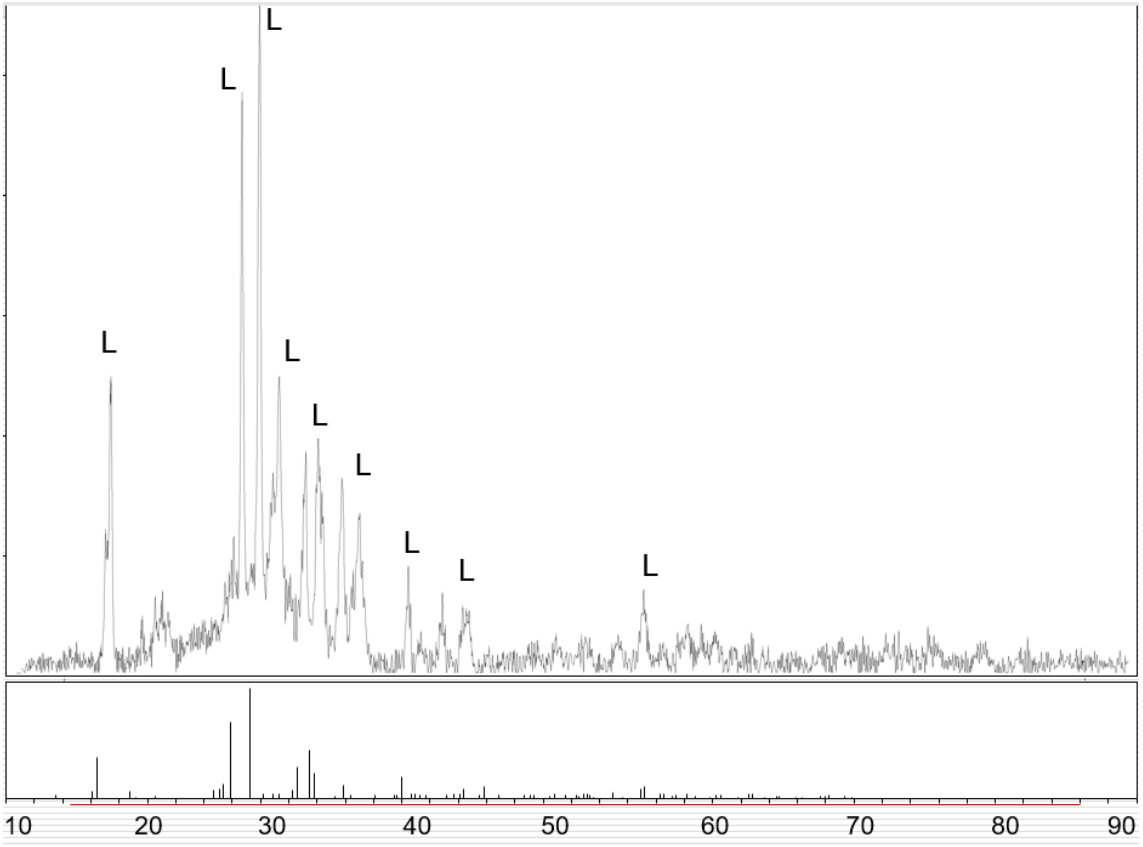

Figure 2. XRD pattern of the sample sintered at 1120°C

The location and intensity of the peaks in the graph are in full agreement with JCPDS card No. 00-038-1423. This demonstrates that the amorphous powders prepared by the sol-gel method successfully crystallized at 1120°C and transformed into the targeted tetragonal leucite phase. The presence of the leucite phase indicates that the material's coefficient of thermal expansion has increased to a level suitable for metal substrates.

3.2. Microstructural Analysis (SEM)

Scanning Electron Microscope (SEM) images taken from the fracture surfaces of the sintered samples provided information about the internal structure of the material.

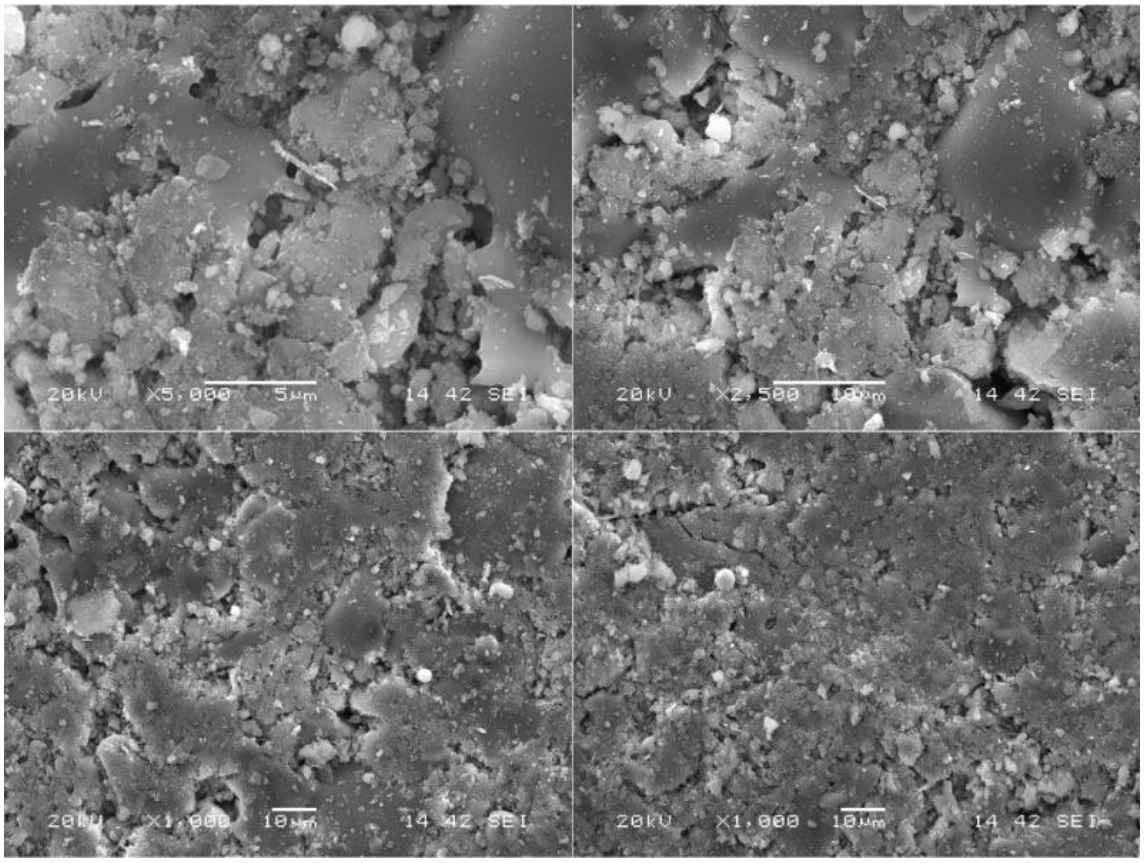

Figure 3. SEM micrograph of sintered dental porcelain

The images show crystal grains dispersed throughout the glass matrix, along with occasional pores (porosity). Despite vacuum sintering, the failure to achieve complete densification (disintegration) suggests that the sintering temperature or time should be optimized. Leucite crystals serve as reinforcing elements within the glass phase, strengthening the structure.

4. Conclusions

In this study, the sol-gel method was successfully applied as an alternative synthesis route for the production of leucite-based feldspathic dental porcelains that combine aesthetic and mechanical properties in dentistry. Using potassium carbonate (K_2CO_3), aluminum alkoxide, and tetraethylorthosilicate (TEOS) as starting materials, homogeneous and high-purity porcelain powders with the targeted stoichiometric composition were synthesized. Unlike the high-temperature and multi-stage processes required by traditional fritting methods, the sol-gel process allowed for molecular mixing at lower temperatures, demonstrating an advantageous process in terms of energy efficiency.

Characterization studies of the produced powders demonstrated that vacuum sintering at 1120°C provided sufficient thermal energy for the crystallization of the amorphous structure and the development of the targeted phases. X-Ray Diffraction (XRD) analyses confirmed the successful formation of tetragonal leucite ($KAlSi2O_6$) crystals, the primary reinforcing phase of dental porcelain, in the sintered

samples. The presence of the leucite phase is critical for ensuring compatibility of the material's coefficient of thermal expansion with metal substrates and increasing mechanical strength.

Sintering behavior and microstructural analyses (SEM), it was observed that heat treatment under vacuum was effective in reducing porosity, but partial cracking and fragmentation occurred in the samples. This suggests that the 40-bar pressure applied during the pressing phase may have been insufficient for particle packing or that volumetric changes during sintering were not fully controlled. It was concluded that improvements such as increasing the pressing pressure, incorporating suitable organic binders, or optimizing the sintering regime are necessary to fully ensure physical integrity.

In conclusion, this study has demonstrated the high potential of the sol-gel method in dental ceramic production. The method offers economic and technological advantages over traditional methods through the use of pure raw materials and low processing temperatures. It is anticipated that by improving the shaping parameters in future studies, these sol-gel-derived porcelains could be promising biomaterial candidates for clinical applications.

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Fabrication and Phase Analysis of PMMA-Modified Al_2O_3–SiO_2 Composite Ceramics via Sol-Gel Method

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ABSTRACT

This study presents the sol-gel-based synthesis and characterization of composite ceramic materials composed of alumina (Al_2O_3) and silica (SiO_2), modified with polymethyl methacrylate (PMMA) as an organic binder and porosity modifier. Two distinct precursor systems were prepared with varying silica contents to produce Al_2O_3–SiO_2 and Al_2O_3–$3SiO_2$ composites. Aluminum alkoxides and TEOS were used as primary precursors for Al_2O_3 and SiO_2, respectively, and PMMA was dissolved in acetone and incorporated into the mixed sols.

After gelation and drying at 105 °C, the materials were ground, uniaxially pressed into disc-shaped pellets, and sintered at 1500 °C. The crystalline phases were analyzed by X-ray diffraction (XRD), revealing the formation of mullite ($Al_6Si_2O_{13}$), sillimanite (Al_2SiO_5), and cristobalite (SiO_2) depending on the silica ratio in the formulation.

The results demonstrated that the sol-gel method enables the successful integration of PMMA into oxide-based ceramic matrices, promoting the formation of advanced phases suitable for high-temperature applications. The presence of different crystalline phases confirms the impact of SiO_2 content on phase evolution during sintering.

Keywords : PMMA, Composite ceramics, Sol-gel synthesis, Aluminum alkoxide, TEOS, XRD

1. Introduction

Alumina–silica ceramics are widely used in high-temperature applications owing to their thermal stability, chemical inertness, and mechanical durability, with mullite ($3Al_2O_3{\cdot}2SiO_2$) being especially valued for its low thermal expansion, high creep resistance, and excellent thermal-shock performance [1]. Achieving homogeneous mixing of Al_2O_3 and SiO_2 precursors is critical for obtaining controlled mullite formation and minimizing undesired secondary phases, a challenge well-documented in aluminosilicate processing studies [2].

The sol–gel method provides significant advantages over conventional solid-state processing by enabling molecular-level precursor mixing, lowering reaction temperatures, and promoting uniform structural development [3,4]. Furthermore, the incorporation of organic polymers into sol–gel systems has been shown to influence porosity, diffusion, and crystallization pathways, offering tunability in ceramic microstructure evolution [5]. Among polymer additives, polymethyl methacrylate (PMMA) is particularly suitable in ceramic processing due to its clean thermal degradation and ability to modify porosity through controlled burnout [6,7].

Although PMMA-assisted sol–gel systems have been used in oxide ceramics, their influence on phase evolution in alumina–silica compositions with varying silica content remains insufficiently explored, despite recent efforts demonstrating the potential of polymer-modified gels in tailoring mullite formation [8,9]. This study aims to clarify these effects by synthesizing Al_2O_3–SiO_2 and Al_2O_3–$3SiO_2$ composites via a

PMMA-modified sol–gel route and evaluating their crystalline phase development after high-temperature sintering.

2. Materials and Method

2.1. Materials

Aluminum alkoxide (aluminum isopropoxide) (AIP, ≥98%) and tetraethyl orthosilicate (TEOS, 98%) were used as aluminum and silicon precursors. PMMA powder (average Mw ≈ 120,000 g/mol) was employed as the polymeric modifier and pore-forming agent. Nitric acid (HNO_3) served as the catalyst for hydrolysis reactions, and ethanol (EtOH) was used as the solvent.

2.2. Precursor Preparation

Aluminum alkoxide (aluminum isopropoxide) served as the alumina precursor, while TEOS (tetraethyl orthosilicate) provided silica. The aim was to produce an Al_2O_3-SiO_2-based composite material by bonding the obtained Al_2O_3 and SiO_2 with the help of PMMA.

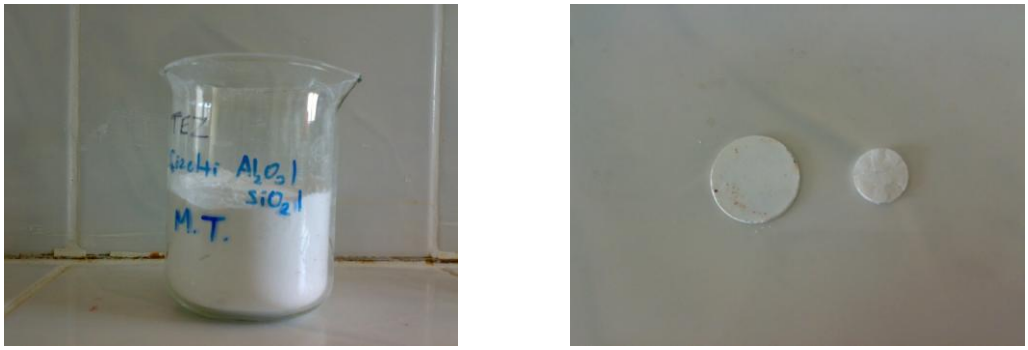
- Al_2O_3–SiO_2 (stoichiometric alumina–silica ratio)
- Al_2O_3–$3SiO_2$ (silica-rich composition)

2.3. Production of Samples

2.3.1. Preparation of Al_2O_3-SiO_2 Solution with PMMA Addition

To prepare the Al_2O_3 sol, 2 mol of Al-alkoxide was used, and a 0.5 mol/L concentration of Al-alkoxide was prepared in a 250 ml volume. Isopropyl alcohol was added to 51.0625 g of Al-alkoxide, and the solution was brought up to 250 mL. It was stirred on a magnetic stirrer for 1 hour. The pH was adjusted by adding a sufficient amount of acetic acid. To prepare the SiO_2 sol, 1 mol of TEOS was used, and a 0.5 mol/L concentration of TEOS was prepared in a 250 ml volume. Ethyl alcohol was added to 26.04125g TEOS, bringing the solution to 250 ml. It was stirred on a magnetic stirrer for 1 hour. The pH was adjusted by adding a sufficient amount of acetic acid

Acetone was added to 7.7g PMMA, bringing the solution to 250 ml. It was stirred on a magnetic stirrer for 1 hour. The prepared Al_2O_3 and SiO_2 solutions, along with PMMA, were combined to produce an Al_2O_3-SiO_2-PMMA-based composite material. The prepared mixture was remixed in a 500 ml beaker with a magnetic stirrer and allowed to gel. The resulting gel was placed on a tray and left to dry for three days to form a powder. The resulting powder was then dried in an oven at 105 °C for 3 days. The prepared powder was ground. These powders were pressed into coins using a hydraulic press. These pressed samples were dried for 1 day. They were then sintered at 1500 °C and ground to a particle size of below 90 µm. XRD analysis was performed on this sintered material (Figure 1).



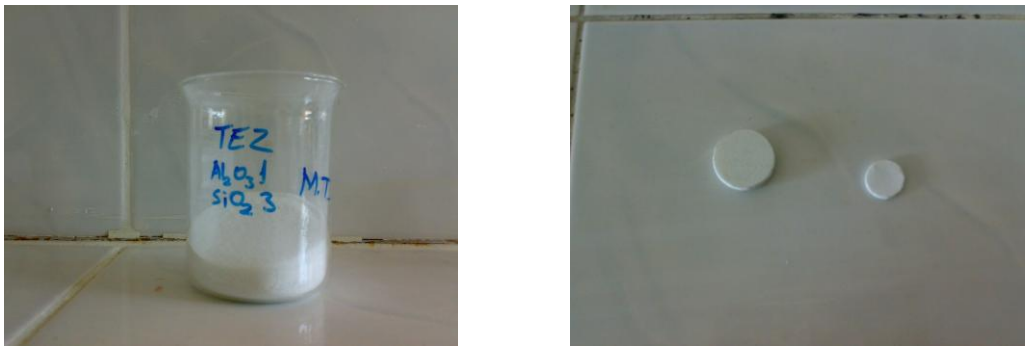
(a) (b)

Figure 1. a) Solution of Al_2O_3-SiO_2, b) Samples obtained before and after sintering (1500 °C)

2.3.2. Preparation of Al_2O_3-$3SiO_2$ Solution with PMMA Addition

To prepare the Al_2O_3 sol, 2 mol of Al-alkoxide was used, and a 0.5 mol/L concentration of Al-alkoxide was prepared in a 250 ml volume. Isopropyl alcohol was added to 51.0625 g of Al-Sec-Butoxide, and the solution was brought up to 250 mL. It was stirred on a magnetic stirrer for 1 hour. The pH was adjusted by adding a sufficient amount of acetic acid. To prepare the SiO_2 sol, 3 mol of TEOS was used, and a 0.5 mol/L concentration of TEOS was prepared in a 250 ml volume. Ethyl alcohol was added to 78.12375 g TEOS, bringing the solution to 250 ml. It was stirred on a magnetic stirrer for 1 hour. The pH was adjusted by adding a sufficient amount of acetic acid

The prepared Al_2O_3 and SiO_2 solutions, along with PMMA, were combined to produce an Al_2O_3-SiO_2-PMMA-based composite material. The prepared mixture was remixed in a 500 ml beaker with a magnetic stirrer and allowed to gel. The resulting gel was placed on a tray and left to dry for three days to form a powder. The resulting powder was then dried in an oven at 105°C for 3 days. The prepared powder was ground. These powders were pressed into coins using a hydraulic press. These pressed samples were dried for 1 day. They were then sintered at 1500 °C and ground to a particle size of below 90 µm. XRD analysis was performed on this sintered material (Figure 2).



(a) (b)

Figure 2. a) Solution of Al_2O_3-$3SiO_2$, b) Samples obtained before and after sintering (1500 °C)

3. Results and Discussion

3.1. XRD Analysis

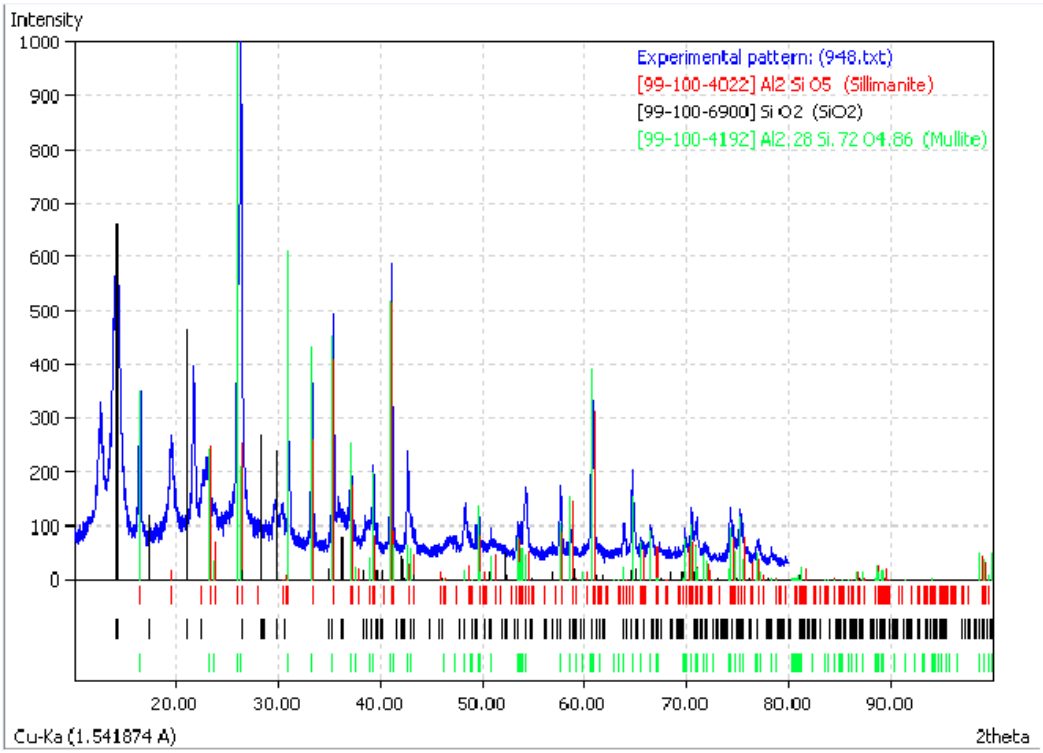


Figure 3. XRD analysis of Al_2O_3-SiO_2 samples sintered at 1500°C

The comparative XRD analysis of the Al_2O_3–SiO_2 and Al_2O_3–$3SiO_2$ composites is broadly consistent with previous reports on alumina–silica ceramics produced via sol–gel and related routes. Sol–gel derived systems with Al_2O_3/SiO_2 ratios close to the stoichiometric 3:2 mullite composition typically yield mullite as the dominant or even single crystalline phase after sintering in the range 1400–1600 °C, with only minor residual alumina or silica phases, reflecting efficient interdiffusion and reaction between the two oxides [10]. This trend is in good agreement with the present Al_2O_3–SiO_2 composition, where mullite peaks dominate the diffraction pattern and secondary phases are only weakly developed, indicating that the PMMA-modified sol–gel route still allows sufficient homogeneity for advanced mullitization at 1500 °C.

In contrast, several studies have shown that shifting the composition towards silica-rich regimes leads to the stabilization of SiO_2-rich crystalline or glassy phases and a reduction in mullite content, especially when the Al_2O_3/SiO_2 ratio departs significantly from the mullite window [11].The predominance of cristobalite and the reduced relative intensity of mullite peaks observed in the Al_2O_3–$3SiO_2$ composite match this behaviour, confirming that excess silica tends to remain as cristobalite or SiO_2-rich domains rather than fully reacting into mullite at 1500 °C. Similar composition-dependent phase assemblages, where silica-rich formulations retain cristobalite while only partially transforming to mullite, have been reported in both sol–gel derived gels and compositions based on natural aluminosilicate or sillimanite sources [12,13]. The detection of sillimanite in the silica-rich sample is also compatible with the aluminosilicate phase fields described for Al_2O_3–SiO_2 systems, where intermediate 1:1 aluminosilicate structures can transiently form or persist under non-stoichiometric or kinetically constrained conditions [14]. Overall, the present results reinforce the view that silica content is a critical parameter governing the phase evolution pathway in alumina–silica ceramics: compositions near the mullite stoichiometry favour extensive mullitization, whereas silica-rich formulations promote the coexistence of mullite with

cristobalite and other aluminosilicate secondary phases, even when processed via a polymer-modified sol–gel route.

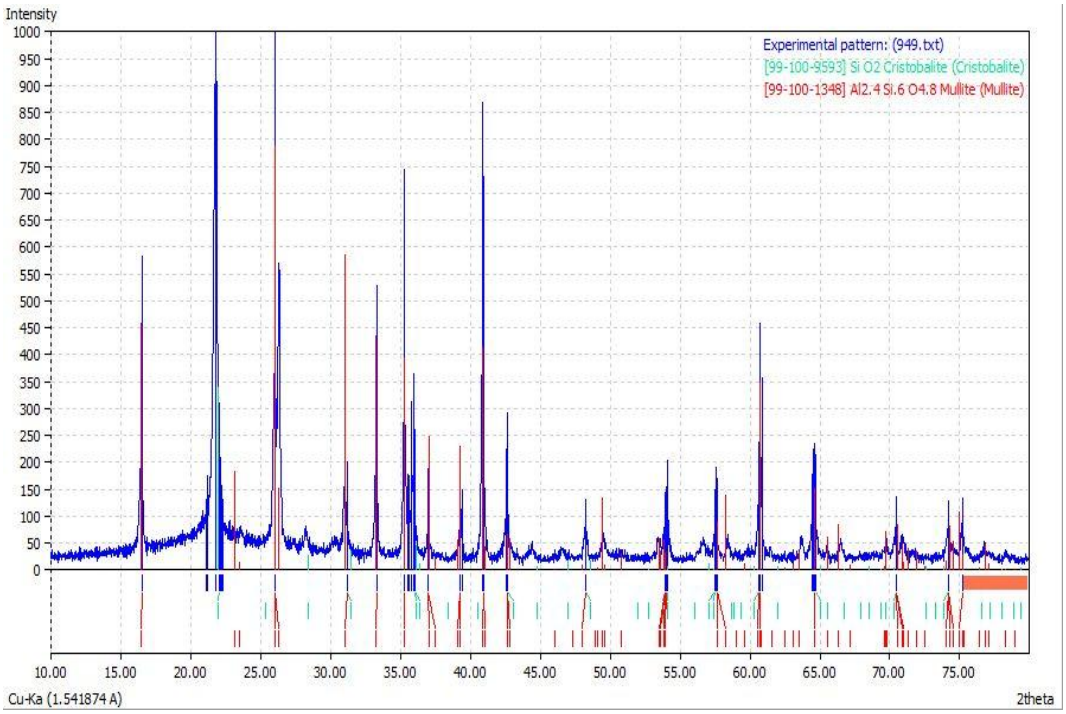


Figure 4. XRD analysis of Al_2O_3-$3SiO_2$ samples sintered at 1500°C

The XRD pattern of the Al_2O_3–$3SiO_2$ composite sintered at 1500 °C (Figure 4) exhibited strong cristobalite peaks, confirming the dominant presence of SiO_2-rich phases due to the silica-excess formulation. Mullite reflections were also detected, although with significantly lower intensities compared to cristobalite, indicating partial but incomplete reaction of alumina and silica during sintering. The high SiO_2 content suppressed full mullite conversion and promoted cristobalite stabilization. These findings demonstrate that the phase evolution in silica-rich aluminosilicates is strongly controlled by the precursor stoichiometry, even when sol–gel processing and PMMA-induced porosity enhance diffusion and reactivity [15,16].

PMMA-assisted sol–gel processing provided, homogeneous precursor mixing, Improved diffusion pathways due to PMMA burnout, Favorable conditions for mullite nucleation, despite these benefits, the high silica content prevented complete mullite formation, causing cristobalite to dominate the final phase composition.

4. Conclusions

The main conclusions of the study may be presented in:

PMMA-modified alumina–silica composites were successfully synthesized via a sol–gel method and sintered at 1500 °C. The study demonstrated that PMMA effectively integrates into the sol–gel matrix, enhances homogeneity, and promotes improved diffusion during sintering through controlled pore generation.

XRD results confirmed that:

- **Stoichiometric Al_2O_3–SiO_2** systems predominantly formed mullite,
- **Silica-rich Al_2O_3–$3SiO_2$** systems produced mullite together with sillimanite and cristobalite.

These outcomes highlight the strong influence of silica content on phase evolution and underscore the effectiveness of PMMA-assisted sol–gel processing for producing advanced, thermally stable ceramic materials suitable for high-temperature engineering applications.

5. Acknowledge

Please collate all acknowledgements in a separate section at the end of the article, before the references.

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Investigation of the Effect of Y_2O_3–Al_2O_3 Additions on the Production of Boron Carbide by Spark Plasma Sintering

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ÖZET

Bor karbür, üstün fiziksel ve kimyasal özellikleriyle bilinmektedir; ancak yüksek erime noktası, güçlü kovalent bağ yapısı ve toz parçacıkları üzerinde bulunan ince oksit tabakası nedeniyle yoğunlaştırılması oldukça zordur. Bu zorlukların üstesinden gelmek amacıyla, sinterleme sıcaklığını düşürmek ve kırılma tokluğunu artırmak için karbon, metal oksitler ve saf metaller gibi katkı maddeleri kullanılmaktadır. Bu katkı maddelerinin homojen bir şekilde dağılması son derece önemlidir; çünkü aşırı veya dengesiz katkı dağılımı, son malzemenin mekanik özelliklerini olumsuz etkileyebilir. Bu çalışmada, bor karbüre alumina ve itriya katkılarının yüksek homojenlikte dağılımını sağlamak amacıyla çöktürme yöntemi kullanılmıştır. Karşılaştırma amacıyla, toz karışımları geleneksel bilyalı öğütme yöntemiyle de hazırlanmıştır. Tüm karışımlar, 1750°C ile 1850°C arasındaki sıcaklıklarda, sabit argon atmosferi altında Kıvılcım Plazma Sinterleme (SPS) yöntemi ile sinterlenmiştir. Yapılan yoğunluk ölçümleri ve mikroyapı analizleri sonucunda, çöktürme yöntemiyle hazırlanan numunelerin, bilyalı öğütme yöntemiyle hazırlananlara göre daha yüksek yoğunluk ve sertlik değerlerine sahip olduğu belirlenmiştir. Bu durum, çöktürme yönteminin bor karbür kompozitlerinin sinterleme davranışı ve mekanik performansını geliştirmede etkili olduğunu göstermektedir.

Anahtar Kelimeler : Sinterleme, Toz Hazırlama, Bor Karbür

Investigation of the Effect of Y_2O_3–Al_2O_3 Additions on the Production of Boron Carbide by Spark Plasma Sintering

ABSTRACT

Boron carbide is known for its exceptional physical and chemical properties; however, its densification remains a significant challenge due to its high melting point, strong covalent bonding, and the presence of a thin oxide film on powder particles. To overcome these issues, additives such as carbon, metal oxides, and pure metals are commonly introduced to lower the sintering temperature and improve fracture toughness. Uniform dispersion of these additives is essential, as excessive or uneven distribution can degrade the mechanical properties of the final material. This study investigates the use of a precipitation method to achieve a highly homogeneous distribution of alumina and yttria additives in boron carbide. For comparison, powder mixtures were also prepared using conventional ball milling. All mixtures were sintered via Spark Plasma Sintering (SPS) at temperatures ranging from 1750°C to 1850°C under a constant argon atmosphere. The precipitation-based samples demonstrated superior densification and higher hardness values compared to their ball-milled counterparts, indicating the effectiveness of the precipitation technique in enhancing the sintering behavior and mechanical performance of boron carbide composites.

Keywords: Sintering, Powder Preparation, Boron Carbide

1. Introduction

Boron carbide (B4C) ranks among the hardest engineering ceramics, surpassed only by diamond and cubic boron nitride, and is therefore highly valued in applications requiring extreme hardness-to-weight ratios. In addition to its hardness, B4C possesses low density (~2.52 g/cm³), high elastic modulus, strong chemical inertness, and excellent neutron absorption capability, making it well-suited for structural armor, nuclear shielding, and abrasive machining tools. [1–5]

Yet, a major barrier to the widespread industrial application of B4C is its notoriously poor sintering behavior. The inherently strong covalent bonding within the B–C lattice limits bulk diffusion, requiring extremely high temperatures for densification. The existence of a naturally formed B_2O_3 layer on powder surfaces further restricts grain contact and inhibits diffusion-driven neck growth. Even at sintering temperatures approaching 2300–2400°C, conventional pressureless sintering often achieves insufficient densification and may result in exaggerated grain coarsening that deteriorates mechanical performance.

To overcome these challenges, researchers have introduced additives capable of modifying sintering kinetics and promoting enhanced diffusion. Carbon-based additives can help reduce oxide impurities, while metal oxides such as Y2O3 and Al2O3 may form transient liquid phases or intergranular phases, which enhance mass transport and reduce sintering temperature. Rare-earth oxides, including yttria, have been particularly effective in improving fracture toughness through grain-boundary engineering. [6–10]

However, the benefits of additive incorporation strongly depend on their spatial distribution and particle-scale integration. Several studies have shown that conventional mechanical mixing cannot guarantee homogeneity, often resulting in localized additive aggregation that produces intergranular defects and inconsistent grain bonding. An alternative approach is chemical precipitation onto powder surfaces, which enables molecular-scale coating and significantly improves microstructural uniformity. [11–12]

The present study explores this precipitation-based incorporation of Al2O3 and Y2O3 precursors onto B4C powders and compares its effectiveness against traditional ball milling. By examining densification behavior, microstructure, and hardness, we aim to elucidate the direct relationship between additive uniformity and sintering performance in B4C ceramics.

2. Materials and Method

Commercial B4C powders were employed as the base material. Aluminum nitrate nanohydrate and yttrium nitrate hexahydrate served as precursor salts for precipitation, with alumina (Al_2O_3) and yttria (Y_2O_3) selected as sintering additives due to their ability to enhance grain boundary diffusion, reduce surface oxide contamination, and suppress abnormal grain growth.

In the precipitation route, aqueous solutions of Al and Y precursors were deposited onto B_4C powders by adjusting the pH with ammonia solution. The resulting precipitates were filtered, washed with alcohol to remove residual impurities, and calcined under controlled atmospheres (air and argon) to generate oxide coatings on B_4C particles. For comparison, counterpart samples were prepared by conventional ball milling, where B_4C, $Al2O3$, and Y_2O_3 powders were mixed in ethanol, dried, and sieved to achieve uniform particle size distribution.

All powder mixtures were consolidated via Spark Plasma Sintering (SPS) at 1750–1850 °C with a 5-minute dwell under argon atmosphere. A uniaxial pressure was applied during consolidation, and densification kinetics were tracked through SPS displacement curves. Scanning electron microscopy (SEM) with energy-dispersive spectroscopy (EDS) was used to examine grain morphology, additive dispersion, and porosity. Relative densities were determined using Archimedes' method.

3. Results and Discussion

The precipitation process proved effective in modifying the surface chemistry of the B4C powders. The choice of precipitation pH was critical: aluminum nitrate begins precipitating above pH 5, while yttrium nitrate requires a pH exceeding 8. Therefore, a final pH of 9.5 ensured full precipitation of both species, leading to consistent oxide deposition on particle surfaces.
An important observation was the role of calcination atmosphere. Calcination in air resulted in additional oxide formation and larger agglomerates, whereas treatment under argon suppressed unwanted reactions and yielded finer, more uniformly distributed precipitates. This clearly demonstrates that reducing oxygen availability during calcination helps preserve nanoscale dispersion and maintains higher additive uniformity.

SEM micrographs revealed that the precipitation method produced a conformal oxide coating on B4C grains, facilitating intimate additive contact along grain boundaries. In contrast, ball-milled powders exhibited significant additive clustering, non-uniform surface coverage, and the presence of irregularly shaped agglomerates. This microstructural heterogeneity in the ball-milled powders translated into inferior sintering and mechanical outcomes.

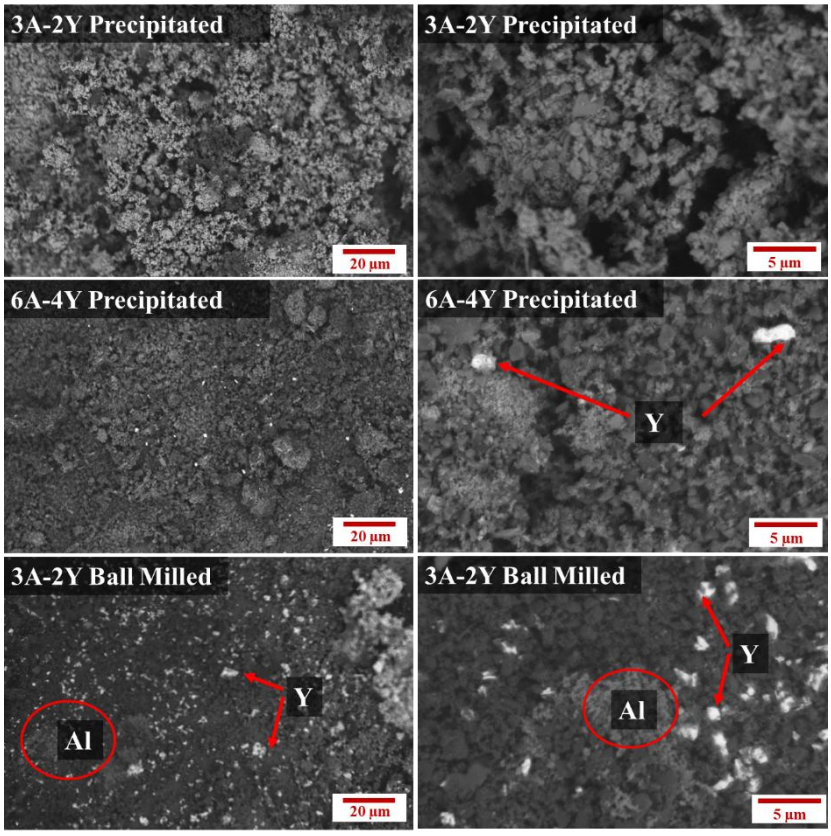

Figure 1. Precipitation process schematic and SEM image of B4C powders with uniformly distributed Al2O3 and Y2O3 after precipitation. [12]

Precipitation-assisted samples consistently achieved higher relative densities than their ball-milled counterparts. At 1850 °C, precipitated specimens reached densities exceeding 98% of the theoretical value, while ball-milled samples remained less dense and contained noticeable porosity. Table 1 summarizes the density values of samples sintered at 1750 and 1850 °C. Additive-containing ball-milled samples showed improved densification compared to pure B4C, but precipitation-prepared specimens achieved the highest densities—approximately 6–7% higher than pure B4C and 3–4% higher than ball-milled ones. No significant differences were found between the 3A–2Y and 6A–4Y compositions.

Table 1. Sintering studies and density results

Sample	Density	Temperature
Pure Boron Carbide	88%	1750°C 5 Min
%3A-%2Y Prec	94%	
%6A-%4Y Prec	94%	
%3A-%2Y Ball Mill	90%	
%6A-%4Y Ball Mill	90%	
Pure Boron Carbide	94%	1850°C 5 Min
%3A-%2Y Prec	99%	
%6A-%4Y Prec	99%	
%3A-%2Y Ball Mill	96%	
%6A-%4Y Ball Mill	96%	

Figure 2 presents SEM micrographs of specimens sintered at 1850 °C for 5 minutes. Pure ball-milled B4C exhibited limited densification, with weak neck formation and a lack of pore closure, characteristic of the intermediate sintering stage. In contrast, the precipitated sample showed particle coalescence and partial pore closure, indicative of advanced sintering progression and consistent with its higher density. Overall, precipitation-prepared samples exhibited fine-grained and homogeneous microstructures with additives uniformly distributed along grain boundaries, whereas ball-milled samples contained residual porosity and localized additive agglomerates.

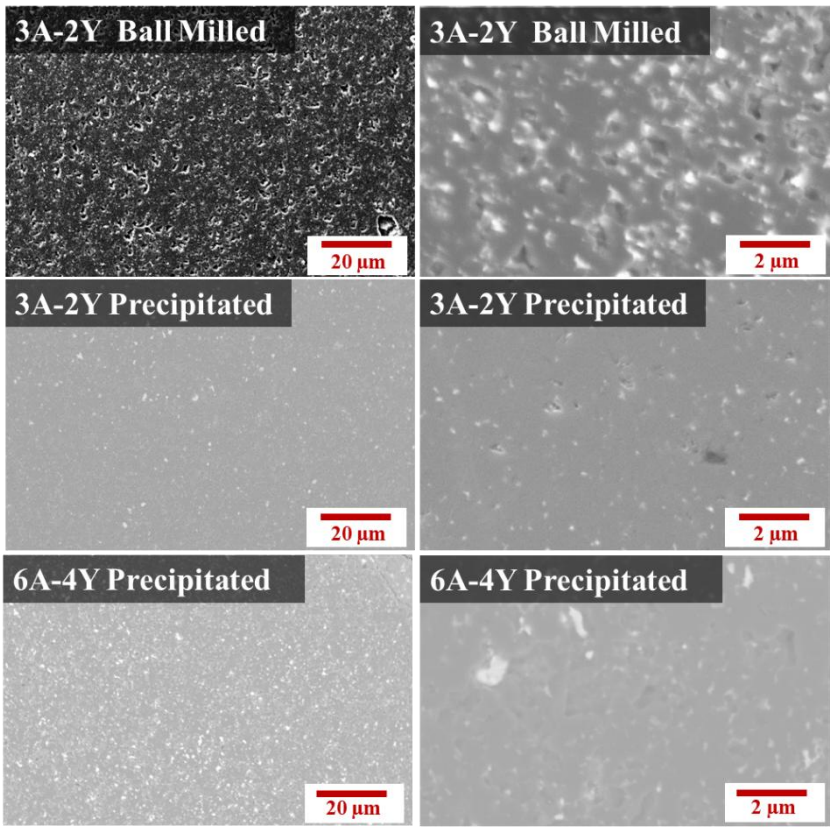

Figure 2. SEM images of ball milled and precipitated B_4C at 1850°C for 5 min

4. Conclusions

This study establishes that precipitation-mediated additive incorporation is a highly effective method for improving the microstructural quality and densification behavior of B4C ceramics. The main conclusions are:

- The precipitation method ensures nanoscale, homogeneous distribution of Al2O3 and Y2O3 on B4C powder surfaces, enabling enhanced mass transport during sintering.
- The processing atmosphere during calcination plays a decisive role in microstructural evolution, with argon proving superior to air in retaining fine dispersion.
- Compared to ball milling, precipitation enhances sintering kinetics, resulting in significantly higher densities and hardness values.
- The improved microstructural uniformity reduces porosity, suppresses abnormal grain growth, and promotes microstructural stability.
- Overall, precipitation processing offers a promising and scalable pathway for producing high-density, high-performance B4C ceramics suitable for demanding structural and protective applications.

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Hemostatic Performance of PHEMA Cryogels: A TEG-Based Evaluation of Blood Interaction

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ÖZET

Biyomalzemelerin kan uyumluluğunu değerlendirmek için birçok test yöntemi bulunmaktadır, ancak bu testler koagülasyon sisteminin farklı bölümleri üzerindeki etkileriyle ilgilidir. Tromboelastografi, kanın elastikiyetini pıhtılaşmanın başlangıcından fibrinolizin sonuna kadar kantitatif olarak ölçmekte ve yalnızca koagülasyon kaskadı başlangıcına odaklanan standart laboratuvar testlerine kıyasla ek bilgiler sağlamaktadır. Çalışmamız kapsamında PHEMA plaka kriyojeller üretilmiş ve insan tam kanı ile etkileşimleri tromboelastogram yöntemi ile değerlendirilmiştir. Elde edilen sonuçlara göre kriyojel malzemeleri reaksiyon süresini ve pıhtılaşma süresini sırasıyla %18,48 ve %30,21 oranında azaltmıştır. Alfa açısı, maksimum genlik ve G değeri de %34'lere varan oranda artmıştır. Tromboelastogram sonuçlarına göre kriyojel ile temas halindeki kanın pıhtılaşma eğilimi artmıştır. Bu nedenle üretilen PHEMA kriyojeller hemostatik ajanlar olarak ümit vericidir.

Anahtar Kelimeler : Biyomalzeme, Kanama durdurucu, Kriyojel, Poli (2-hidroksietil-metakrilat) Tromboelastografi.

ABSTRACT

There are many test methods to assess the hemocompatibility of biomaterials, but these tests relate to their effects on different parts of the coagulation system. Thromboelastography quantitatively measures the elasticity of blood from the beginning of coagulation to the end of fibrinolysis and provides additional information compared to standard laboratory tests that focus only on the beginning of the coagulation cascade. In our study, PHEMA-based plate cryogels were produced, and their interaction with human whole blood was evaluated by the thromboelastogram method. According to the results, cryogel materials decreased the reaction time and coagulation time by 18.48% and 30.21%, respectively. Alpha angle, maximum amplitude, and G value also increased by up to 34%. According to the thromboelastogram results, the coagulation tendency of the blood in contact with the cryogel was increased. Therefore, the produced PHEMA cryogels are promising as hemostatic agents.

Keywords: Biomaterial, Cryogel, Hemostatic agent, Polyhydroxyethyl methacrylate, Thromboelastography.

1. Introduction

Biomaterials are natural or synthetic materials that are used to perform or support the functions of living tissues in the human body, and that are in constant or intermittent contact with body fluids (e.g., blood) (Bhat & Kumar, 2013; Chong et al., 2023). Polymeric biomaterials, in particular, are preferred thanks to their ability to produce in various forms such as fibers, gels, films, and sponges (Cheng et al., 2018; Chong et al., 2023; Rasouli et al., 2019; Henderson et al., 2013). Cryogels are gel matrices, consisting of interconnected pores ranging from 10 to 200 µm, prepared with partially frozen monomer or polymer solutions (Plieva et al., 2011; Jespersen, 2014; Nayak et al., 2018; Lozinsky, 2003). The interaction of biomaterials with blood determines their intended functions in vivo. For most applications, blood compatibility (i.e., no effect on blood clotting) is required; however, for some applications, such as bleeding control in trauma and surgical injuries, promotion of blood clotting is desired (Weber et al., 2023). Therefore, understanding and controlling biomaterial-blood interactions for different applications is critical.

There are many routine test methods to assess the hemocompatibility of biomaterials, such as prothrombin time (PT), thrombin clotting time (CT), and partial thromboplastin time (PTT), but these tests are related to their effects on different parts of the coagulation system. A thromboelastogram (TEG) is a test method that quantitatively measures blood elasticity from the onset of clotting until fibrinolysis. This method differs from routine laboratory tests, which focus solely on the onset of the clotting cascade, and provides additional information. Furthermore, the test can provide information about the all coagulation system using a small amount of blood (360 µL) and in as little as 30 minutes (Peng, 2010; Vig et al., 2001; Donahue & Otto, 2005; Salooja & Perry, 2001; Luddington, 2005; Greaves, 2004).

The TEG method is widely used during surgery and in the clinic (Peng, 2010). However, there are limited studies on its use to evaluate the hemostatic properties of biomaterials. For example, Osman et al. (2019) investigated the hemostatic performance of nanoparticle-embedded poly(acrylamide-methyl methacrylate) cryogels using the TEG method.

This study aimed to demonstrate the hemostatic performance of PHEMA cryogels and to further develop TEG for biomaterials research. For this purpose, PHEMA-based cryogels were produced, and their interaction with human whole blood was evaluated using the TEG method. The results showed that the coagulation tendency of blood in contact with the produced cryogels increased at the end of 30 minutes.

2. Materials and Method

2.1. Materials

2-hydroxyethyl methacrylate (HEMA) monomer was purchased from Fluka A.G. (Buchs, Switzerland). N, N, N', N'-tetramethylethylenediamine (TEMED) and N, N'-methylenebis(acrylamide) (MBAAm) were provided by Merck (Darmstadt, Germany). Ammonium persulfate (APS) was obtained from Sigma-Aldrich (St. Louis, USA). Distilled water was supplied by Tekkim (Bursa, Turkey). All reagents were used as received, without further purification.

2.2. Preparation of the Cryogels

The cryogel production was performed according to the methodology established in our previous study (Kanmaz et al., 2024), with minor adaptations as required for the present work. A concise overview of the procedure is provided. The mold consisting of two glass plates to be used in production was prepared by leaving a 2 mm gap between the glasses. For the cryogelation solution, MBAAm was dissolved in distilled

water, and 1.3 mL of HEMA monomer was added to the solution. The mixture was placed in an ice bath, and 0.02 g of APS was added. After adding TEMED, the prepared cryogel mixture was poured between glass plates. The mixture was polymerized at −18 °C for 24 hours. After the time period was completed, the cryogels were brought to room temperature. The produced cryogels were washed with water to remove unreacted monomers. The produced gel was cut to 6 mm in diameter so that it could be used in TEG measurements. The final product is shown in Fig. 1.

Figure 1. Produced final PHEMA cryogel

2.3. Blood collection from volunteers

The determination of the effectiveness of the produced cryogels on bleeding was carried out by the Bursa Uludağ University Faculty of Medicine Clinical Research Ethics Committee with the decision numbered 2023-6/14 dated 2 March 2023.

Volunteers who will donate blood were selected from healthy individuals aged between 20 and 55, who were non-smokers, had not consumed alcohol in the last ten days, had not taken any medication in the last 10 days, and had no acute infection/chronic disease, or problems related to donating blood.

Blood samples were collected from the antecubital vein after at least 8 hours of fasting, using a 21-gauge needle and gentle venous pressure applied to the upper arm. Three tubes (approximately 24 ml) of blood were collected from each volunteer, and all experiments were completed within 3 hours of collection.

Vacutainer tubes containing sodium citrate buffer were used for blood collection. The tubes were prepared by adding 0.8 ml of 0.106 M sodium citrate solution. Following blood collection, anticoagulated whole blood samples with a citrate/blood ratio of 1:9 were obtained (Fig. 2). Three tubes of blood samples collected from the volunteers were combined into a single tube to homogenize the sample.

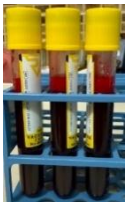

Figure 2. Anticoagulated whole blood samples collected from volunteers

2.4. Characterization

2.4.1. SEM Analyses

The morphologies of the produced cryogel were examined using Carl Zeiss AG-EVO 40 XVP Scanning Electron Microscope. Dried cryogels were coated with gold–palladium for SEM analysis.

2.4.2. Thromboelastography

Thromboelastogram (TEG) measurements were performed using the TEG®5000 Thrombelastograph® Hemostasis System (HAEMONETICS CORPORATION, MA, USA). First, 1400 µL of blood was divided equally into two tubes. Then, cryogel was added to one tube. The tube without the cryogel was used as the control sample. Both tubes were incubated for 30 minutes. 20 µL of 0.2 M $CaCl_2$ solution was added to the two-channel transparent containers of the TEG device. Then the incubated blood samples were placed in the channels of the TEG device. All tests were conducted in seven independent replicates. Statistical analysis was performed using a paired samples t-test.

3. Results and Discussion

3.1. Morphological Characteristics

The PHEMA cryogel was synthesized by polymerization of HEMA and MBAAm. The SEM image of PHEMA cryogels is shown in Fig. 3. Supermacropores generated by ice crystal dissolution are visible in the SEM image. Such a porous network enhances the suitability of cryogels for applications in tissue engineering and drug delivery (Savina et al., 2021; Sharma et al., 2015).

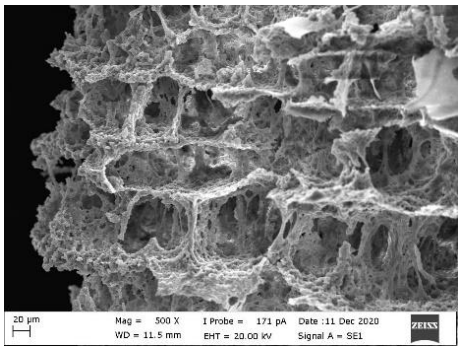

Figure 3. SEM images of PHEMA cryogel (500 X)

3.2. Effects of the PHEMA Cryogels on Hemostatic Parameters

Unlike conventional coagulation tests that are limited to examining the initiation of the coagulation cascade, thromboelastography provides a dynamic assessment of blood elasticity across the full spectrum of hemostasis, extending from coagulation onset to fibrinolysis (Peng, 2010). In our study, PHEMA-based plate cryogels were produced, and their interaction with human whole blood was evaluated by the thromboelastogram method. An example thromboelastogram graph is given in Fig. 4. Effects of THE produced PHEMA cryogel on hemostatic parameters are given in Table 1. According to the results, cryogel materials decreased the reaction time and coagulation time by 18.48% and 30.21%, respectively. Alpha angle, maximum amplitude, and G value also increased by up to 34%. The general coagulation index increased by 1.17 with the use of cryogel. According to the thromboelastogram results, the coagulation tendency of the blood in contact with the cryogel was increased.

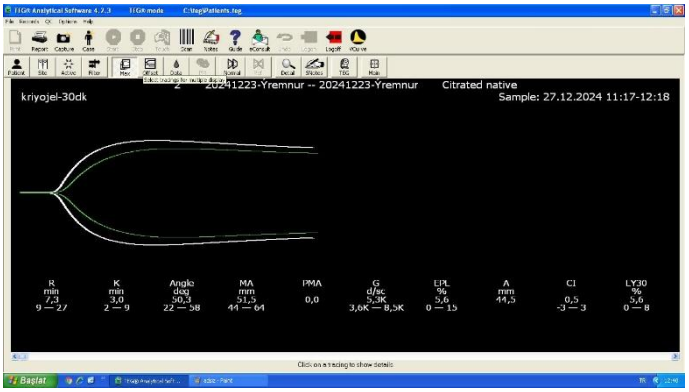

Figure 4. An example of thromboelastogram experiment

Table 1. Effects of produced PHEMA cryogel on thromboelastogram parameters

Values	Control	Cryogel	Difference
R (min)	9.89±2.13	8.03±1.71	-18.49 (%)
K (min)	6.86±2.10	4.59±0.89	-30.21 (%)
α (degree)	32.46±5.84	41.09±5.85	28.41 (%)
MA (mm)	35.39±4.77	42.24±5.31	19.95 (%)
G	2.79±0.59	3.71±0.85	34.12 (%)
CI	-1.93±0.94	-0.76±0.67	1.17

The significance levels and the comparison of the TEG results based on the paired t-test are shown in Fig. 5. The results obtained are statistically significant at the 95% confidence level. According to Fig. 3, the decrease in R and K values and the increase in MA, α angle, G, and CI values can be clearly observed. Shifts in TEG parameters (i.e., decreased R and K, increased α, MA, G, and CI) are consistent with the expected performance of effective hemostatic materials (Kim et al., 2021).

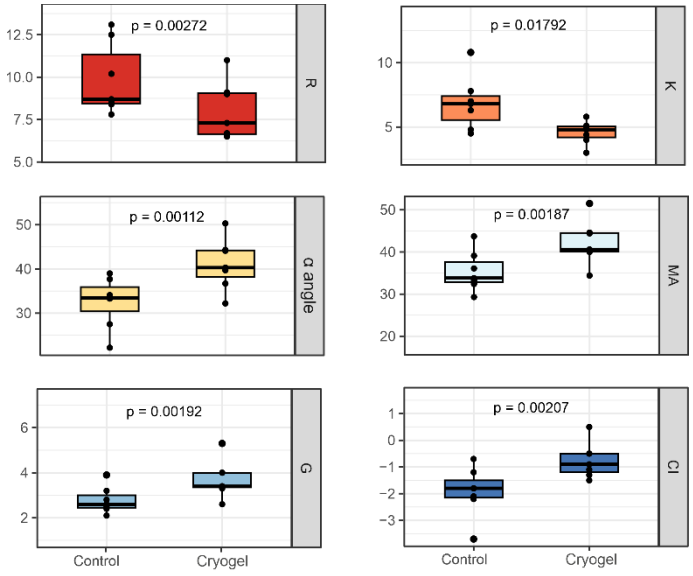

Figure 5. A Comparison of TEG Results

4. Conclusions

In this study, the blood interaction of PHEMA cryogels was investigated using the TEG method. According to SEM images, a macro-porous cryogel structure was successfully produced. TEG studies revealed that the cryogel application supported rapid clot formation, strong clot structure, and short clotting time. Statistically significant changes were observed in TEG parameters. Overall, the TEG findings confirm that the cryogel material has the capacity to accelerate hemostasis and may serve as a promising candidate as a hemostatic material. In future studies, it is aimed to shorten the test time to 30 minutes and thus examine the effectiveness of cryogel in shorter periods.

5. Acknowledge

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Control of Porous Titania Membrane Properties via Sintering: Microstructure and Filtration Performance

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ABSTRACT

This study investigates how sintering conditions influence the microstructure and water permeability of porous titania membranes fabricated by tape casting. To increase membrane thickness, two approaches were tested: lamination of three green tapes and sequential tape casting of up to three layers. Sequential tape casting produced mechanically stable membranes, whereas lamination resulted in weak interfacial bonding and sudden failure during filtration. Green tapes were sintered at 500–1100 °C for 1–3 h, and the effects on pore structure and filtration performance were evaluated. Increasing the sintering temperature from 1000 to 1100 °C enlarged the average pore size (170–264 nm) but reduced porosity, while extending the sintering time at 1000 °C increased porosity without significantly altering pore size. Water permeability correlated with both pore size and porosity, underscoring the importance of microstructural tailoring for membrane optimization.

Keywords : Titania, Tape casting, Porous membranes, Microstructure, Water permeability.

1. Introduction

Porous ceramics exhibit excellent chemical, thermal, and mechanical stability, making them suitable for a wide range of applications, including catalyst supports, filtration, and energy-related devices [1-3]. Their functional performance is strongly governed by structural parameters such as pore size, porosity, and connectivity, which in turn influence properties such as permeability, strength, and selectivity [1, 4]. Among these applications, filtration is particularly critical, as pore size distribution and porosity directly determine flux and separation efficiency in porous ceramic membranes [5, 6].

The pore characteristics of ceramics can be tailored through several factors, including raw material properties, the use of additives, fabrication methods, and sintering conditions [7]. Tape casting has emerged as a versatile technique for fabricating flat, thin, and multilayer ceramic membranes with thicknesses ranging from tens to hundreds of micrometers [8, 9]. In this method, slurry composition, drying behavior, and subsequent thermal treatment play decisive roles in defining the microstructure and final membrane performance.

Titania (TiO_2) is particularly attractive for porous membrane applications due to its chemical stability, photocatalytic activity, and potential for separation and purification processes [10, 11]. The sintering process plays a central role in tailoring the microstructure of titania membranes, as both temperature and duration influence pore size, porosity, and mechanical integrity. However, increasing membrane thickness remains a challenge: lamination may introduce interfacial weaknesses, whereas sequential tape casting provides a promising alternative for producing mechanically stable multilayer membranes [12, 13].

In this study, we investigate the fabrication of porous titania membranes by tape casting, with emphasis on increasing thickness through two approaches: lamination of multiple green tapes and sequential tape casting of dried tape layers. The effects of sintering temperature and time on pore structure and filtration behavior are systematically analyzed, and the correlation between microstructural

features and water permeability is discussed. The findings highlight the importance of microstructural tailoring for optimizing the performance of titania membranes in filtration applications.

2. Materials and Method

2.1. Starting material

Commercial TiO_2 powder (Kronos 1171, Germany; mean particle size 0.26 µm; specific surface area 9.0 $m^2.g^{-1}$) was used. Polyvinyl butyral (PVB, Mowital B60H) and polyethylene glycol (PEG 600) served as binder and plasticizer, respectively. An azeotropic ethanol/toluene mixture (50/50 vol%) was used as the tape-casting solvent.

2.2. Fabrication of porous titania membrane

TiO_2 was dispersed in the solvent and ball-milled (zirconia media) for ~2 h. Binder was added and milled for 24 h, followed by plasticizer addition and a further 24 h of mixing. The slurry was tape-cast on Mylar using a stainless-steel doctor blade (~30 cm min^{-1}) and dried.

To increase thickness, two approaches were applied: (i) Lamination: three individual green tapes were stacked and laminated; (ii) Sequential tape casting: three successive layers were cast sequentially onto previously dried green tapes. Green sheets were cut to size and sintered at 500–1100 °C (1 h) and at 1000 °C for 1 and 3 h.

2.3. Characterization and permeability testing

Final microstructure and thickness were examined by FESEM (Zeiss SIGMA VP). Average pore size was obtained from FESEM images using ImageJ. Open porosity was measured by the Archimedes immersion method in deionized water. Phase composition was determined by XRD (Philips X'Pert PRO PW1730, Cu K_α, λ = 1.5406 Å, 40 kV, 30 mA). Water permeability was evaluated in a dead-end stirred cell (Amicon 8010) connected to compressed N_2 (Figure 1). The feed side was held at constant pressure, the permeate at atmospheric pressure, at 25 °C and transmembrane pressure (TMP) up to 0.4 bar. Permeation flux was calculated as

$$j = \Delta V/(t.A) \quad (1)$$

where ΔV is the collected permeate volume, t the filtration time, and A the membrane area.

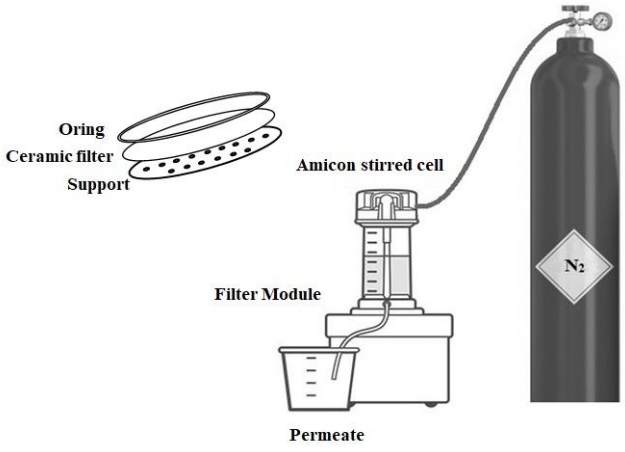

Figure 20:schematic of water permeability test under nitrogen gas pressure.

3. Results and Discussion

3.1. Influence of layering techniques

Figure 2 shows scanning electron microscopy images of the fractured cross-sections of the membranes after pressure-induced failure in the pressure cell, highlighting the distinct differences in interfacial bonding between the two fabrication strategies. In the sequential tape casting approach (Figure 2a), the interfaces between the layers were well integrated, resulting in a dense and homogeneous cross-section with no visible separation. This indicates that during sequential deposition, the subsequent slurry layer adheres effectively to the previously dried green tape, forming a consolidated structure upon sintering. In contrast, the laminated membranes (Figure 2b) exhibited clear debonding at the interfaces of the stacked layers. The weak interfacial bonding resulted in pronounced separation lines within the fracture surface, which compromised the structural integrity of the membrane. The top-view SEM image of the laminated sample (Figure 2c) further confirms this observation, showing the three layers distinctly separated at the fracture site.

The mechanical stability of the membranes was further assessed under hydrostatic nitrogen pressure (Figure 1). The laminated membranes failed at pressures below 0.2 bar, indicating premature delamination under stress. By comparison, the membranes prepared through sequential tape casting withstood pressures up to 0.4 bar before failure, demonstrating their superior resistance to pressurization. These results clearly show that sequential tape casting provides stronger interfacial bonding and higher mechanical reliability compared to lamination, making it a more effective strategy for fabricating multilayer porous titania membranes intended for filtration applications.

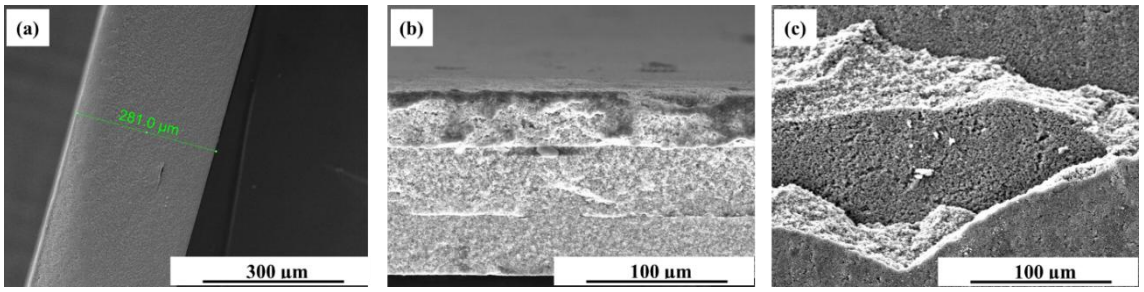

Figure 21: FESEM micrographs of samples prepared by sequential tape casting (a) and lamination, showing cross-sectional (b) and top (c) views.

3.2. Crystalline structure and microstructural analysis

Figure 3 presents the XRD patterns of porous titania sheets sintered at different temperatures (500–1100 °C for 1 h) and at 1000 °C for different durations (1 and 3 h). At sintering temperatures below 1000 °C, the samples predominantly exhibited the anatase phase. However, when the sintering temperature increased to 1100 °C, anatase was completely transformed into rutile. This anatase-to-rutile transformation is a well-known thermally driven phase transition in titania, and the results clearly demonstrate that temperature is the dominant factor controlling the crystalline phase. Sintering time also influenced phase transformation: extending sintering time at 1000 °C from 1 h to 3 h enhanced the conversion of anatase to rutile, confirming the time-dependent nature of the process.

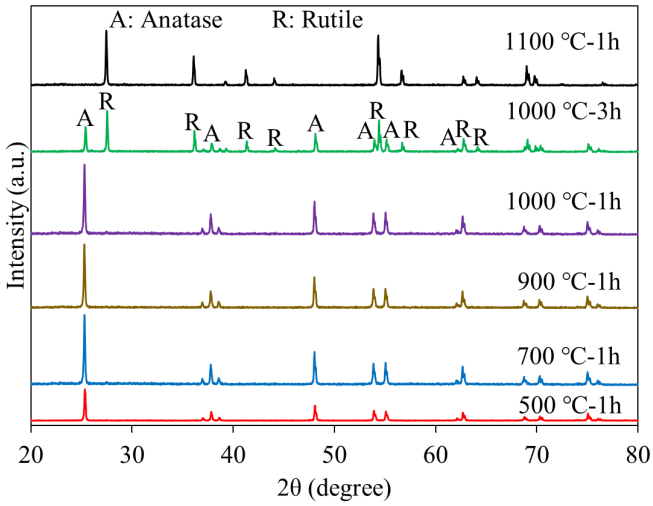

Figure 22: XRD patterns of titania sheets sintered at 500 to 1100 °C for 1h and 1000 °C for 3 h.

The corresponding microstructures of the sintered sheets are shown in Figure 4. With increasing sintering temperature, grains coalesced and grew significantly, leading to a denser structure. A marked increase in average grain size was observed as the temperature rose from 1000 °C to 1100 °C, indicating accelerated grain growth in this range. Prolonged sintering time also promotes grain coarsening, as shown in Figures 4b and 4d, which can be attributed to grain boundary migration processes that are strongly time dependent.

Interestingly, the effect of sintering time on porosity differed from that of temperature. While higher temperatures tended to densify the structure and reduce porosity, increasing the sintering time slightly increased the open porosity (Table 1). This phenomenon can be explained by the anatase-to-rutile phase transformation. Since rutile has a higher density than anatase, the formation of rutile grains alongside remaining anatase induced localized shrinkage and structural rearrangement, thereby increasing the fraction of open pores [14]. Thus, partial phase transformation significantly influenced the porosity of the sheets, even under constant sintering temperature.

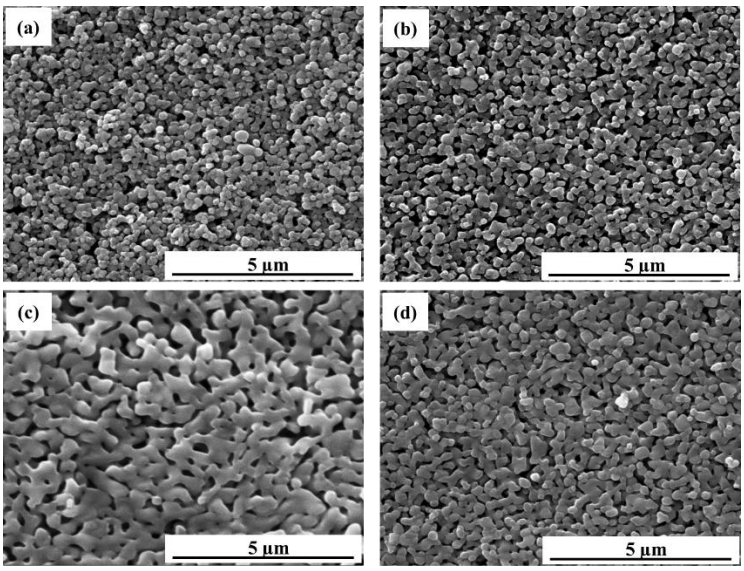

Figure 23: FESEM images of porous titania sheets sintered at 900 (a), 1000 (b), 1100 (c) for 1 h and 1000 °C for 3 h (d).

3.3. Permeability study

The results of water permeability measurements are summarized in Table 1. No data were obtained for membranes sintered below 900 °C, as these samples exhibited insufficient mechanical strength and failed even under pressures lower than 0.2 bar. With increasing sintering temperature from 900 °C to 1100 °C, the water permeability of the membranes progressively improved. This trend can be explained by changes in pore structure: although the total porosity decreased, the fraction of open pores increased, and the average pore size rose markedly from 170 nm at 1000 °C to 264 nm at 1100 °C. At 1000 °C, prolonging the sintering time from 1 h to 3 h also resulted in higher permeability. This improvement is attributed to microstructural rearrangements induced by the partial anatase-to-rutile transformation, which facilitated the formation of additional open pores.

The maximum operating pressure showed a comparable dependence on sintering conditions. Membranes sintered at 1000–1100 °C exhibited enhanced structural stability, withstanding pressures up to 0.4 bar. These results emphasize the close relationship between sintering parameters, microstructural evolution, and filtration behavior, highlighting the importance of carefully optimizing processing conditions to achieve mechanically robust and highly permeable porous titania membranes.

Table 5: Permeability performance of porous titania sheets in the Amicon stirred cell

Sintering temperature (°C)	Sintering time (h)	Open porosity (%)	Pore size (nm)	Permeability ($L/m^2.h.bar$)	Maximum operating pressure (bar)
900	1	52	165	335	0.2
1000	1	50	170	348	0.3
1100	1	43	264	589	0.4
1000	3	57	173	432	0.3

4. Conclusions

This study demonstrates that sequential tape casting is a more effective strategy than lamination for fabricating multilayer porous titania membranes, due to its stronger interfacial bonding and higher mechanical stability. Sintering strongly influences the microstructure: raising the temperature from 1000 °C to 1100 °C enlarged the average pore size from about 170 nm to 260 nm and increased water flux accordingly, while extending the dwell time from 1 h to 3 h at 1000 °C mainly increased open porosity (from 50% to 57%) without significantly changing pore size, due to partial anatase-to-rutile transformation. Overall, the results highlight the tight link between processing, structure, and performance, emphasizing that precise control of both sintering temperature and time is essential for producing robust, high-permeability titania membranes for filtration applications.

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Additive Manufacturing Technologies and Materials: A State-of-the-Art Review

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ABSTRACT

Additive manufacturing (AM), also commonly known as three-dimensional (3D) printing or rapid prototyping, has advanced significantly over the past decade. Thanks to the design freedom it offers, AM enables the production of parts that are difficult or even impossible to produce using traditional manufacturing methods such as formative manufacturing and subtractive manufacturing. The constraints and limitations encountered in traditional manufacturing are eliminated with this technique. With advantages such as reduced material usage, minimized waste, the ability to produce complex geometries, elimination of storage needs, rapid production, ease of customization, and the potential to consolidate multi-part assemblies into a single or minimal number of parts, AM offers unique opportunities. According to the ASTM-F42 committee guidelines, AM is classified into seven categories. These categories are material jetting, binder jetting, vat photopolymerization (including stereolithography [SLA] and digital light processing [DLP]), powder bed fusion (including selective laser sintering [SLS], selective laser melting [SLM], and electron beam melting [EBM]), material extrusion (including fused deposition modeling [FDM]), direct energy deposition (including laser engineering net shaping [LENS] and electron beam additive manufacturing [EBAM]), and sheet lamination (including laminated object manufacturing [LOM]). Additionally, AM are classified into three categories based on the material used: solid, liquid, and powder. 3D parts made from various printing materials, such as metals, polymers, and ceramics, have a wide range of uses in a broad spectrum of industries, from aerospace and automotive to healthcare and consumer goods. This review aims to provide an overview of various aspects of AM technologies and materials, highlighting the advances made over the past decades.

Keywords : Additive manufacturing, 3D printing, Materials

1. Introduction

In recent years, rapid advancements in technology have led to fundamental changes in manufacturing methods. One of the most significant examples of these changes is additive manufacturing technologies. Generally known as 3D printing, additive manufacturing (AM) has emerged as a transformative technology in the manufacturing industry. Unlike traditional manufacturing methods, AM offers significant advantages such as design flexibility, less material waste, customized production, and the ability to produce complex geometries with relative ease (Kaikai et al., 2023, Pereira et al., 2023). Currently, AM is primarily used for the low-volume production of complex parts. However, as production volume increases and part complexity decreases, traditional production methods such as casting and forging become more suitable and feasible.

Although the origins of AM date back to the 1980s, developments in both hardware and materials over the past decade have significantly expanded its range of applications. Initially developed for rapid prototyping, this technology is now widely used in various sectors such as aerospace, automotive, biomedical engineering, and construction. It offers more cost-effective, sustainable, and functional alternatives to conventional techniques (Zhou et al., 2024). The materials used in this process also show significant diversity, ranging from plastics and metals to ceramics and composite materials.

Thermoplastics, photopolymers, metals, ceramics, and composite materials are being developed and optimized to meet the specific requirements of different AM techniques.

This review provides an overview of the current state of additive manufacturing technologies, examining different production techniques and types of materials used in the process.

2. Comparison of Traditional Manufacturing and Additive Manufacturing

The fundamental difference between traditional manufacturing and additive manufacturing lies in their production approach and material usage (Kaikai et al., 2023). Traditional manufacturing methods are generally based on subtractive processes, where unwanted material is removed from a workpiece or shaped using molds. Formative manufacturing is a production method used in processes such as molding and plastic injection, where molten material is injected into a mold and takes shape under specific temperature and pressure conditions. In this method, one of the most critical factors is the cost of the mold. Subtractive manufacturing is a production method where material is gradually removed from a solid workpiece using cutting tools to achieve the desired shape. This method results in significant material waste and directly increases production costs. However, additive manufacturing is a production technique in which material is added layer by layer. One of the major advantages of this method is that it eliminates the need for molds and minimizes material waste, enabling a faster and more efficient production process (Pereira et al., 2023).

Figure 1 shows the schematic representation of different production methods.

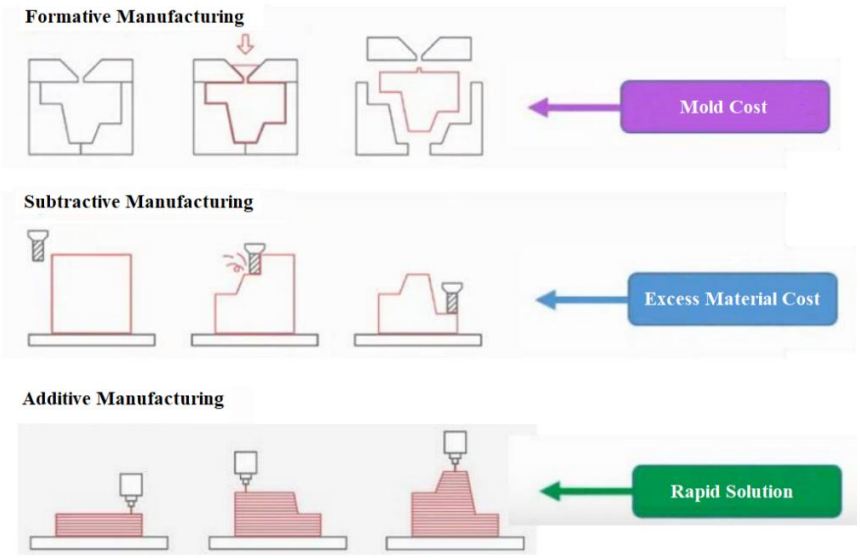

Figure 1. Schematic representation of different production methods (Redwood et al. 2020).

A comparison between 3D printing and traditional manufacturing in terms of cost, complexity/customization, and production volume is shown in Figure 2.

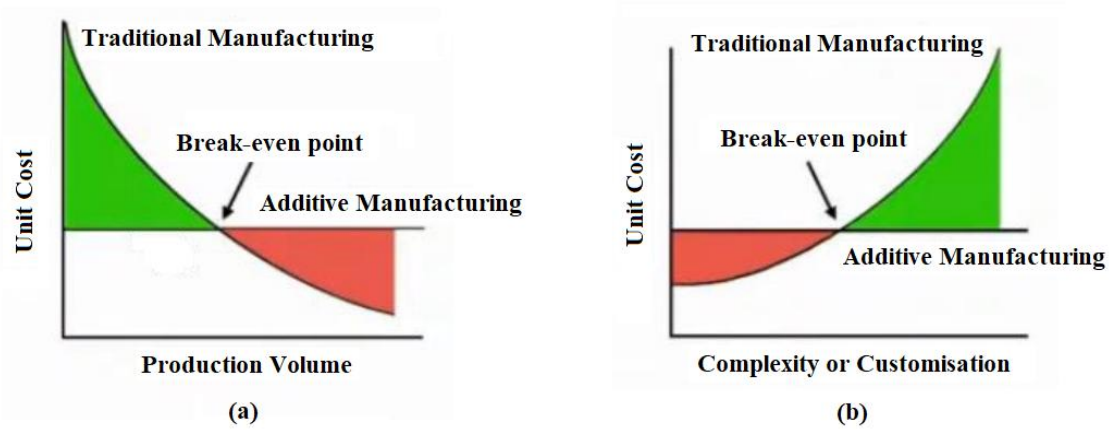

Figure 2. A comparison between 3D printing and traditional manufacturing in terms of cost, complexity/customization, (a) and production volume (b) (Shang & Sun, 2020).

As can see Figure 2 observed that the unit cost of additive manufacturing generally remains constant regardless of production volume. In contrast, in conventional manufacturing, costs decrease as production volume increases. This indicates the existence of an optimization point, up to which additive manufacturing can be more efficient than conventional production methods. However, beyond this point, at higher production volumes, conventional manufacturing becomes more advantageous. In terms of complexity and customization, the cost of additive manufacturing tends to remain stable, while in conventional manufacturing, the unit cost increases as complexity rises. In this case, additive manufacturing stands out as the preferred method. That is, in situations involving high complexity, additive manufacturing should be considered the more suitable option.

2.1. Additive Manufacturing

Additive Manufacturing (AM) is a rapidly developing technology that has entered the manufacturing sector in recent years. It is also commonly known as rapid prototyping or 3D printing. According to ASTM F2792-10, additive manufacturing is defined as a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies (ASTM, 2010). To put it simply, it can be compared to building with LEGO bricks. By adding material only where needed, the desired product can be created efficiently.

Figure 3. Schematic representation of additive manufacturing as LEGO bricks*.*

2.1.1. The Advantages of Additive Manufacturing

The advantages of additive manufacturing are presented in Table 1.

Table 1. Advantages of additive manufacturing.

Reducing multi-part assemblies to a single component or to the lowest possible number
Eliminating the need for inventory
Rapid production of parts with complex geometries
Shortening production preparation time

Avoiding costs associated with molds, dies, and tooling
Producing high-surface-quality parts with minimal waste
Fast production of models, prototypes, and final parts

2.1.2. The Importance of Additive Manufacturing for Industries

The importance of additive manufacturing for industries are presented in Table 2.

Table 2. The importance of additive manufacturing for industries.

Direct manufacturing of designs
Ability to produce designs with complex internal structures
Production of lightweight parts with lattice structures or hollow interiors
Manufacturing that minimizes material waste and scrap
Shortening R&D and product development cycles, thereby accelerating time-to-market
Production with tight tolerances
On-demand manufacturing
Shortening of the supply chain

3. Additive Manufacturing Production Stages

Additive manufacturing is not limited to a single production method; rather, it is a general term encompassing multiple production technologies. The process begins with creating a model using computer-aided design (CAD) software. Once the design is completed, it is converted into an STL format that additive manufacturing machines can interpret. While conventional manufacturing typically involves generating CAM data, additive manufacturing primarily uses STL files. Recently, newer file formats such as AMF and 3MF have also become popular. Converting to STL means translating the model into a language understandable by the printer. Next, the model needs to be prepared for printing. When the STL file is sent to the printer, the machine recognizes the model, but the build orientation, angle, and locations for support structures must be determined. Specialized software is used to position the model in the desired orientation and to add support structures where needed. After this preparation, the printer starts the manufacturing process. Following production, post-processing steps are performed as necessary. These may include smoothing rough surfaces, heat treatment, or painting to achieve the final product (Kanishka & Acherjee, 2023).

The additive manufacturing production stages are presented in Figure 4.

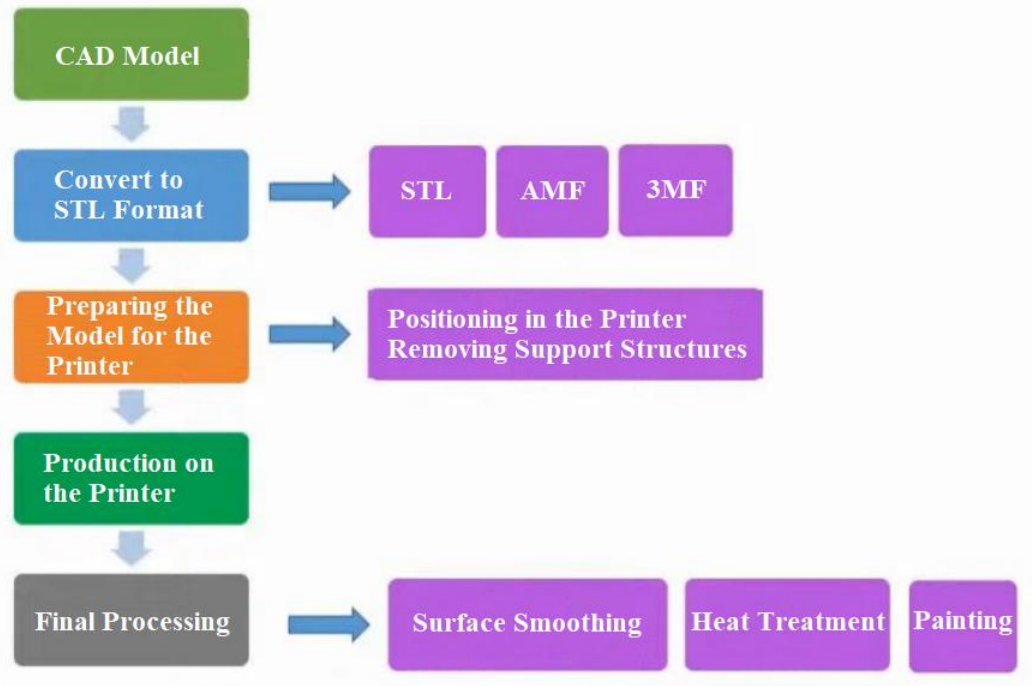

Figure 4. Additive manufacturing production stages.

4. Additive Manufacturing Materials

Materials used in additive manufacturing (3D printing) vary depending on the process type and application area. These materials can be metals, polymers, composites, or ceramics. In general, materials are divided into three states: solid, liquid, and powder. The most common materials include plastic filaments (PLA, ABS, PETG), resins, metal powders (stainless steel, titanium, aluminum), and composite materials. Plastic materials are preferred for prototyping and low-cost parts, while metal powders are used in aerospace, automotive, and medical device production for their durability and performance.

The solid-state method, which includes FDM (Fused Deposition Modeling), the liquid-state method, which includes technologies such as SLA (Stereolithography) and DLP (Digital Light Processing), the powder-state method, which uses materials in powder form, such as in SLS (Selective Laser Sintering), SLM (Selective Laser Melting), EBM (Electron Beam Melting), and LENS (Laser Engineered Net Shaping) technologies.

The materials used in additive manufacturing are presented in Figure 5.

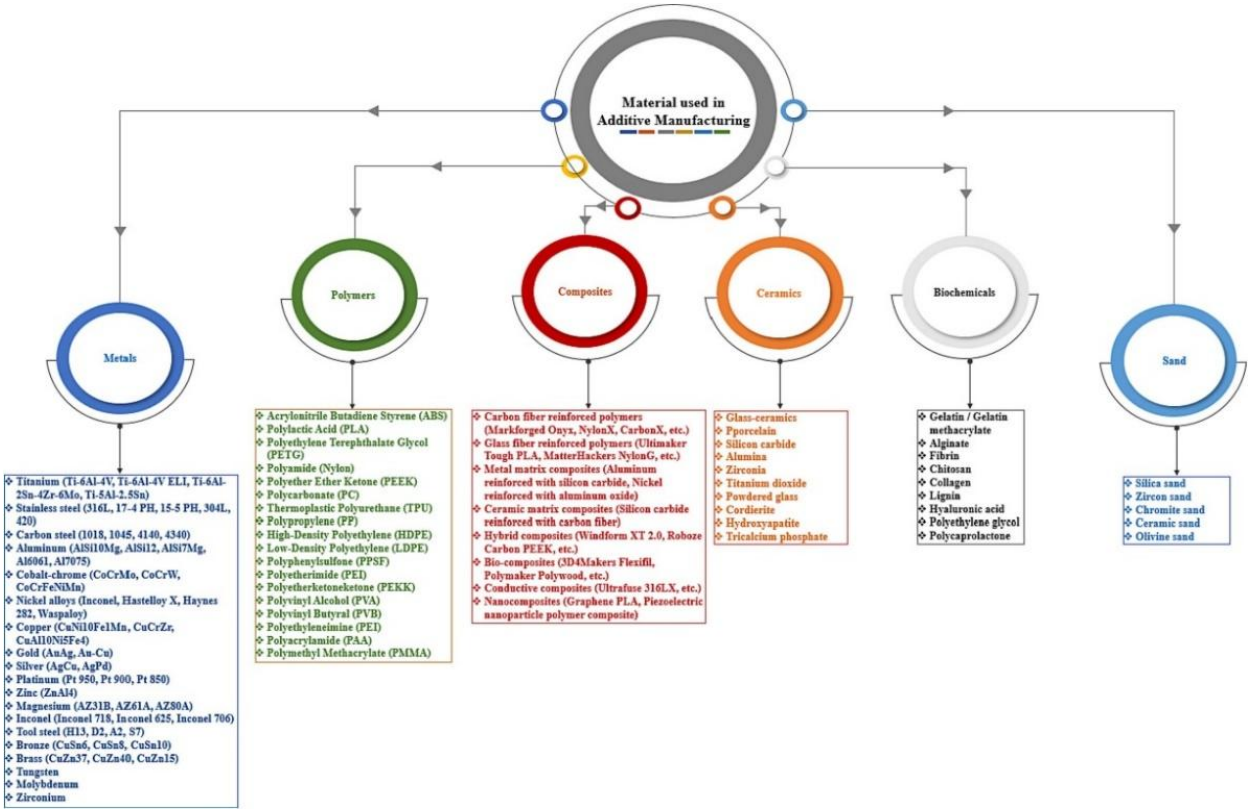

Figure 5. Additive manufacturing materials (Kanishka & Acherjee, *2023).*

5. Additive Manufacturing Technologies

According to ASTM standards, additive manufacturing is classified into different categories. The overall classification of additive manufacturing is shown in Figure 6.

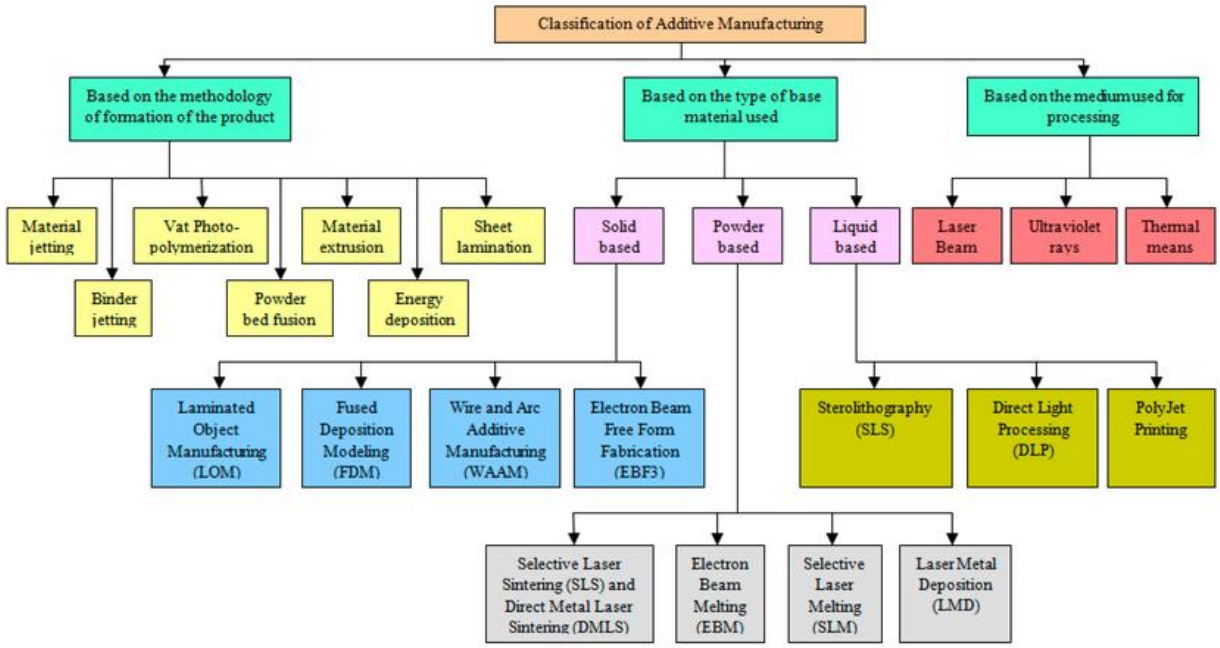

Figure 6. Classifacition of additive manufacturing (Saleh Alghamdi et al. 2021).

5.1. Material Jetting

In the material jetting technology, material is sprayed onto a build platform. This system uses jetting print heads. It works by depositing very small droplets of a polymer layer by layer onto the surface, similar to the inkjet print heads used in inkjet printers. These droplets solidify immediately (using UV light or heat), thus forming precise layers (Elkaseer et al., 2022).

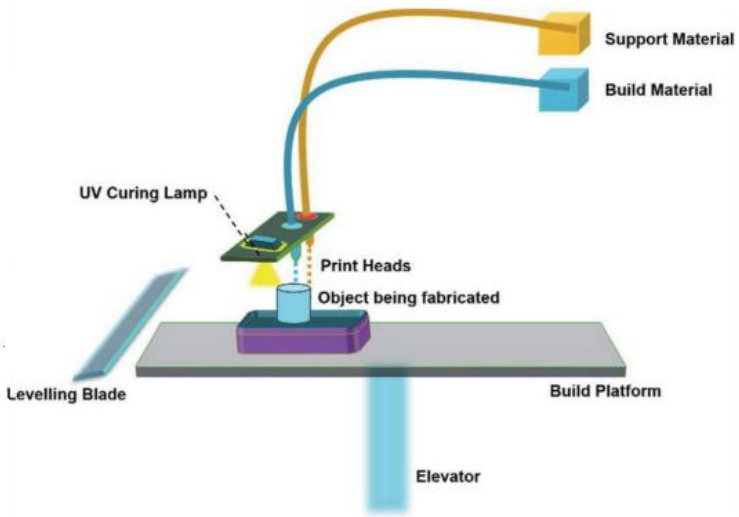

Figure 7. Schematic illustration of material jetting working principle (Loughborough University, 2025).

5.2. Binder Jetting

Binder jetting is a method of building a part layer by layer by spraying liquid binder droplets onto a powdered material, similar to inkjet printing (Ziaee & Crane, 2019).

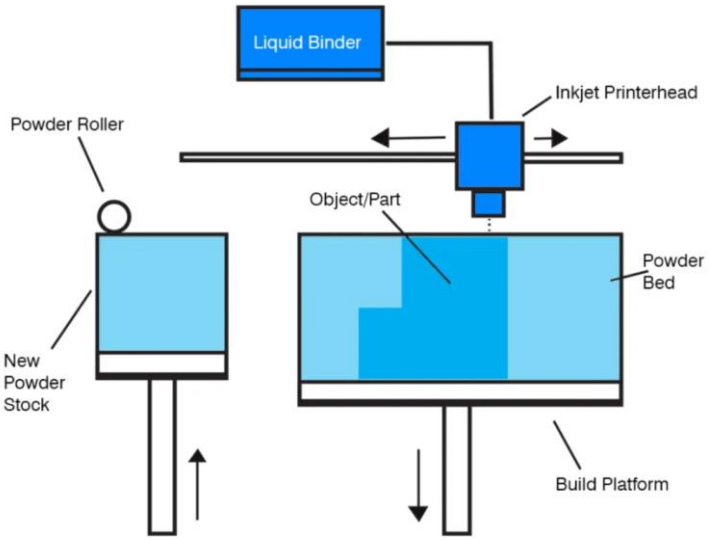

Figure 8. Schematic illustration of binder jetting working principle (Thrimana, 2018).

5.3. Vat Photopolymerization

Vat photopolymerization includes two main technologies: Stereolithography (SLA) and Digital Light Processing (DLP).

5.3.1. Stereolithography (SLA)

SLA is a method based on curing liquid photopolymer resin layer by layer using a UV laser. The laser draws the desired shape on the surface of a platform submerged in the resin, causing the resin to harden. Layers are built up successively to form the part (Lakkala et al., 2023, Husna et al., 2024).

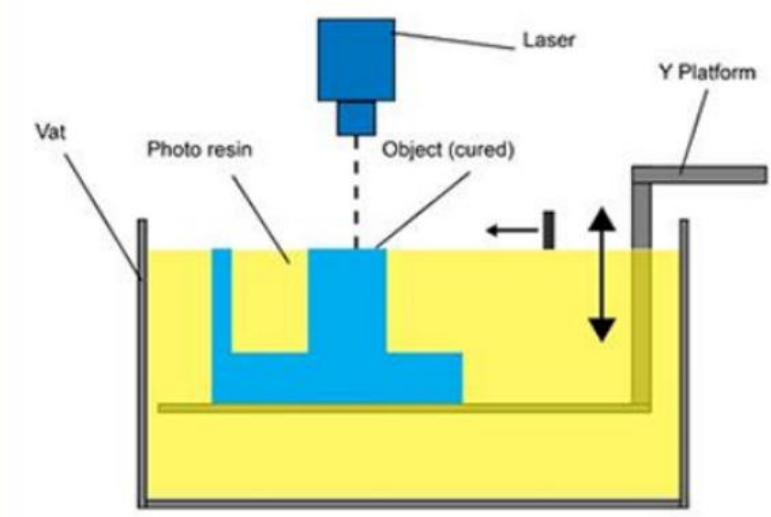

Figure 9. Schematic illustration of SLA working principle (Loughborough University, 2025).

5.3.2. Direct Light Processing (DLP)

DLP is a method that uses a projector or digital light source to cure the entire resin surface or a large area of it layer by layer using UV light in a single exposure. In this way, instead of scanning each layer with a laser, the layer is cured all at once through light projection (Chaudhary et al., 2023, Yi et al., 2025).

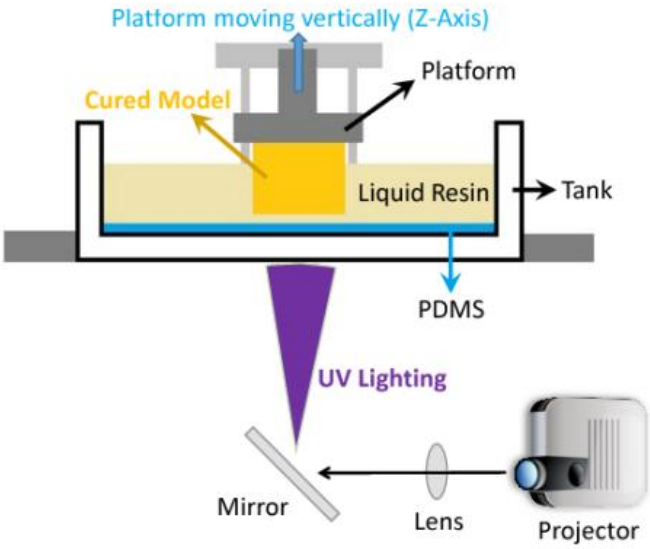

Figure 10. Schematic illustration of DLP working principle (Pazhamannil et al. 2022).

5.4. Powder Bed Fusion

Powder Bed Fusion includes three main technologies: Selective Laser Sintering (SLS), Selective Laser Melting (SLM) and Electron Beam Melting (EBM).

5.4.1. Selective Laser Sintering (SLS)

SLS is a method in which high-energy laser beams are directed onto metal powders to fully melt and fuse them together (Morano & Pagnotta, 2023,Yehia et al. 2024).

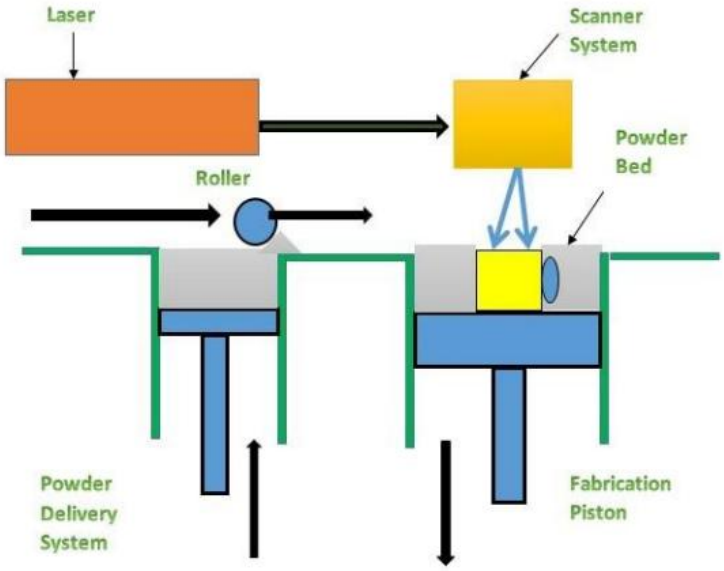

Figure 11. Schematic illustration of SLS working principle (Rasaki et al. 2021).

5.4.2. Selective Laser Melting (SLM)

SLM is a method in which metal powders are melted and fully fused together layer by layer. Using a high-power laser beam, the metal powders are completely melted and then solidified (Gao et al., 2023, Soni et al., 2024).

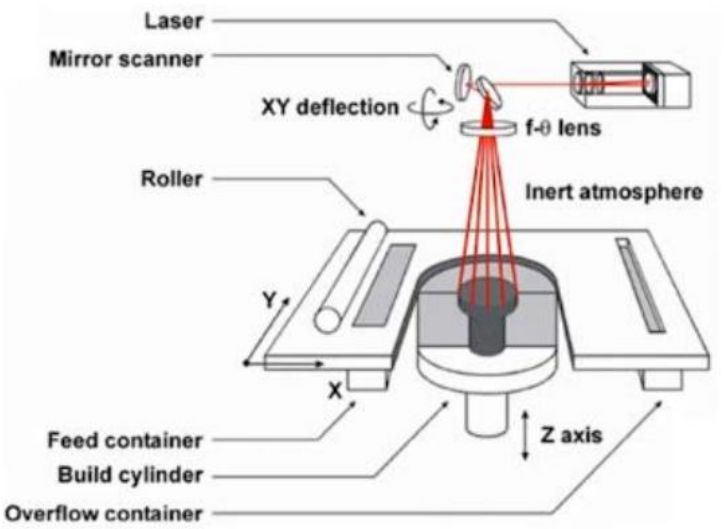

Figure 12. Schematic illustration of SLM working principle (Lian et al. 2018).

5.4.3. Electron Beam Melting (EBM)

EBM is a method in which the final product is obtained by melting metal powder using a high-energy electron beam under vacuum conditions (Zhang et al., 2017, Jiao et al., 2024).

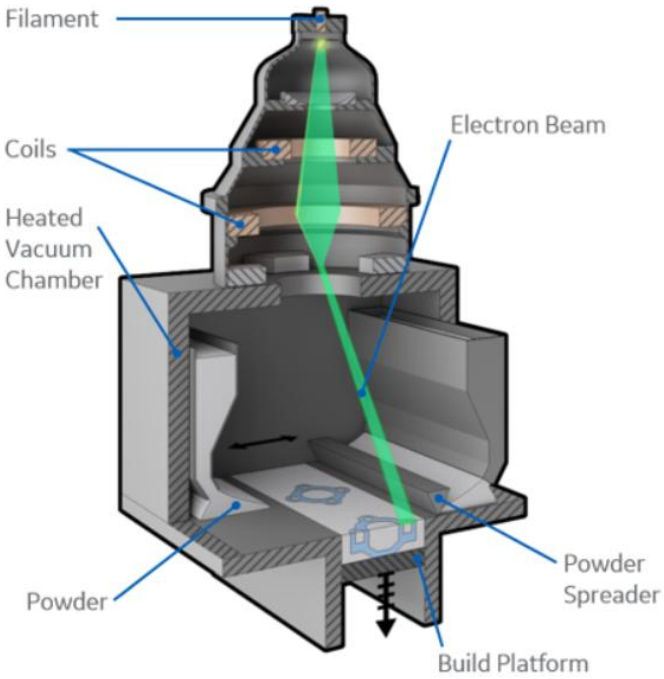

Figure 13. Schematic illustration of EBM working principle (Manufacturing Guide, 2025).

5.5. Material Extrusion (Fused Deposition Modeling - FDM)

FDM is the most well-known and widely used technique among additive manufacturing technologies.

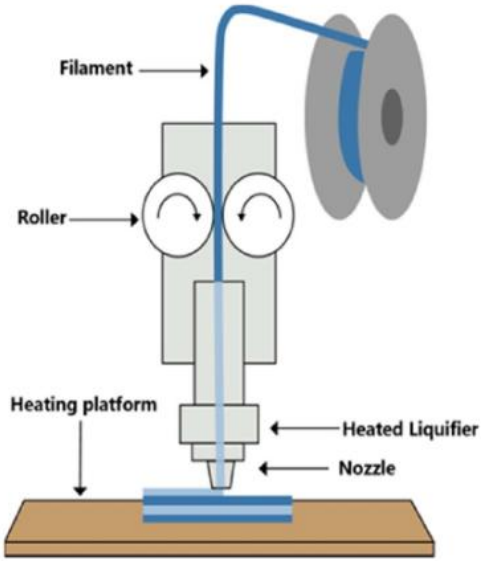

Figure 14. Schematic illustration of FDM working principle (Peng et al. 2024).

This method is particularly common in most desktop 3D printers. It creates the part by melting thermoplastic filament (such as PLA or ABS) in a heated nozzle and depositing it layer by layer. Typically,

the thermoplastic material in filament form (e.g., PLA, ABS) is fed from a spool into the heated nozzle. The filament is melted at the hot end, usually at temperatures between 180°C and 260°C. The molten polymer is extruded from the nozzle and deposited onto the build platform in layers. As the print head moves in the X-Y plane, the build platform moves down along the Z-axis, allowing the part to be built layer by layer. The extruded polymer rapidly cools and solidifies, thus forming the final structure (Daminabo et al., 2020, Vicent et al., 2021).

5.6. Direct Energy Deposition

5.6.1. Laser Engineering Net Shaping (LENS)

LENS is a method in which a metal wire is melted using an electron beam to create a structure layer by layer. The electrons are accelerated in a vacuum environment, and when they strike the target material, the resulting heat melts the metal wire, allowing it to be shaped accordingly (Izadi et al., 2020).

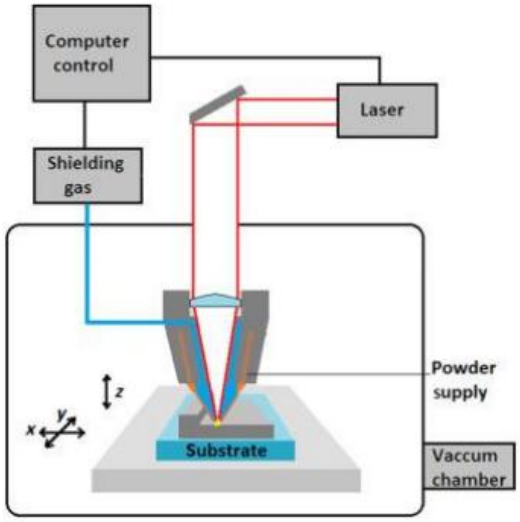

Figure 15. Schematic illustration of LENS working principle (Antolak-Dudka et al. 2019).

5.6.2. Electron Beam Additive Manufacturing (EBAM)

EBAM is a method in which metal powders are melted and fully fused together layer by layer. Using a high-power laser beam, the metal powders are completely melted and then solidified (Gong et al., 2014).

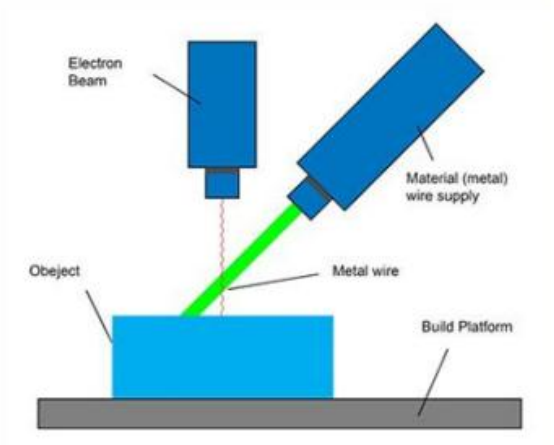

Figure 16. Schematic illustration of EBAM working principle (Loughborough University, 2025).

5.7. Sheet Lamination (Laminated Object Manufacturing - LOM)

LOM is a manufacturing method in which a sheet material fed from a roll is cut according to the shape of each layer and then bonded (laminated) onto the previous layer to build the part layer by layer (Dermeik & Travitzky, 2020).

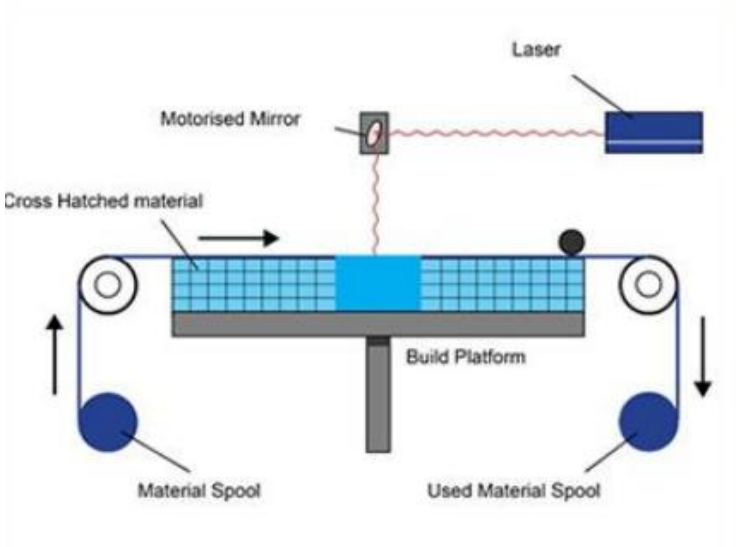

Figure 17. Schematic illustration of LOM working principle (Loughborough University, 2025).

6. Conclusions

Additive manufacturing technologies significantly shorten product development cycles in many industries, icluding aerospace, biomedical, and automotive, by enabling the production of complex geometries and rapid prototyping. Today, AI integration and sustainability have become key focus areas for additive manufacturing technologies. Within the framework of the circular economy, considerable efforts are being made to use recycled raw materials, minimize material waste, and adopt biodegradable materials. As a result, additive manufacturing is transforming into a smart, sustainable production platform. Nonetheless, challenges such as printing speed, material variety, cost, and post-processing requirements remain areas needing improvement.

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Characterization of the Structural Behavior of Carbon Fiber–PPS Based Hybrid Fabrics Depending on Braiding Parameter

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ÖZET

Bu çalışmada, yüksek performans ve hafiflik gerektiren uygulamalar için hibrit örgü termoplastik kumaşların geliştirilmesi hedeflenmiştir. Özellikle yüksek sıcaklığa dayanıklı bir mühendislik termoplastiği olan polifenilen sülfid (PPS), karbon elyaf ile örgü(braiding) tekniği kullanılarak hibrit yapıda bir araya getirilmiştir. Üretilen örgü yapılar sıcak pres prosesine tabi tutulmuştur. Bu aşamada PPS termoplastik bileşeni eritilerek lif yapısı arasında matris olarak görev yapması sağlanmış ve kompozit plakalar elde edilmiştir. Çalışma esnasında farklı örgü açıları elyaf oranları ile örülen ürünler incelenmiştir. Bunun sonucunda 45° açı ile elde edilen yapıların mekanik dayanım açısından optimum sonuç verdiği görüldüğünden 45° örgü açısı kabul edilmiştir. Ayrıca üretim sürecinde karşılaşılan homojen elyaf dağılımı bozuklukları ve hedeflenen örgü açısından sapmalar, makine ayar parametreleri (motor hızı, çekim hızı, pitch değeri) ile örgü geometrisi (kukla sayısı ve örgü açısı) arasındaki ilişkiler sistematik olarak incelenerek optimize edilmiştir. Sonuçta PPS takviyeli hibrit örgü kumaşlar, üretilebilirlik açısından umut verici çözümler sunmaktadır.

Anahtar Kelimeler : Hibrit örgü kumaş, Karbon elyaf, Kompozit plaka, PPS

ABSTRACT

In this study, the development of hybrid braided thermoplastic fabrics for applications requiring high performance and lightness was aimed. Polyphenylene sulfide (PPS), a high-temperature-resistant engineering thermoplastic, was combined with carbon fiber in a hybrid structure using the braiding technique. The braided structures produced were subjected to a hot-pressing process. At this stage, the PPS component was melted to act as a matrix within the fiber structure, forming composite plates. Products braided at different angles and fiber ratios were examined. It was found that structures with a 45° braiding angle provided optimum mechanical performance, and thus the 45° angle was adopted. Non-uniform fiber distribution and deviations from the targeted angle observed during production were systematically analyzed and optimized by evaluating the relationships between machine parameters (motor speed, take-up speed, pitch) and braiding geometry (spindle number and braiding angle). PPS-reinforced hybrid braided fabrics offer promising solutions in manufacturability.

Keywords: Carbon fiber, Composite plate, Hybrid braided fabric, PPS

1. Introduction

The demand of industries for lightweight and high-performance materials is increasing the use of composite materials. As a result, the use of textile composites has also been growing in many sectors. In textile composites, various textile products such as yarn, knitted or braided fabric, and woven fabric can be used together with suitable resin to produce composite materials.

In this study, hybrid fabrics were developed using the braiding technique. Braiding is a method in which continuous fibers are interlaced by winding around each other on a braiding machine.

The difference from weaving is that in weaving, the yarns interlock at right angles, whereas in braiding they cross each other at specific angles. By optimizing this angle, the desired strength properties can be achieved. [1]

In this study, the braiding method was preferred over weaving for fabric production due to several factors:

- lower production cost,
- ability to achieve the targeted strength properties,
- capability to produce closer shape to the desired final shape.

2. Materials and Method

Hybrid textile structures can be manufactured through several approaches, with commingling being one of the most widely studied methods. To ensure a homogeneous distribution of components, it is generally preferred that each filament bundle within the braided structure maintains a consistent ratio of reinforcement and matrix materials. In a study similar in scope to the present work, commingled yarns were produced by blending continuous carbon fibers with thermoplastic filaments of polyphenylene sulfide (PPS). The research focused on evaluating how process parameters such as overfeeding, air pressure, and production speed influence fiber mixing within the yarn cross-section. The findings demonstrated that commingling parameters strongly affect blend uniformity, and a direct correlation was established between process conditions and the degree of homogeneity achieved. Furthermore, it was highlighted that the mechanical performance of such hybrid yarns is primarily governed by the tensile properties of the carbon fibers, while PPS contributes chemical resistance, thermal stability, and flame retardancy, making it a competitive thermoplastic matrix for high-performance aerospace and automotive applications.

In this study, however, commingling was not employed. Instead, in order to achieve lower production costs and improved processing efficiency, carbon and PPS fibers were directly wound onto the braiding machine bobbins at predetermined ratios, and the hybrid fabrics were subsequently produced through braiding. This approach allowed for controlled fiber proportions without requiring additional commingling steps.[2]

2.1. PPS (Polyphenylene Sulfide)

Polyphenylene sulfide (PPS) is a high-performance engineering thermoplastic widely recognized for its excellent thermal resistance, chemical stability, flame retardancy, and dimensional stability. With its low thermal expansion coefficient, high hardness, and strong resistance to creep and wear, PPS has become an attractive matrix material for advanced composite applications. In particular, PPS reinforced with carbon fibers has been extensively applied in aerospace, automotive, and aeronautical industries, where lightweight structures with superior mechanical performance are required. Compared to other high-temperature thermoplastics such as polyetherimide (PEI) and polyetheretherketone (PEEK), PPS provides a favorable balance between performance and processing cost, making it one of the most commercially viable matrix systems. [3]

Thermal characterization plays a crucial role in the processing of carbon/PPS composites. Differential Scanning Calorimetry (DSC) results show that PPS exhibits a glass transition temperature of approximately 90 °C and a melting point near 285 °C. Thermogravimetric Analysis (TGA) further confirms that the degradation temperature of PPS is significantly higher than the processing window, ensuring structural integrity during thermoforming. Based on DSC and TGA findings, as well as industrial validation, the optimal forming temperature for carbon/PPS composites has been determined as 320 °C. To prevent

the deterioration of mechanical properties during cooling, the formed parts must be held at 220 °C for 10 minutes under controlled conditions.

Overall, the combination of carbon fibers and PPS provides a robust and reliable hybrid system with high tensile strength, excellent chemical and thermal resistance, and strong processing efficiency, thereby offering significant potential for structural components in demanding industrial applications.[4]

2.2. Carbon Fiber

Carbon fibers are the most widely used reinforcements in advanced composites, particularly due to their outstanding strength-to-weight ratio, high tensile strength, and high tensile modulus values. These properties, combined with excellent fatigue resistance, low thermal expansion, and dimensional stability, make carbon fibers an indispensable material for structural applications in aerospace, automotive, and defense sectors. The performance of hybrid composites is largely determined by the carbon fiber phase, as it governs stiffness and tensile strength, while the polymeric matrix contributes toughness and chemical resistance.

In braided composite structures, carbon fibers serve as the primary reinforcement. Modern braiding technologies enable the production of biaxial and triaxial braids in which carbon fibers can be combined with thermoplastic or thermoset matrix systems. The braiding angle, fiber type, and yarn architecture strongly influence the final properties of the composite. For example, biaxial braids are generally used for torsional load-bearing applications, whereas the introduction of 0° yarns in triaxial braids enhances flexural strength. Moreover, the undulations created by the textile architecture may reduce in-plane properties compared to non-crimp fabrics, but optimized braiding patterns or unidirectional braids (UD-braids) can mitigate these effects and improve load transfer efficiency.

Another critical factor is fiber handling during the braiding process. Carriers in the braiding machine must maintain constant fiber tension to avoid irregularities in the braid. Unequal yarn tension or fiber damage from sharp guiding elements can compromise composite quality. To address this, advanced carrier designs employ low-curvature guiding systems that reduce fiber breakage and preserve the flat geometry of rovings, ultimately improving the mechanical performance of carbon fiber braids. The versatility of carbon fiber braiding has led to its adoption in diverse fields. Applications range from aerospace stiffener profiles and helicopter landing gear to automotive crash components and high-performance sporting goods. Reports indicate that braided landing gear structures can reduce weight by up to 20%, while braided components in luxury cars improve crash energy absorption. These examples highlight carbon fibers' ability to deliver lightweight, damage-tolerant, and structurally efficient solutions when integrated into braided architectures.[5]

2.3. Method

The technical characteristics of braided products are defined by the braiding geometry, which is determined by parameters such as the type of fiber material, thickness, braiding angle, braiding speed, machine settings, and the number of carriers.[6]

To achieve the required flexibility for different application areas, various combinations of hybrid ratios, braiding angles, and braiding speeds can be applied, each of which has an impact on the mechanical properties of hybrid fabrics. In this project, the effects of braiding angle and technical fiber ratio were specifically investigated.

Different process settings were applied on the braiding machine to obtain various angle values. Hybrid fabrics were produced at braiding angles of 30°, 45°, and 60°, with two different technical fiber ratios of 60% and 50%.

2.3.1. Process

Figure 24. Fiber winding onto the bobbin

Figure 25. Insertion of bobbins into the machine

Figure 26. Bobbins mounted into the machine

Figure 27. Adjustment of machine settings

Figure 28. Braided product

Figure 29. Cut and prepared fabric

Figure 30. Hot-Press machine adjustment

Figure 31. Placement of fabrics into the hot-press machine

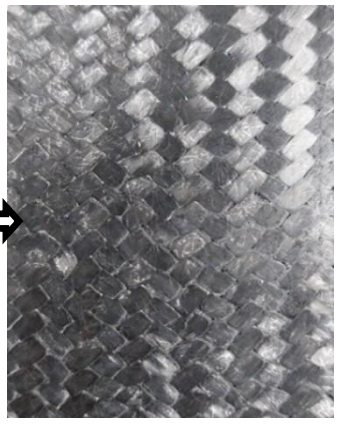

Figure 32. Final plate form

The preparation of the braided structures began with the winding of fibers onto individual bobbin carriers. To achieve hybridization and ensure a homogeneous distribution of the thermoplastic matrix, specific fiber ratios were applied during this stage. For one series of samples, each bobbin was wound with 60% carbon fiber as the technical reinforcement and 40% PPS fiber as the thermoplastic matrix. For the second series, a balanced ratio of 50% carbon fiber and 50% PPS fiber was used. Once all bobbins were prepared, they were mounted onto the circular braiding machine to complete the setup for braiding. Following this step, the machine parameters, such as speed and operational mode, were adjusted via the control interface to ensure proper synchronization and uniform carrier movement. Through multiple trial runs, the appropriate settings were identified and entered into the system in order to achieve the desired braiding angles. This configuration provided consistent tension and positioning of the fibers, enabling accurate control over the braiding process.

Braiding was performed at three different angles —30°, 45°, and 60°— in order to investigate the influence of braiding geometry on the structural performance of the hybrid fabrics. The variation in braiding angle was achieved by altering the process parameters of the machine, allowing the fibers to be interlaced at controlled orientations. After braiding, the produced sleeves were cut into suitable lengths to obtain fabric samples for further processing.

The fabrics were then pressed in a hot-press machine in order to obtain composite plates. Prior to pressing, the operational parameters of the press, including temperature and pressure, were precisely adjusted to promote adequate melting and distribution of the PPS matrix throughout the fiber network, after several trial runs based on the Taguchi method were conducted to determine the optimal settings of the hot-press machine. The fabric layers were subsequently placed into the press chamber and subjected to controlled thermal and mechanical conditions. Composite plates were produced through hot-pressing, resulting in hybrid structures with different fiber ratios (60/40 and 50/50 carbon/PPS) and braiding angles (30°, 45°, 60°) for comparative evaluation.

Figure 33. Tensile Test Conducted Along the Braiding Axis

Figure 34. Tensile Test Conducted Perpendicular to the Braiding Axis

In order to evaluate the mechanical performance of the produced composites, tensile tests were conducted on the plates manufactured with different braiding angles (30°, 45°, and 60°) and fiber ratios (60/40 and 50/50 carbon/PPS). Since the final application areas of the hybrid fabrics could not be predetermined, it was essential to characterize their strength in multiple orientations. Therefore, each sample was tested both along the braiding axis and perpendicular to the braiding axis to capture the anisotropic behavior of the structures. This dual-direction testing approach enabled a comprehensive assessment of the influence of braiding geometry and fiber ratio on the tensile response of the

composites. By comparing the results obtained from the different configurations, the role of braiding angle in balancing axial and transverse strength, as well as the contribution of the technical fiber ratio to overall load-bearing capacity, was clearly identified. Based on these observations, the optimal braiding angle and fiber ratio were selected, providing valuable insights into the design of hybrid braided composites for structural applications.

3. Results and Discussion

Table 6. Mean Tensile Strength Results of the Product with 60% Technical Fiber Content

Braiding Angle	**Mean Tensile Strength Results of the Product with 60% Technical Fiber Content**	
	Tensile Strength Test Results in the Braiding Axis Direction	Tensile Strength Test Results in the Transverse Direction to the Braiding Axis
60°	3249 N	5538 N
45°	3755 N	3679 N
30°	4132 N	3189 N

Table 7. Mean Tensile Strength Results of the Product with 50% Technical Fiber Content

Braiding Angle	**Mean Tensile Strength Results of the Product with 50% Technical Fiber Content**	
	Tensile Strength Test Results in the Braiding Axis Direction	Tensile Strength Test Results in the Transverse Direction to the Braiding Axis
60°	1673 N	5320 N
45°	3686 N	3502 N
30°	3958 N	3147 N

It was determined that a braiding angle of 45° provided the most favorable outcome in terms of both tensile strength and homogenization. The reasons for preferring this angle in the manufacturing process are listed below:

- **Balanced Fiber Alignment:** At a 45° braiding angle, the fibers are positioned in both axial and transverse directions in a balanced manner, which optimizes mechanical properties such as tensile strength, impact resistance, and flexibility.

- **High Homogenization:** The lower density variation achieved at 45° results in a more uniform structure throughout the material. This enables the thermoplastic polymer to fully integrate between the fibers, minimizing voids.

- **Pressing Efficiency:** A homogeneous density distribution allows the polymer matrix to spread more effectively during the pressing stage, ensuring that the desired mechanical properties are consistently obtained across the entire plate.

- **Optimum Performance:** The 45° braiding angle ensures optimum performance in terms of both tensile strength and homogenization, thereby improving the overall quality standards of the final composite product. This leads to uniform density throughout the material and excellent integration between polymer and fibers.

Although the test results indicated that the 60° braiding angle exhibited the highest transverse tensile strength and the 30° braiding angle provided the highest axial tensile strength, the 45° angle was chosen due to several technical advantages. In many applications, it is not sufficient for the material to demonstrate high tensile strength in only one direction.[7] Since fibers are arranged both axially and transversely at 45°, this angle enables multidirectional load-bearing capacity, ensuring balanced load transfer and stable mechanical performance in both orientations. Moreover, the difference in mechanical performance between axial and transverse directions is more balanced at 45° compared to other angles, making the material more reliable and durable against loads applied from different directions. Particularly in complex loading scenarios (impact, compression, or multidirectional forces), the multidirectional load-bearing capacity at 45° contributes to preserving the overall structural integrity of the composite.

In this study, the effect of braiding parameters on the structural behavior of carbon/PPS-based hybrid fabrics was systematically investigated. Evaluations carried out with different braiding angles and technical fiber ratios demonstrated, through tensile testing, that braiding parameters are a significant determinant of the product's characteristics. The test results showed variations in strength depending on the testing direction; however, when both directions were considered, the 45° braiding angle yielded the optimum performance. Furthermore, the configuration with 60% technical fiber content outperformed the 50% ratio, indicating superior mechanical properties at higher reinforcement content. The findings confirm that braiding parameters play a critical role in defining the mechanical performance of hybrid fabrics, and future studies will aim to further enhance the strength characteristics of the products.

3.1. Discussion

The experimental findings revealed that the 45° braiding angle offers the most balanced mechanical performance compared to 30° and 60°. While 30° and 60° angles provided higher tensile strength in the axial and transverse directions respectively, the 45° configuration achieved a more uniform distribution of load-bearing capacity in both orientations. This balance is particularly critical in engineering applications where composites are subjected to multidirectional stresses rather than uniaxial loading. The superior performance of the 45° angle demonstrates that optimizing braiding geometry is not only a matter of maximizing strength in one direction but of achieving structural reliability under complex service conditions.

The influence of fiber ratio was also significant, as the 60% carbon / 40% PPS configuration outperformed the 50/50 ratio. This result underlines the importance of reinforcement content in determining the overall tensile capacity of hybrid fabrics. Nevertheless, increasing the proportion of thermoplastic fibers enhances processability and matrix distribution, suggesting that a trade-off must be considered between mechanical performance and manufacturing flexibility. Such findings provide valuable guidance for tailoring hybrid composite designs based on the intended application.

These observations are consistent with previous studies in the literature, which reported that intermediate braiding angles often deliver more balanced strength characteristics, while higher reinforcement content leads to improved stiffness and tensile capacity. The present results extend this knowledge by highlighting the role of PPS as a thermoplastic matrix in achieving good fiber-matrix integration and reducing void formation during hot-pressing.

From an application standpoint, the identified optimum configuration—45° braiding angle with 60% carbon fiber content—offers significant potential for aerospace and automotive components, where lightweight structures must withstand both axial and transverse loading. The multidirectional performance and enhanced homogeneity achieved in this study suggest that such hybrid braided composites can contribute to safer, more reliable, and more efficient structural designs.

4. Conclusions

This study demonstrated that both braiding angle and fiber ratio play decisive roles in determining the mechanical performance of carbon/PPS hybrid braided composites. Among the tested configurations, the 45° braiding angle provided the most balanced mechanical behavior, offering uniform strength in both axial and transverse directions while ensuring good homogeneity of fiber distribution. In terms of fiber content, specimens with 60% carbon fiber and 40% PPS exhibited superior tensile strength compared to those with a 50/50 ratio, confirming the influence of reinforcement proportion on load-bearing capacity.

Overall, the findings highlight that optimization of braiding parameters is essential for tailoring hybrid composites to meet performance requirements in advanced structural applications. The identified optimum configuration—45° braiding angle with 60% carbon fiber—provides valuable design guidance for lightweight, high-performance components in aerospace and automotive industries.

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Validating Ballistic Impact Limits of Fiber-Metal Laminated Glare Composites as Lightweight Aerospace-Grade Material: Experimental and Simulation Studies

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ABSTRACT

Fiber-metal laminate composite materials offer unique advantages over traditional aerospace materials like monolithic aluminum or carbon fiber composites. GLARE composites are utilized in aerospace applications for their exceptional damage tolerance and lightweight properties to address sustainability concerns. This study investigates the ballistic impact limit of aerospace-grade GLARE 4A-3/2-0.4 composites. Finite element analysis models were calibrated using a two-dimensional ballistic phase diagram for conical projectile impacts on aerospace-grade Al 2024-T3. The ballistic response of the GLARE configuration was further examined under high-velocity impacts by spherical projectiles, with ballistic limit velocities determined through simulation and confirmed by gas-gun experiments. Post-impact damages were characterized using non-destructive ultrasonic inspection, optical microscopy, and computed tomography to provide insights into failure mechanisms. A 3-D ballistic limit diagram was constructed to analyze the effects of aluminum layer thickness and projectile diameter on impact resistance. The outcome of this study offers a valuable toolset for optimizing the structural design and enhancing the impact resilience of sustainable aerospace-grade laminated materials.

Keywords : Fiber-metal laminate (FML), Ballistic impact, Aerospace materials, Composite Failure, Finite element analysis (FEA), Support vector regression (SVR).

1. Introduction

Ballistics inseparably connects applied physics and the mechanics of materials to study the behavior of a projectile within the barrel, in flight, and upon impact with a target. Ballistics is commonly divided into three main categories: internal, external, and terminal ballistics. Internal ballistics concerns the mechanical and chemical processes that occur within a firearm during firing, including ignition, gas expansion, and projectile acceleration. This stage is critical for optimizing muzzle velocity and ensuring consistent performance across varying environmental conditions [1]. External ballistics examines the behavior of a projectile in flight, from the moment it exits the barrel until it reaches the target, taking into account factors such as aerodynamics, gravity, and atmospheric conditions. During this stage, trajectory, stability, and impact accuracy are analyzed, especially for long-range or high-velocity projectiles [2]. Terminal ballistics focuses on the interaction between the projectile and the target, including penetration behavior, energy transfer, and the resulting deformation of both materials. This stage is essential for the design of protective systems and the development of projectiles tailored for specific penetration or fragmentation effects [3,4,5]

A ballistic impact is generally defined as a low-mass, high-velocity collision caused by a projectile propelled by an external source. This type of impact encompasses several physical phenomena and is influenced by multiple factors, including the projectile's and the target's configuration, mass, and material properties, as well as the angle of incidence at which the projectile strikes [6]. According to classification based on impact velocity, impact events are divided into three types. Low-energy impacts are referred to as low-

velocity impacts, which may cause localized deformation without complete penetration [7]. High-energy impacts, often coined as high-velocity impacts, are more commonly known as ballistic impacts, where the projectile possesses enough kinetic energy to cause penetration or structural damage [8]. The third category, known as hypervelocity impacts, involves extremely high energy levels and can result in severe fragmentation, melting, or vaporization of materials upon impact [9,10,11].

Ballistic impact plays a critical role in the aerospace industry, with applications that span both the protection of aircraft in war theaters and the mitigation of environmental threats such as bird strikes. Within this framework, the study of terminal ballistics is essential for informing the design and development of advanced structural materials that exhibit a favorable balance between lightweightness and superior mechanical performance [12, 13]. Materials such as aramid fibers (e.g., *Kevlar*) and ultra-high molecular weight polyethylene (UHMWPE; e.g., *Dyneema*, *Spectra*) are widely utilized due to their exceptional energy absorption and impact resistance characteristics [14]. In addition, ceramic composites including alumina, boron carbide, and silicon carbide as well as titanium alloys, are employed in aerospace applications where ballistic protection must be achieved without compromising weight efficiency [15]. Among these, GLARE (Glass Laminate Aluminum Reinforced Epoxy) composites represent a significant innovation, offering improved damage tolerance, fatigue resistance, and reduced structural weight, thereby enhancing both the survivability and fuel efficiency of modern aircraft platforms [16].

GLARE composite material represents a prominent example of impact-resistant materials employed in the aerospace industry. As part of the Fiber Metal Laminate (FML) composites, GLARE consists of alternating layers of aluminum alloy sheets and unidirectional (UD) S-glass fiber prepregs embedded in an epoxy matrix. The number, orientation, and stacking sequence of the UD prepreg layers can be tailored according to specific engineering requirements and performance objectives. GLARE exhibits a combination of desirable properties, including high structural efficiency, enhanced damage tolerance, superior impact and fatigue resistance, as well as excellent flame and corrosion resistance [17, 18]. Due in part to these characteristics, it has found widespread application in civil transport aircraft, particularly in structural elements such as upper and lower wing skins, fuselage panels, passenger floors, bulkheads (straight or curved), firewalls, and cargo barriers [19, 20].

GLARE is produced in six primary grades, categorized into two subgroups: Group A (GLARE 1, 2, and 3) and Group B (GLARE 4, 5, and 6). The subgroup classification is based on the orientation of the prepreg fibers and the intended application. Group A grades are designed for high static load-bearing applications, while Group B grades are optimized for enhanced impact and fatigue resistance [21]. Among these, GLARE 4 has been the subject of extensive research due to its superior performance in resisting ballistic and fatigue-induced damage. It has been utilized in critical structural components, such as the fuselage panels of the Airbus A380 [22, 23].

Numerous factors influence the ballistic limit of composite materials, including material composition, layer configuration, and projectile characteristics. Extensive research has been conducted to evaluate the ballistic performance of various GLARE grades. The inclusion of bonding materials within laminated structures has been shown to enhance ballistic resistance. For example, one study reported an average increase of 1.5% in the ballistic limit for bonded panels compared to unbonded configurations [24]. In addition, the thickness of the aluminum layers and the geometry of the impacting projectile significantly affect the ballistic performance of GLARE composites. A comparative study examined the ballistic behavior of GLARE under flat and conical projectile impacts, with the objective of assessing the damage mechanisms and protective capabilities of the laminates under different impact conditions [25]. Furthermore, the ballistic performance of alternative Fiber Metal Laminates (FMLs), such as those incorporating ultra-high molecular weight polyethylene (UHMWPE) fiber composites combined with 2024-T3 aluminum sheets, has been investigated. This research evaluated the energy absorption capacity and failure modes of the FMLs when subjected to various projectile types under dynamic loading conditions [26].

Among the various GLARE grades, GLARE 5 has been the subject of the most extensive ballistic studies. Multiple investigations have explored how fiber orientation affects the ballistic limit of GLARE 5 composite materials. One such study demonstrated that the fiber orientation plays a critical role in the ballistic

impact response of GLARE 5 fiber-metal laminate (FML) beams. Specifically, the unidirectional [90°$_4$] configuration exhibited the lowest impact resistance, while the cross-ply [0°/90°] configuration showed the highest contact resistance due to its enhanced energy dissipation capability [27]. In addition to fiber orientation, both experimental and numerical studies have been conducted to assess the effect of material thickness on ballistic performance. For instance, investigations into the influence of thickness and stacking sequence on the ballistic behavior of GLARE 5 plates have focused on damage evolution, C-scan imaging, projectile velocity profiles, and ballistic limit velocity (V_{50}) [28, 29]. Another study revealed that the V_{50} value increases parabolically with increasing specimen thickness but decreases with higher metal volume fractions, indicating a trade-off between structural weight and ballistic protection [30]. In addition to GLARE 5, ballistic limit estimation studies have also been conducted for the GLARE 4A-3/2-0.5 configuration. Numerical simulations using ANSYS LS-DYNA have been employed to model the ballistic response of this material. These simulations enabled the prediction of critical parameters such as ballistic limit velocity, impact force, and absorbed energy, while also illustrating key damage mechanisms observed during impact events [31].

This study presents a validation of the ballistic impact limit for GLARE 4A-3/2-0.4 composite laminates. Finite element models were initially developed in ABAQUS and calibrated using a reference two-dimensional ballistic phase diagram for conical projectile impacts on 6.35 mm-thick Al 2024-T3 plates. Model accuracy was cross-validated through comparison with LS-DYNA simulations. The ballistic response of the three-layer GLARE configuration was then investigated under high-velocity impacts by spherical projectiles (3 cm diameter), with ballistic limit velocities determined through simulation and confirmed by gas-gun experiments. Post-impact damage in the tested specimens was characterized using non-destructive ultrasonic inspection, with optical microscopy and computed tomography (CT) providing additional three-dimensional insights into damage morphology and failure mechanisms across different impact velocities. A three-dimensional ballistic limit diagram was constructed to map the influence of aluminum layer thickness and projectile diameter on impact resistance. The results demonstrate the feasibility of integrating finite element analysis with experimental validation for accurate prediction of ballistic performance in GLARE composites. The approach offers a valuable toolset for optimizing the structural design and enhancing the impact resilience of aerospace-grade laminated materials.

2. Materials And Methods

The aerospace-grade 2024-T3 aluminum alloy sheets used in the fabrication of the GLARE material were chemically milled from an initial thickness of 1.8 mm to a final thickness of 0.4 mm. The resulting laminate comprises three aluminum sheet layers interleaved with two unidirectional (UD) glass fiber-reinforced prepreg layers, each arranged in a [0/90/0] fiber orientation. The composite utilizes a commercial-grade FM94-27% S2-Glass 187-460 prepreg, with a nominal cured ply thickness (CPT) of approximately 0.13 mm. The detailed stacking sequence of the GLARE 4A configuration is depicted in Figure 1.

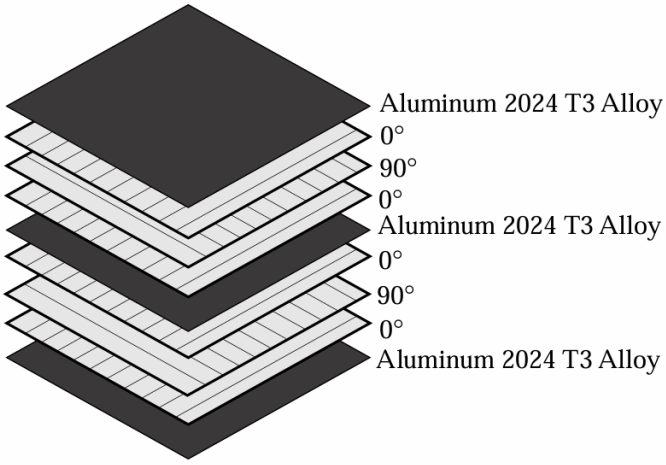


Figure 1. The stacking Sequence of the GLARE 4A-3/2-0.4 composite material.

The GLARE 4A-3/2-0.4 composite specimens were fabricated using a controlled thermal cure cycle. During the process, a constant pressure of 6.9 bar and a vacuum level of 650 mmHg were applied. The temperature was initially increased at a controlled rate of 0.5–3.5 °C/min until reaching 125 °C. The curing was then carried out at a constant temperature of 125 °C for a duration of 90 to 120 minutes. Following the cure, the specimens were cooled to room temperature at a rate of 0.5–3.5 °C/min. The detailed thermal cure cycle of the GLARE composite is illustrated in Figure 2.

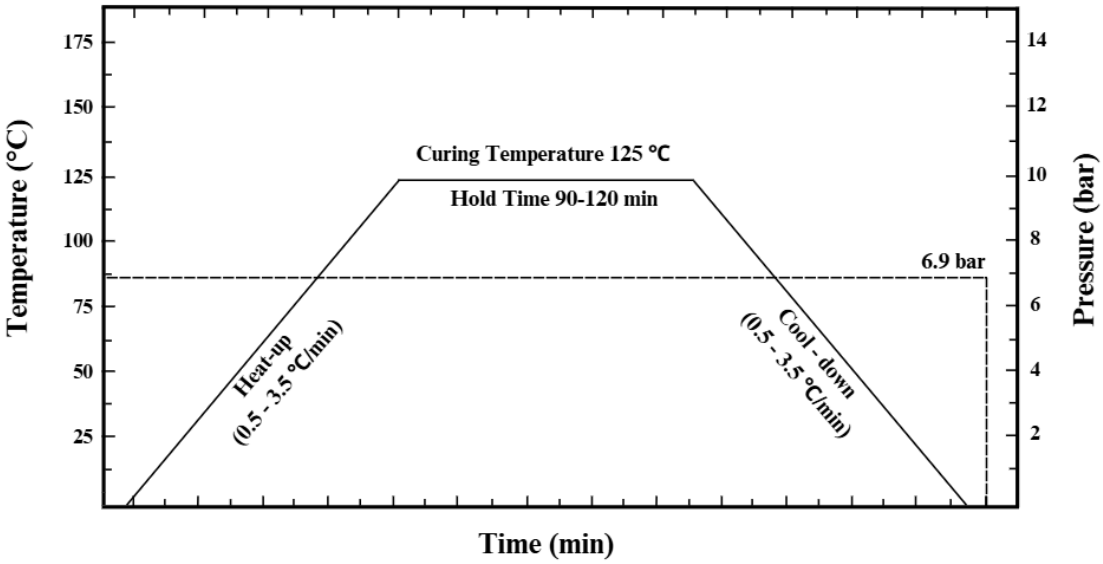


Figure 2. The thermal cure cycle of the GLARE composite.

An experimental test setup utilizing a gas gun system was established to evaluate the ballistic performance of the GLARE composite material. The schematic representation of the setup is provided in Figure 3, detailing the configuration and positioning of all critical components. The projectile velocity was controlled by varying the amount of propellant in the cartridge, with three shots conducted at velocities of 95.97 m/s, 141.49 m/s, and 103.20 m/s, respectively. Projectile velocity was measured using a high-precision chronograph synchronized with two LED photovoltaic detectors positioned 2 m apart. The measurement system was located 10 m from the target. A high-speed camera, placed adjacent to the specimen fixture, recorded the experimental sequence and captured detailed visual data of the impact events. Additionally, an aluminum witness plate was mounted 150 mm behind the target to assess projectile fragmentation and residual velocity. The fracture behavior and post-impact dynamics of the target were analyzed using the high-speed camera operating at 46,000 frames per second (fps) with a resolution of 256 × 176 pixels.

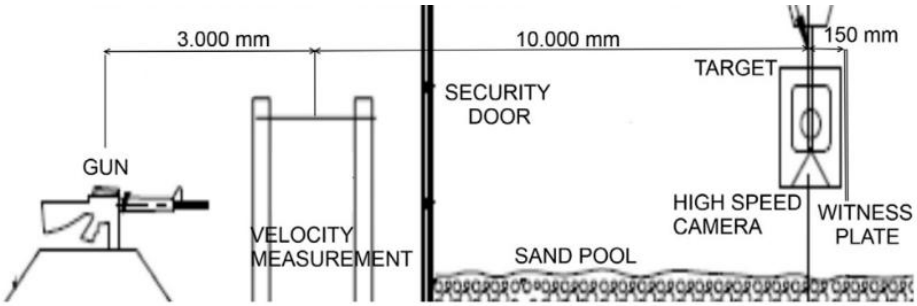


Figure 3. The schematic representation of the ballistic impact test setup [32].

The ballistic impact limit phase diagram of the aerospace-grade Al material was validated through finite element simulations conducted using ABAQUS software. The geometric and material parameters of the projectile, including its caliber and shape, as well as the thickness of the target aluminum plate, were

modeled in accordance with the experimental ballistic phase diagram. The finite element models of the projectile and the target plate are presented in Figure 4. For the 6.35 mm caliber projectile, a central porosity of approximately 0.45 mm was defined. The porosity distribution within the target plate was designed to be maximal at the center and gradually decrease toward the periphery. This gradient reflects the intended impact location at the plate center, enabling detailed analysis of localized damage mechanisms and energy dissipation during high-velocity impact.

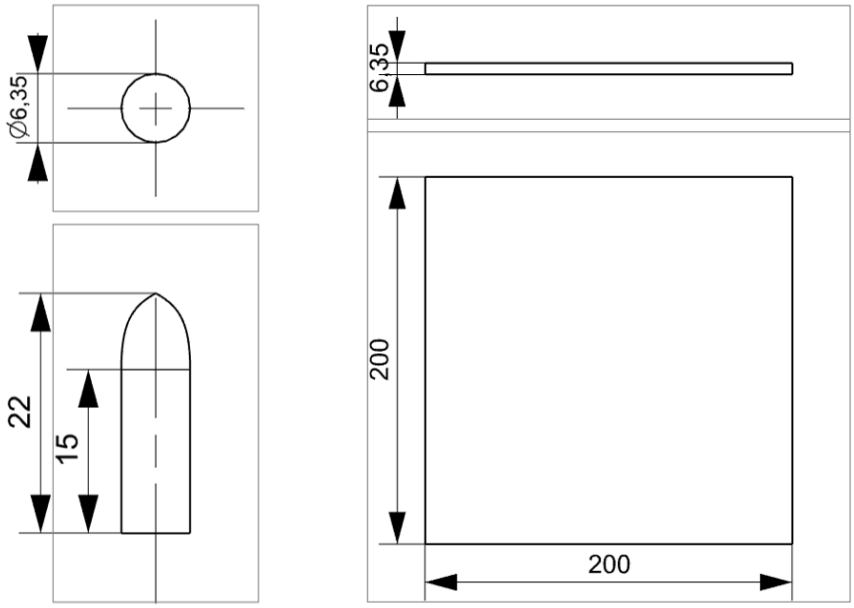


Figure 4. 2D engineering drawings of the conical projectile and target aerospace-grade Al material used in finite element models. All dimensions are given in millimeters.

The ballistic impact behavior of the GLARE composite was further validated using LS-DYNA finite element analysis software. A spherical steel projectile with a diameter of 3 cm was employed in the simulation. The GLARE composite model was constructed by explicitly defining the orientation and material properties of each constituent layer, including the aluminum sheets and fiber-reinforced prepregs, in accordance with the characteristics of the projectile and the experimental setup. Upon completion of all material and geometric definitions, the simulation was finalized. The mesh structure consisted of 814 elements for the composite specimen and 189 elements for the projectile, with a total of 908 nodes defined in the computational domain. The material properties utilized in the simulations are summarized in Table 1, Table 2, and Table 3.

Table 1. Material properties of Al 2024-T3 used in finite element modeling.

Parameter	Notation	Property Value
Density (kg/m³)	ρ	2770
Poisson's ratio	v	0.33
Young's Modulus (GPa)	E	73.084
Static Yield Limit (MPa)	A	369
Strain Hardening Modulus (MPa)	B	684
Strain Hardening Exponent	n	0.73
Strain Rate Coefficient	C	0.0083

Table 2. Material properties of steel used in finite element modeling.

Parameter	Notation	Property Value
Density (kg/m³)	ρ	7600
Poisson's ratio	v	0.33
Young's Modulus (GPa)	E	207

Table 3. Material properties of glass fiber reinforced polymer matrix prepreg used in finite element modeling.

Parameter	Notation	Property Value
Density (kg/m³)	ρ	2000
Poisson's Ratio	*PRBA* (v_{21})	0.0575
	PRCA (v_{31})	0.0575
	PRCB (v_{32})	0.33
Young's Modulus (GPa)	*EA* (E_1)	54
	EB (E_2)	9.4
	EC (E_3)	9.4
Shear Modulus (GPa)	*GAB* (G_{12})	5.6
	GBC (G_{23})	5.6
	GCA (G_{31})	5.6
Shear Strength (MPa)	*SC* (S_{12})	76
Longitudinal Tensile Strength (MPa)	*XT* (S_1)	1900
Transverse Tensile Strength (MPa)	*YT* (S_2)	57
Transverse Compressive Strength (MPa)	*YC* (C_2)	285

Ultrasonic testing was employed to investigate internal damage within the material with greater precision. The non-destructive testing (NDT) technique operates on the principle of partial or complete reflection (echo) resulting from variations in acoustic impedance, defined as a material's resistance to the propagation of sound waves [33]. High-frequency ultrasonic waves in the range of 0.2–25 MHz were utilized to detect internal discontinuities and defects. In this study, an automated squirter-type through-transmission ultrasonic inspection method was implemented. A transducer with a central frequency of 5 MHz was employed and positioned at a 0° incidence angle to ensure optimal wave propagation and accurate signal interpretation.

X-ray computed tomography (CT) was employed to analyze the internal damage structure of the material in detail. CT is a non-destructive imaging technique that utilizes the differential transmission of X-rays through materials with varying densities, enabling visualization of internal features without compromising the integrity of the specimen. In this study, a X3000 Industrial CT Scanning System was utilized. During the scanning procedure, the X-ray source was operated at a voltage of 150 kV and a current of 200 µA. The specimen was rotated through 360°, and images were acquired from multiple angular positions. These projections were reconstructed into a three-dimensional (3D) volumetric model using efX-CT software developed by North Star Imaging company. The reconstructed CT data were analyzed to identify internal defects such as cracks, porosity, and delaminations within the composite structure.

A high-resolution Epson Perfection V700 flatbed scanner was utilized to digitally analyze the surface properties of the composite material. This scanner is capable of achieving a maximum resolution of 6400 × 9600 dpi, allowing for detailed surface imaging. During the scanning process, the specimen was secured on a flat substrate and positioned on the scanner's glass bed. The scanning was conducted at a resolution of 4800 dpi, with 48-bit color depth for full-color imaging. For high-precision surface texture analysis, scans were also performed in 16-bit grayscale format. The scanner employs a CCD (Charge-Coupled Device) sensor in conjunction with LED-based illumination, providing high-fidelity image acquisition. The resulting digital images were subsequently processed and analyzed to evaluate surface features and potential surface-level damage.

3. Results And Discussion

To validate the accuracy of the reference ballistic impact phase diagram of Al material, a series of simulations replicating key points from the diagram were conducted using ABAQUS Explicit analysis software [34]. Four representative impact conditions were selected: (a) 300 m/s velocity at 0° incidence; (b) 200 m/s velocity at 0° incidence; (c) 500 m/s velocity at 40° incidence; and (d) 200 m/s velocity at 20° incidence. The selection of these points, featuring variations in both velocity and impact angle, was critical to comprehensively assess the reliability of the phase diagram. The chosen impact conditions and their corresponding simulation results are illustrated in Figure 5. For Point (a), the phase diagram predicts the perforation of the plate by a projectile traveling at 300 m/s with perpendicular impact, which the simulation results confirm by demonstrating projectile penetration. Point (b) involves a projectile velocity of 200 m/s at normal incidence, where the phase diagram indicates no perforation; this outcome is similarly validated by the simulation, showing the projectile failing to penetrate the plate. At Point (c), the projectile impacts at 500 m/s with a 40° inclination, resulting in perforation as predicted by the phase diagram and corroborated by simulation. Finally, Point (d), representing an impact at 200 m/s and 20° inclination, demonstrates no penetration in both the phase diagram and simulation outcomes. The strong agreement between the ABAQUS Explicit simulation results and the ballistic phase diagram confirms the accuracy and consistency of the phase diagram. Therefore, these results substantiates the phase diagram as a reliable tool for predicting ballistic impact behavior in further assessments.

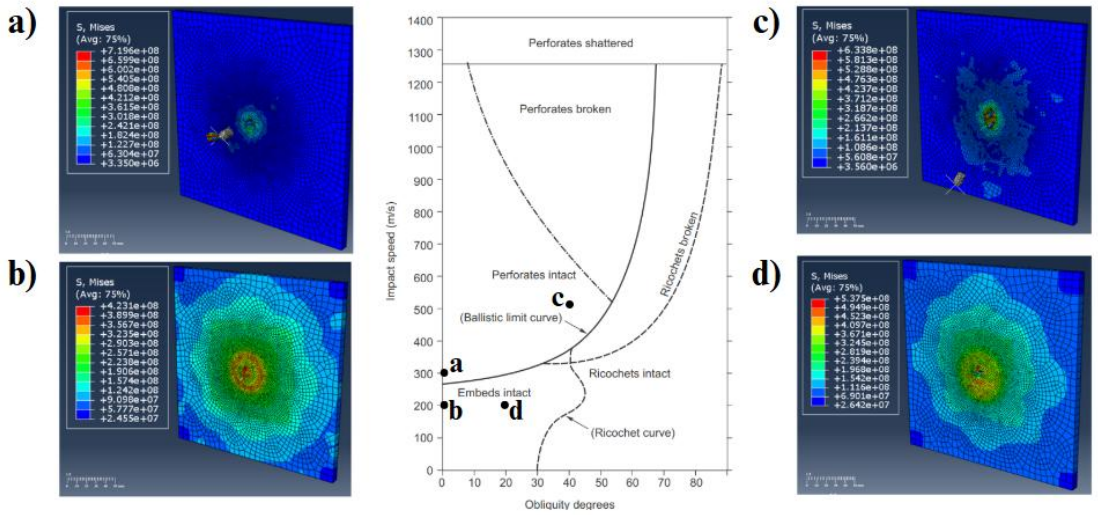


Figure 5. The validation of ballistic phase diagram for the conical projectile and Al target plate with ABAQUS used to calibrate the finite element model [34].

The results of these simulations demonstrated that the phase diagram accurately corresponds with the finite element models implemented in ABAQUS. The subsequent objective is to assess the compatibility

of the phase diagram with LS-DYNA, which will be employed for ballistic simulations involving GLARE composite materials. The use of two distinct finite element software packages for this validation process is motivated by several considerations. Primarily, to evaluate the accuracy of LS-DYNA in modeling ballistic impacts on GLARE composites; a reliable reference ballistic test is necessary. The ballistic limit phase diagram of the aluminum plate serves as this benchmark. However, to ensure both the credibility of the phase diagram and the consistency of simulation outcomes of LS-DYNA, an independent verification tool was required [34]. Therefore, ABAQUS Explicit analysis was utilized to confirm that the phase diagrams of LS-DYNA, and ABAQUS yield mutually consistent results. Without this cross-validation via ABAQUS, relying solely on LS-DYNA would have been inadequate to fully validate the phase diagram or to accurately predict the ballistic performance of GLARE composites.

To further validate the phase diagram using LS-DYNA, a finite element analysis approach consistent with the previous ABAQUS modeling was adopted. In this model, the target plate was defined as a projectile shell, while the impacting object was represented as an ogival-nosed projectile. The mesh configuration included 5,625 elements for the Al plate and 875 elements for the projectile. Material properties corresponding to 2024-T3 aluminum for the plate and the projectile were assigned. For consistency and comparative purposes, two specific test conditions were selected for the LS-DYNA simulations as previously evaluated in ABAQUS: (a) a projectile velocity of 300 m/s at 0° impact angle and (b) a projectile velocity of 200 m/s at 0° impact angle. These two conditions were chosen for two primary reasons. First, their inclusion in the ABAQUS analyses enables a direct comparison between ABAQUS and LS-DYNA results under identical boundary conditions. Second, both test cases involve normal (perpendicular) impacts, which aligns with the planned experimental configuration utilizing a gas gun to launch projectiles perpendicularly into GLARE composite specimens. Given that oblique impact angles are not being considered in the current experimental design, angled cases such as points (c) and (d) from the phase diagram were excluded from the LS-DYNA analysis. The selected impact scenarios and the corresponding LS-DYNA simulation results are illustrated in Figure 6.

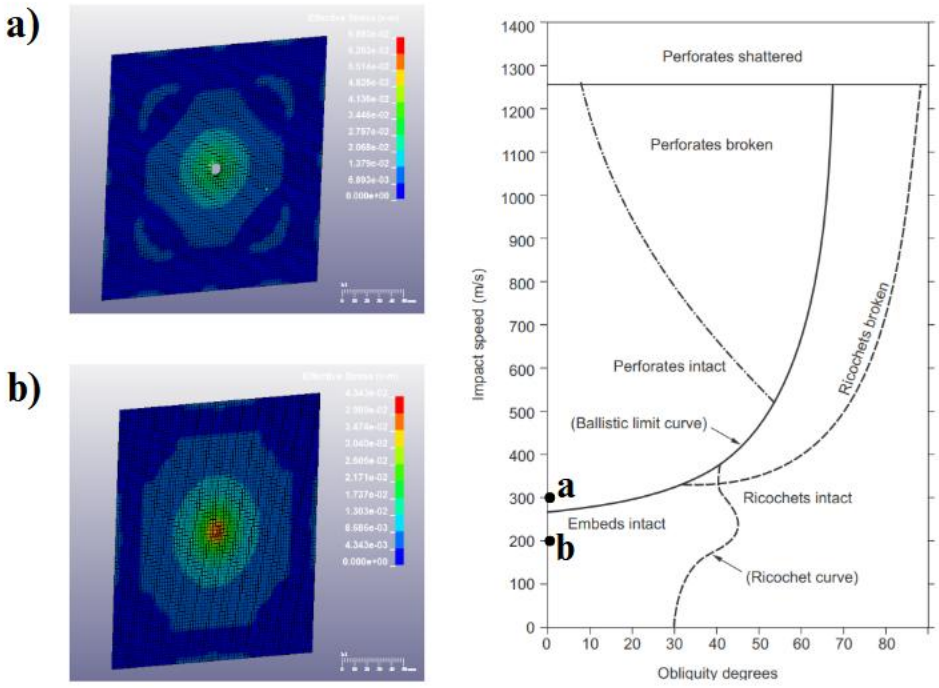


Figure 6. Finite element modeling results with LS-DYNA for (a) 300 m/s velocity at 0° inclination with perforation, and (b) 200 m/s velocity at 0° inclination without perforation, used for model calibration..

Based on the analysis results presented in Figure 6, the projectile impacting the Al plate at a velocity of 300 m/s and a 0° inclination (Point A on the phase diagram) was observed to achieve full perforation. This result is in strong agreement with both the predictions of the ballistic limit phase diagram and the

corresponding simulation outcomes obtained from ABAQUS. Similarly, for the second selected case (Point B), where the projectile velocity was 200 m/s at a 0° inclination, the projectile failed to penetrate the plate. This finding is likewise consistent with both the phase diagram and ABAQUS simulation results. These observations indicate a high level of correlation and consistency between the ballistic limit phase diagram for 2024-T3 aluminum, the ABAQUS Explicit analyses, and the LS-DYNA simulations [34]. As a result, LS-DYNA is validated as a reliable tool for modeling ballistic impact phenomena and can be confidently extended to simulate the ballistic response of GLARE 4A-3/2 composite materials. Therefore, the ballistic limits predicted by these simulations are considered accurate and can serve as a dependable basis for further analytical and experimental investigations.

The ballistic test setup was replicated in a numerical environment by modeling a three-layer GLARE composite system, comprising an aluminum 2024-T3 matrix interleaved with two glass-epoxy prepreg layers. A 3 cm diameter steel sphere was defined as the projectile, with appropriate material properties assigned to accurately reflect realistic ballistic impact conditions. Following the completion of the model definitions, simulations were conducted at three distinct impact velocities to evaluate the ballistic response and damage progression within the composite material. The simulation results, including deformation profiles and failure modes, are presented in Figure 7.

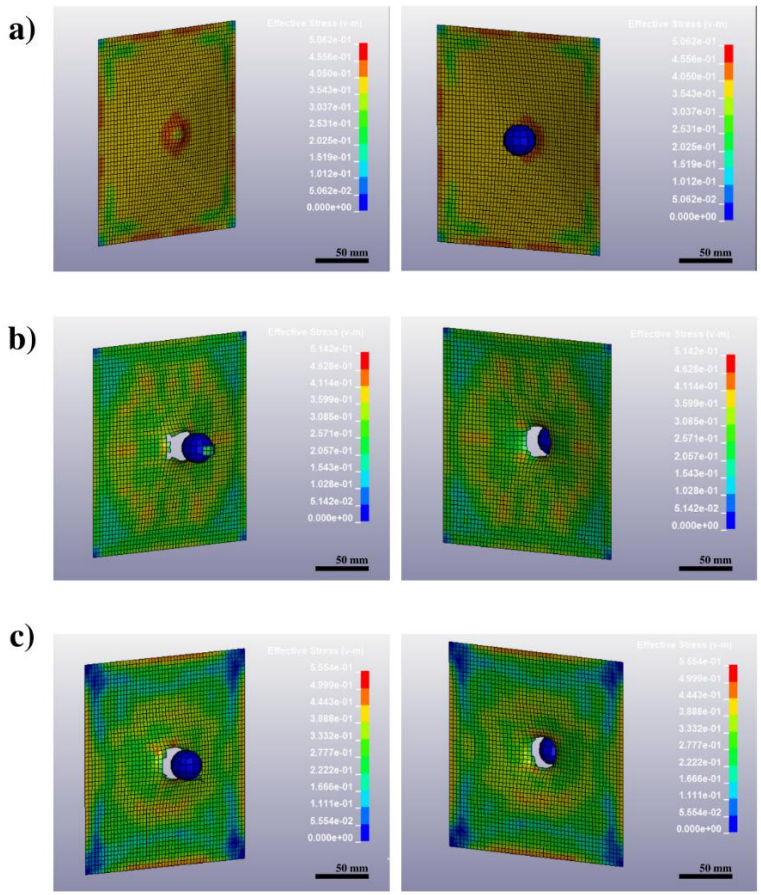


Figure 7. Finite element modeling results for velocities of a) 95 m/s, b) 145 m/s, and c) 105 m/s at 0° inclination. Left and right images represent back and front sides of GLARE specimens, respectively.

As illustrated in Figure 7, three distinct simulation scenarios were developed to determine the ballistic limit of the GLARE 4A-3/2 composite material, with projectile velocity as the primary variable. In the first scenario, the projectile was launched perpendicularly at a velocity of 95 m/s. The results revealed that the projectile failed to fully perforate the laminate, instead embedding within the material. This response

is categorized as “embeds intact” and is shown in Figure 7.a, indicating that the ballistic limit of the GLARE 4A-3/2 composite exceeds 95 m/s. In the second scenario, the impact velocity was increased to 145 m/s. The projectile successfully perforated the laminate without significant deformation, corresponding to a “perforates intact” outcome, as presented in Figure 7.b. This result suggests that the ballistic limit lies below 145 m/s, necessitating further simulations with intermediate velocities. Consequently, a third scenario was conducted at a reduced velocity of 105 m/s. Under this condition, the projectile again perforated the laminate, producing a “perforates intact” outcome, as shown in Figure 7.c. However, unlike the 145 m/s case, the residual velocity of the projectile dropped significantly to approximately 20 m/s after exit. This indicates a near-threshold ballistic condition, suggesting that the ballistic limit of the GLARE 4A-3/2 composite is in close proximity to 105 m/s.

The subsequent phase of this study involved the experimental replication of the simulation scenarios using a gas gun test setup. Three distinct GLARE 4A-3/2 composite specimens, each measuring 200 mm × 200 mm, were prepared and mounted within the gas gun assembly. A 3 cm diameter steel sphere, matching the mass and geometry of the simulated projectile, was used as the impactor. Firing velocities were carefully selected to mirror those employed in the simulations specifically, 95 m/s, 145 m/s, and 105 m/s. During the tests, the actual measured velocities were 95.97 m/s, 141.49 m/s, and 103.20 m/s, respectively.

High-speed video recordings were captured for each test to facilitate detailed observation and analysis. Figure 8 presents selected frames from the ballistic impact tests. In Figure 8.a, the steel projectile traveling at 95.97 m/s is shown just prior to impact (Figure 8.a-left) and immediately after rebounding from the target surface (Figure 8.a-middle and right). The experimental results confirm that the projectile did not penetrate the composite plate at this velocity, indicating an “embeds intact” outcome consistent with the simulation findings. In the second test, shown in Figure 8.b, the projectile velocity was 141.49 m/s. Figure 8.b-left captures the moment before impact, while Figure 8.b-middle and right illustrate the projectile after having fully perforated the GLARE plate. The results clearly indicate a “perforates intact” response, again corroborating the outcome predicted by the corresponding simulation. Figure 8.c presents the third test scenario, in which the steel projectile was fired at a velocity of 103.20 m/s toward the mounted GLARE 4A-3/2 composite specimen. Figure 8.c-left captures the projectile immediately before the impact, while Figure 8.c-middle and right illustrate the moment of contact and the subsequent perforation event. The results indicate that the projectile successfully penetrated the composite, resulting in a “perforates intact” outcome. This behavior closely mirrors that observed in Figure 8.b, further confirming that the ballistic limit of the composite is around 103.20 m/s.

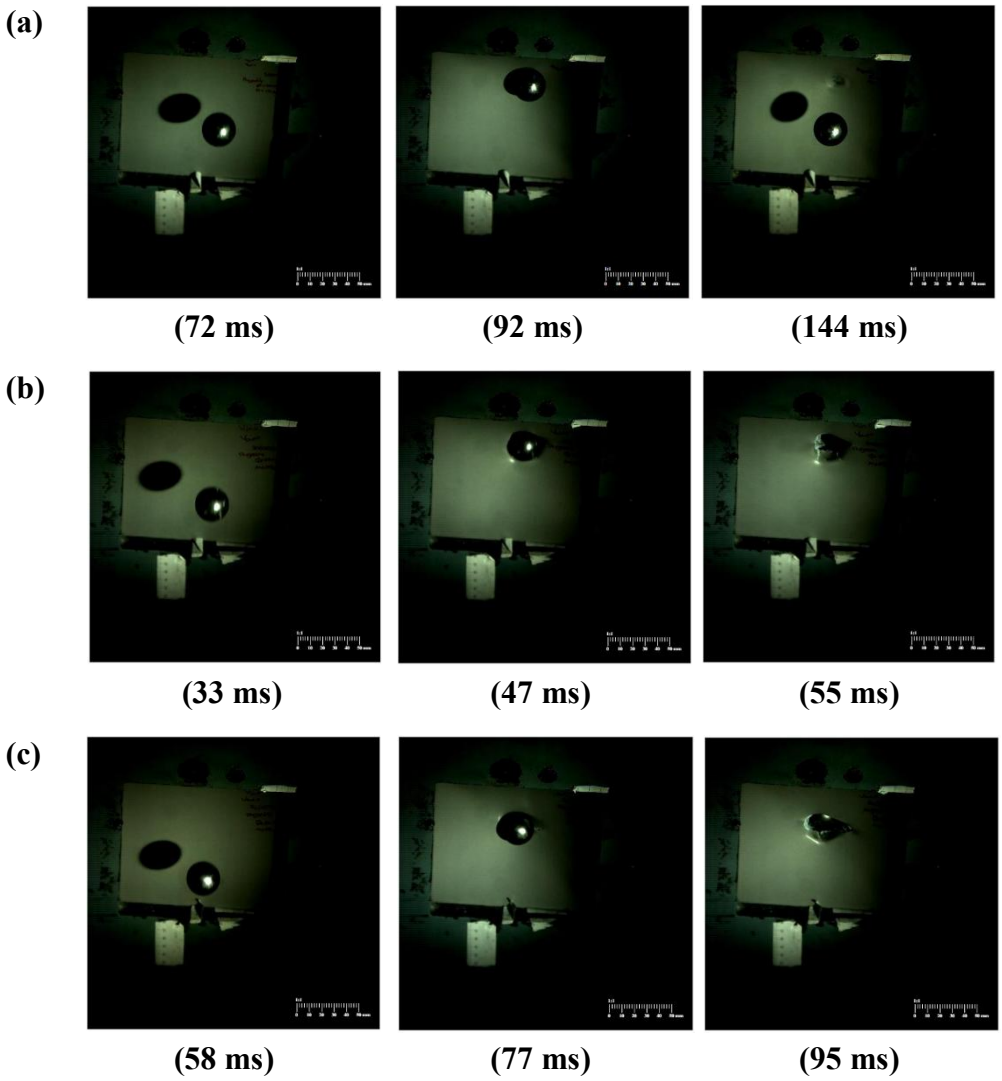


Figure 8. Experimental test results for speeds a) 95.97 m/s, b) 141.49 m/s, and c) 103.20 m/s with obliquity degree of 0°.

In the impact case illustrated in Figure 8.a, the primary reason the projectile remains embedded within the plate rather than achieving full penetration is the activation of fracture and energy-absorption mechanisms intrinsic to the layered architecture of the GLARE 4A 3/2 composite. Upon impact, the high stresses initiate various damage processes, including delamination, fiber breakage, and plastic deformation across the alternating aluminum and glass-epoxy layers [35]. These mechanisms collectively dissipate a significant portion of the kinetic energy of projectile, preventing it from surpassing the internal resistance of material. The resulting “embeds intact” outcome indicates that, while the projectile partially intrudes into the surface, it lacks sufficient residual energy to breach the laminate entirely. Near the ballistic limit, even minor changes in projectile velocity can significantly alter the damage evolution, by accelerating or delaying crack propagation, ultimately determining whether the plate is perforated. Conversely, in the scenarios depicted in Figures 8.b and 8.c, the projectile velocities exceed the ballistic limit, leading to more extensive and rapid progression of damage within the GLARE 4A-3/2-0.4 composite. Under these high-velocity conditions, the energy-absorbing mechanisms of composites are insufficient to arrest the projectile. As a result, the delamination, fiber rupture, and plastic deformation processes are overwhelmed, and the projectile successfully perforates the target [36]. The brief contact duration during high-speed impact further limits the effectiveness of energy dissipation mechanisms, such as interfacial

friction and distributed crack arresting. Although the aluminum and glass-epoxy layers exhibit substantial resistance to shear, tensile, and bending stresses, once the projectile velocity surpasses the critical threshold, these resistive capacities are exceeded, resulting in a “perforates intact” failure mode.

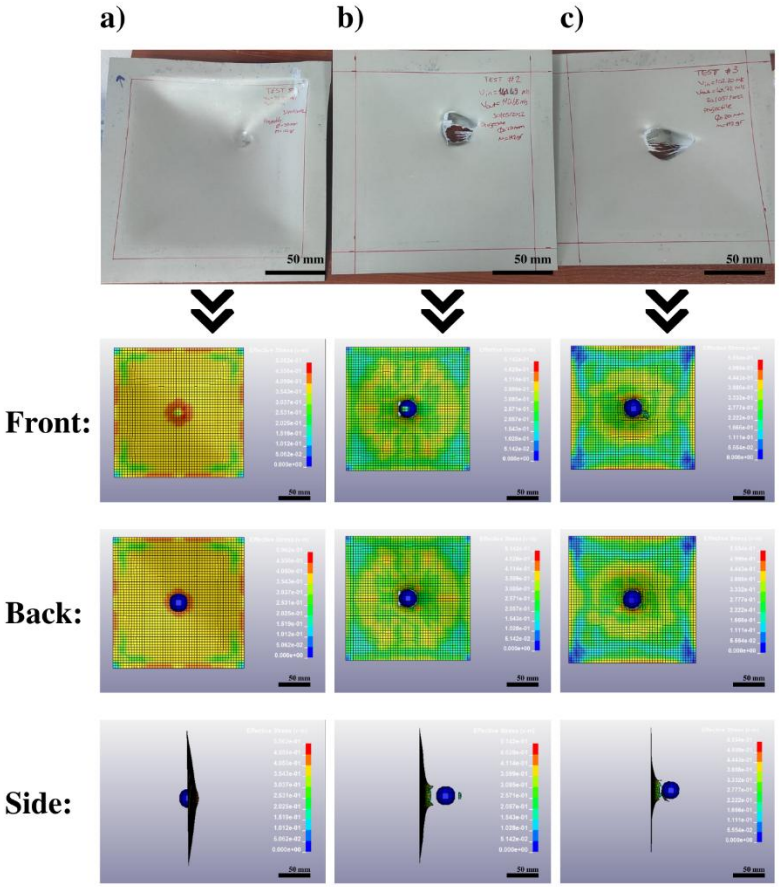


Figure 9. Comparisons of finite element modeling results and experimental test results for the velocities of a) 95 m/s, b) 141 m/s, and c) 103 m/s with the obliquity degree of 0°. The images represent front, back, and side views of GLARE specimens.

The simulation results and their corresponding gas gun experiments are presented in Figure 9. The strong correlation observed between the numerical simulations and the experimental data confirms that the ballistic perforation behavior of the GLARE 4A-3/2-0.4 composite material can be reliably captured using computational methods. Both the simulations and physical tests revealed consistent failure mechanisms, such as interlaminar delamination, fiber breakage, and plastic deformation of the aluminum layers. This outcome demonstrated that the selected material models and finite element strategies were implemented effectively. At lower impact velocities, as shown in Figure 9.a, the projectile does not fully perforate the specimen and instead remains embedded (“embeds intact”), a behavior replicated with high fidelity in the simulation. At increased velocities, as illustrated in Figures 9.b and 9.c, the projectile perforates the composite (“perforates intact”), with both the experimental and numerical results capturing the same damage progression. This high level of agreement underscores the critical importance of accurate numerical calibration particularly with respect to material property definitions, mesh density, contact algorithms, and boundary conditions for achieving predictive fidelity in finite element models of impact phenomena [37]. The results further validate the reliability of the modeling approach for future ballistic performance evaluations of GLARE composites.

Ultrasonic inspection was performed to investigate the internal damage sustained by the material as a result of ballistic impact. The NDT method operates on the principle of partial or complete reflection (echo) of high-frequency sound waves, which occurs due to variations in acoustic impedance, the material's resistance to sound wave propagation. These impedance differences, typically caused by internal flaws such as cracks, delaminations, or voids, disrupt the wave path and are detected as discontinuities [38]. In ultrasonic testing, sound waves in the frequency range of 0.2–25 MHz are used to evaluate internal features of the material. The unit of frequency, hertz (Hz), represents the number of oscillations per second [39]. In this study, an automated squirter-type through-transmission technique was employed. A transducer operating at a frequency of 5 MHz was positioned at a 0° angle relative to the specimen surface to ensure optimal wave propagation and signal reception. The results obtained from the ultrasonic inspection are illustrated in Figure 10.

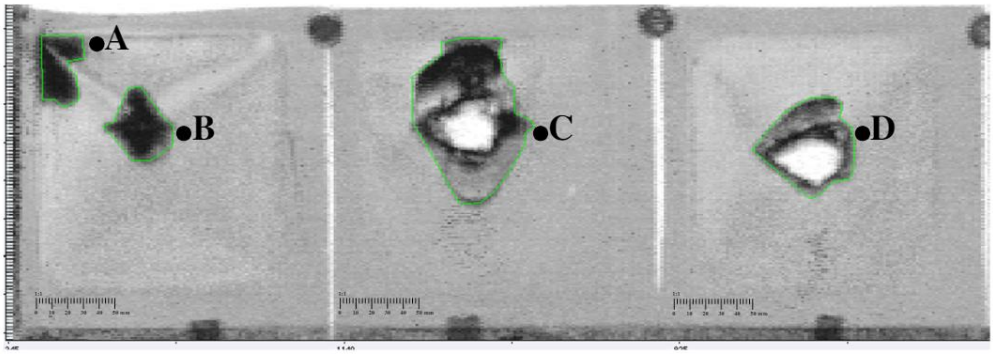


Figure 10. Ultrasonic inspection images of the GLARE specimens corresponding to impact velocities of a) 95.97 m/s, b) 141.49 m/s, and c) 103.20 m/s with obliquity degree of 0°.

Table 4. Calculated delamination areas of GLARE composites for highlighted objects in Figure 10.

OBJECT	DELAMINATION AREA (mm2)
A	837.96
B	1125.94
C	4841.74
D	2401.87

As illustrated in Figure 10 and summarized in Table 4, the three GLARE composite specimens subjected to ballistic impact, along with one undamaged reference panel, were analyzed using ultrasonic inspection. Amongst the tested specimens, the second one, impacted by a steel projectile at a velocity of 141.49 m/s, exhibited the most extensive delamination area, indicating the highest level of internal deformation. The first specimen revealed two distinct zones of deformation: one centrally located at the impact site and another near a fixed corner, likely influenced by boundary effects or stress wave reflections. In contrast, the third specimen displayed a smaller delamination region compared to the second, which may be attributed to the more severe residual (fracture) damage observed in the metal plies of the second specimen [40]. These findings suggest that while both delamination and fracture contribute to energy absorption, their distribution varies with impact velocity and local structural response.

Following the ultrasonic inspection, CT analysis was performed on the GLARE composite specimens to obtain a more comprehensive understanding of the internal damage resulting from ballistic impact. CT is an advanced non-destructive imaging technique that captures multiple two-dimensional radiographic projections at various angles and reconstructs them into a three-dimensional volumetric model of the specimen. This method enables detailed visualization of internal features such as delaminations, cracks, and fiber-matrix separations. In this study, CT imaging provided critical insights into the damage morphology and extent that are not easily detectable through surface or ultrasonic methods. Figure 11 presents representative tomographic images of the impacted GLARE specimens, clearly illustrating the internal damage characteristics induced by different impact conditions.

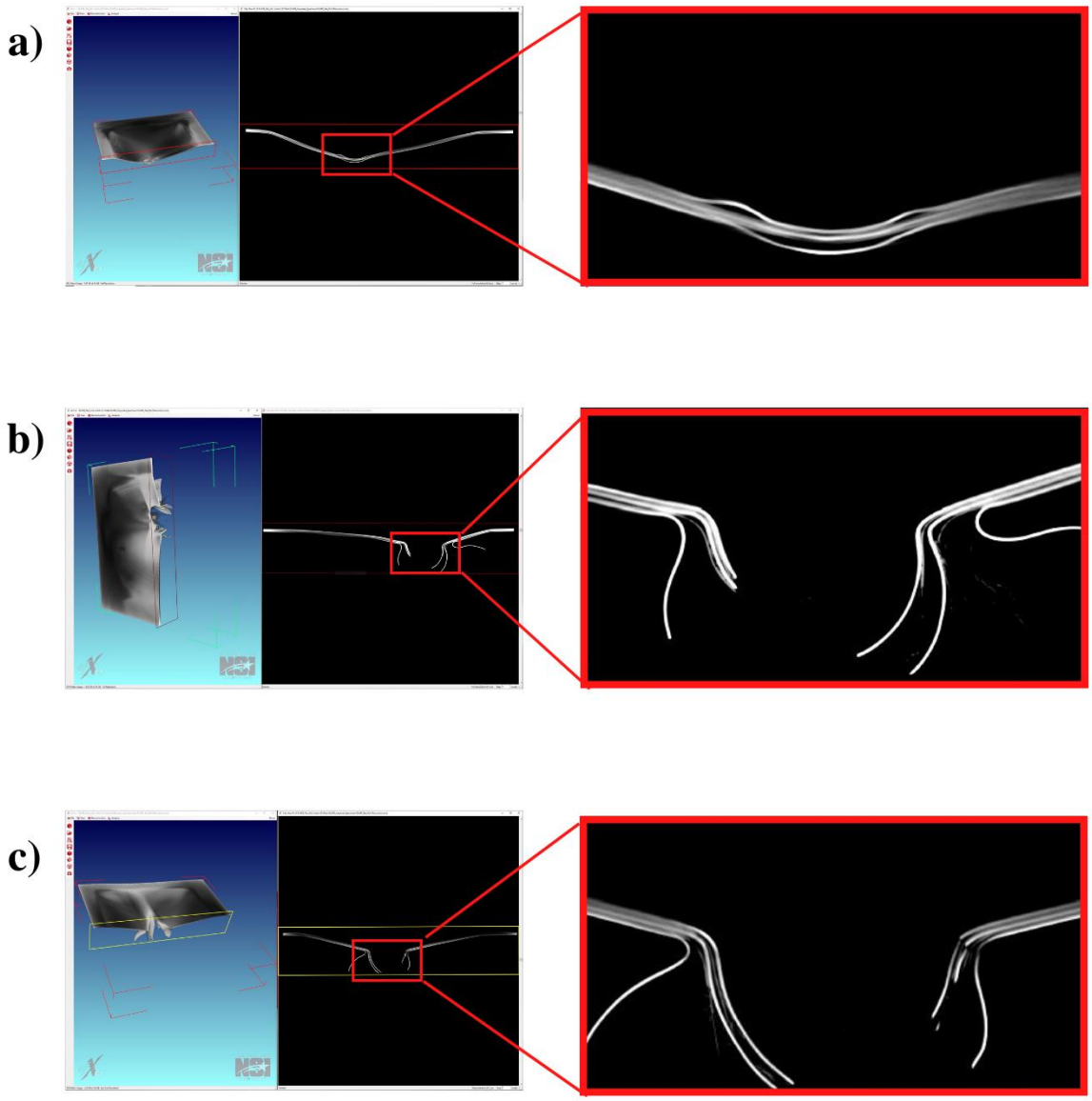
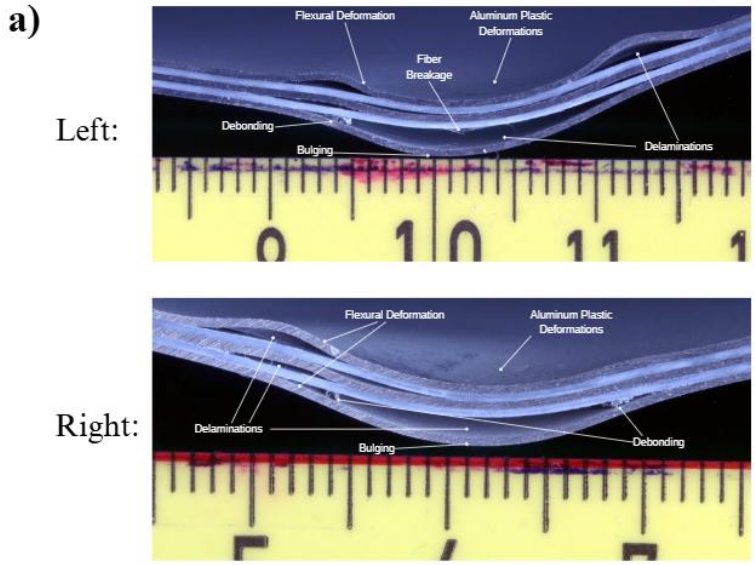


Figure 11. CT images of the impacted GLARE specimens test at the velocities of a) 95.97 m/s, b) 141.49 m/s, and c) 103.20 m/s with the obliquity degree of 0°.

Figure 11.a presents the CT image of the GLARE composite specimen subjected to the impact velocity of 95.97 m/s. Both the outer and inner surfaces of the specimen reveal significant flexural deformation in the composite layers, accompanied by evident plastic deformation in the aluminum plies, an indication of

permanent loss of elasticity. Bulging is observed at the rear impact site, yet no rupture or “petal” formation is present in the aluminum layers. CT imaging also reveals interfacial delamination between the aluminum matrix and the glass-epoxy prepreg layers. Additionally, the prepreg region exhibits localized fiber breakage and debonding within the glass fiber reinforcement. Figure 11.b shows the tomography of a second GLARE specimen impacted at 141.49 m/s. At this higher velocity, the steel projectile successfully perforated all composite layers. The aluminum plies demonstrate severe plastic deformation with through-thickness ruptures and clearly defined petaling on the exit side of the specimen. Cracking is present across the aluminum layers, while extensive delamination and matrix-prepreg separation are apparent. The glass fibers in the prepreg layers sustained considerable damage, including complete fiber breakage, rupture, and interfacial debonding [41]. Figure 11.c illustrates the tomographic reconstruction of the third specimen impacted at 103.20 m/s. The damage mechanisms observed in this specimen closely resemble those in Figure 11.b. All composite layers were penetrated by the projectile, and the aluminum plies experienced progressive plastic deformation resulting in full rupture and cracking. Petaling effects are also visible on the rear side. Similar to the previous case, the glass-epoxy prepreg layers exhibit extensive fiber breakage and debonding, confirming the critical damage progression once the ballistic limit is exceeded [42].

Following the gas-gun ballistic tests, the GLARE composite specimens were sectioned along the impact axis to expose the internal damage zones for detailed examination. After surface preparation and thorough cleaning of the cross-sections, each specimen was scanned using the flatbed scanner. This high-resolution scanning technique enabled the direct visualization of internal damage features associated with the projectile impact, providing valuable insights into the material’s penetration and perforation behavior previously identified through numerical simulations and experimental testing. The scanned cross-sectional images, along with the corresponding damage mechanisms observed within the composite architecture, are presented in Figure 12.



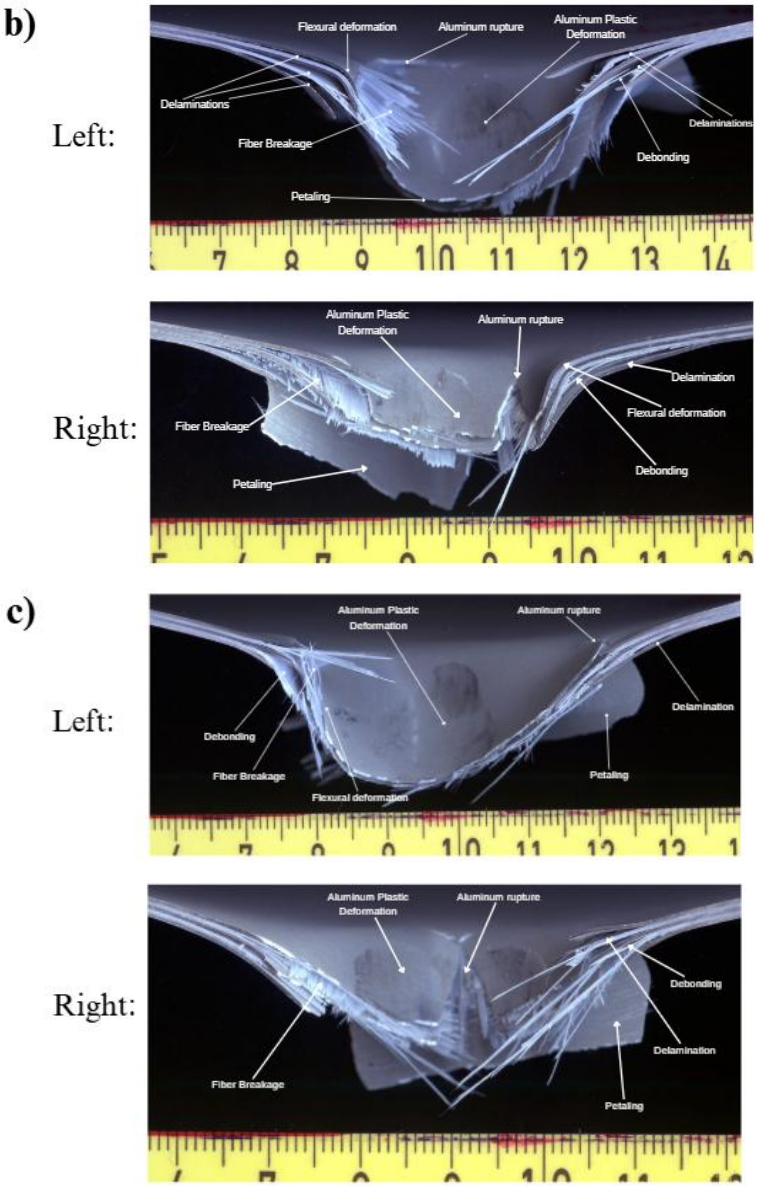


Figure 12. Optical microscope images of the impacted GLARE specimens at the velocities of a) 95.97 m/s, b) 141.49 m/s, and c) 103.20 m/s with the obliquity degree of 0°.

A detailed analysis of the high-resolution optical scans revealed a complex, multi-modal damage evolution within the GLARE laminates. Initial damage was characterized by interfacial debonding at the aluminum–glass/epoxy prepreg interfaces near the impact zone, suggesting that local interfacial shear stresses exceeded the material's critical adhesion threshold. This was accompanied by significant out-of-plane (z-direction) bulging and widespread delamination between the prepreg layers, mechanisms that played a crucial role in dissipating impact energy and promoting lateral damage propagation [43]. Localized fiber breakage and associated flexural deformation were evident within the glass-fiber-reinforced plies, indicating areas where bending stresses and fiber–matrix incompatibilities were most pronounced [44]. The 2024-T3 aluminum interlayers showed distinct signs of plastic deformation, including yield bands and permanent indentations. In specimens subjected to full perforation, classical petaling on the exit face and rupture of the rear aluminum plies were observed, highlighting the interaction between the ductile metal layers and the more brittle composite constituents [45]. These experimentally observed damage features closely align with the failure modes predicted by the finite element simulations and corroborated by high-

speed camera footage. Collectively, the evidence confirms that multiple failure mechanisms develop simultaneously in the multilayer GLARE system, each contributing to the laminate's high energy absorption capacity and residual mechanical integrity.

In the next phase of the study, a detailed parametric investigation was carried out using the previously validated GLARE 4A-3/2-0.4 model, which had demonstrated strong agreement with experimental results. This analysis aimed to quantitatively assess the ballistic performance of different GLARE configurations and to evaluate the effects of variations in specific design parameters on ballistic limit values. Two key parameters were selected for investigation: the thickness of the aluminum layers and the diameter of the steel projectile. The simulation results, including the range of parameter variations and their impact on ballistic limit values, are summarized in Table 5.

Table 5. Calculated ballistic limits of GLARE composites against Aluminum Layer Thickness and steel projectile diameter.

Ball Diameter (mm)	Aluminum Layer Thickness (mm)	Ballistic Limit (m/s)
10	0.2	175.8
10	0.3	205.6
10	0.4	225.2
10	0.5	270.1
10	0.6	295.3
20	0.2	86.3
20	0.3	109.4
20	0.4	126.7
20	0.5	145.8
20	0.6	200.1
30	0.2	70.4
30	0.3	81.3
30	0.4	99.5
30	0.5	110.2
30	0.6	124.1

To investigate the influence of aluminum content within the laminate, the thickness of the Al 2024-T3 layers in the GLARE 4A-3/2-0.4 configuration originally 0.40 mm were varied across a range of 0.20 mm to 0.60 mm (specifically, 0.20 mm, 0.30 mm, 0.50 mm, and 0.60 mm). This parametric variation enabled the evaluation of how changes in the metallic fraction affect the impact energy absorption capacity, while ensuring that the total laminate mass remained within practical constraints. In parallel, the effect of projectile size was examined by replacing the experimentally validated 30 mm diameter steel sphere with smaller alternatives of 10 mm and 20 mm diameter. This allowed for an assessment of how variations in

specific impact energy (J/mm²) influence the laminate's ballistic resistance. For each parameter combination, finite element simulations were conducted in LS-DYNA, incorporating the Johnson–Cook plasticity model for the metallic layers and the Hashin damage criteria for the composite plies [46]. The ballistic limit was determined using incremental velocity simulations within the "embed–perforate" transition regime, following established methodologies. One key result from this parametric study was the validation of a 99.5 m/s ballistic limit for the reference GLARE 4A-3/2-0.4 configuration (Al = 0.40 mm; projectile Ø = 30 mm). Another significant observation was that increasing the aluminum layer thickness or reducing the projectile diameter both led to higher ballistic limits. This improvement is attributed to the increased ductility and energy absorption capacity of thicker aluminum layers, as well as the reduced impact area associated with smaller projectiles. In contrast, when the Al thickness was decreased to 0.20 mm while maintaining the 30 mm projectile diameter, the ballistic limit fell to approximately 70.4 m/s. This sharp decline underscores the critical role of the metallic fraction in maintaining sufficient impact resistance.

Based on the data presented in Table 5, three-dimensional ballistic limit response surfaces were generated to illustrate the combined effects of steel projectile diameter and aluminum layer thickness on the ballistic performance of GLARE laminates. The resulting plot is shown in Figure 13. This figure consolidates the outcomes of the parametric finite element study by simultaneously mapping the ballistic limit as a function of the two governing parameters. Each data point on the surface corresponds to an individual LS-DYNA simulation, wherein Johnson–Cook plasticity and the Hashin failure criteria were employed to model the initiation and evolution of damage in the metallic and composite layers, respectively [46]. The continuous response surface was constructed through interpolation of these discrete, simulation-validated ballistic limit values, yielding a high-fidelity visualization of the laminate's ballistic behavior under varying material and impact conditions. The diagram reveals a pronounced positive correlation between aluminum layer thickness and ballistic limit, whereas increasing projectile diameter exerts an opposing effect, reducing the critical impact velocity. The varying slope of the surface further indicates a multiplicative interaction between the two parameters rather than simple additive influences. Consequently, Figure 13 serves as a predictive design tool, enabling the rapid assessment and optimization of GLARE laminate configurations under diverse threat levels and mass constraints.

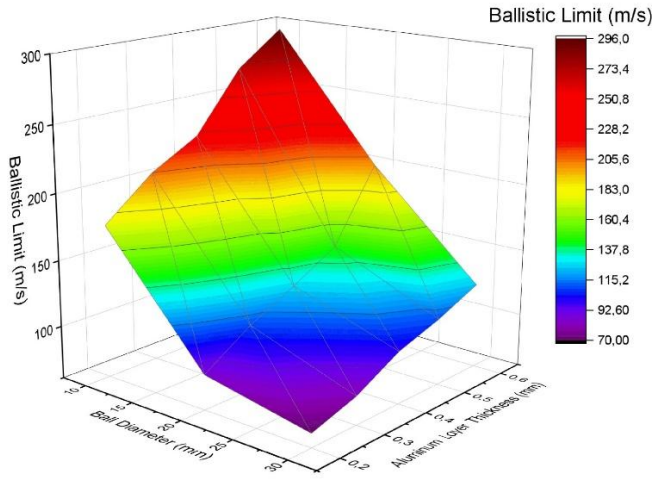


Figure 13. The 3D ballistic limits of the GLARE composites validated for different projectile diameters and aluminum layer thickness

CONCLUSION

As a result of this study, a comprehensive ballistic analysis framework was developed and validated for GLARE 4A-3/2-0.4 composite materials subjected to high-velocity impact by spherical projectiles. The phase diagram incorporating ballistic data for aluminum 2024 was successfully verified using the finite element analyses with ABAQUS and LS-DYNA. A detailed finite element model of the GLARE composite was constructed in LS-DYNA, and ballistic impact simulations were performed using a 30 mm diameter steel sphere. The simulations yielded a ballistic limit velocity of 99.5 m/s for the reference configuration. Complementary ballistic experiments were conducted using a gas-gun setup, and the observed damage mechanisms such as plastic deformation, petaling, and rupture in the aluminum layers were found to correlate well with simulation predictions. The study further explored the effects of varying key design parameters, namely, the thickness of the aluminum layers and the diameter of the projectile. These variations were systematically evaluated through parametric simulations, and the resulting ballistic-limit values were visualized using a 3D response surface. As a final outcome, a computational tool was developed that allows rapid estimation of the ballistic limit for various GLARE composite configurations, offering valuable support for material design and optimization in impact-critical applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contributions

Musa Ethem Haksever: conceptualization, data curation, formal analysis, and writing the original draft. Mustafa Güden: investigation, methodology, validation, and writing the review & editing. Mete Bakır: funding acquisition, project administration, writing the original draft, and writing the review & editing

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Bor Katkısının Yapı Malzemeleri Üzerine Etkilerinin Araştırılması

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ÖZET

Bor ve türevleri dünyada uzun yıllardan beri kullanılmaktadır. Yapılmış olan araştırmalara göre nihai kullanım alanı olan sektörlerde çoğunlukla bor kimyasalları şeklinde tüketildiği gibi, yoğunlaştırılmış bor ürünleri olarak doğrudan da tüketilebilmektedir. Bor ürünleri; uzay ve hava araçları, nükleer uygulamalar, askeri araçlar, yakıtlar, elektronik ve iletişim sektörü, tarım, cam sanayii, kimya ve deterjan sektörü ile seramik ve polimerik malzemeler, nano teknolojiler, otomotiv ve enerji sektörü, metalürji ve inşaat gibi pek çok alanda kullanılmaktadır. Geniş kullanım alanına sahip borun, özellikle yapı malzemesi alanında kullanımı irdelenmiş, kategorilere ayrılmış ve kullanıldığı malzemeye kattığı pozitif özelliklere vurgu yapılmıştır. Çalışmadaki amaç, birlikte kullanıldığı malzemeye önemli nitelikler kazandıran Bor mineralinden ülkemizde yeterince yararlanılamadığı düşüncesiyle, dünyada gittikçe artan Bor tüketiminin yapı malzemesindeki kullanım alanlarını belirleyerek Borun başlıca kullanım özelliklerine ışık tutmak ve yenilikçi malzeme geliştirmeye yol gösterici olmaktır.

Anahtar Kelimeler: Bor, Yapı teknolojisi, İnşaat malzemesi, Mineral, Kolemanit

Research of The Development Processes of High-Performance Mortars

ABSTRACT

Boron and its derivatives have been used in the world for many years. According to the researches, it is mostly consumed in the form of boron chemicals in the sectors where it is the final usage area, and it can also be consumed directly as concentrated boron products. Boron products are used in many areas such as space and air vehicles, nuclear applications, military vehicles, fuels, electronics and communication sector, agriculture, glass industry, chemical and detergent sector, ceramic and polymeric materials, nano technologies, automotive and energy sector, metallurgy and construction. Boron, which has a wide usage area, has been examined, categorized and the positive features it adds to the material it is used in are emphasized. The aim of the study is to determine the usage areas of Boron in construction materials, which is increasing in the world, with the idea that boron mineral, which provides important qualities to the material it is used with, is not sufficiently utilized in our country, and to shed light on the main usage features of boron and to guide the development of innovative materials.

Keywords: Boron, Building technology, Construction material, Mineral, Colemanite

1. Giriş

Ülkemizin deprem kuşağında yer alması ve önlem amaçlı zorunlulukların artması ile birlikte hafif kaya malzemelerinin kullanımı giderek artmaktadır. Yapı ve inşaat sektöründe ana hammadde olarak değerlendirilmeye başlanmış olan hafif kayaçların kendilerine has bazı özellikleri dikkate alınarak sektörde komfor amaçlı ana malzeme olarak sıkça kullanılmaya başlamıştır. Bu amaçla, ülkemizde inşaat endüstrisinde hafif yapı malzemeleri üretimi üzerine yapılan bilimsel çalışmalar ve araştırmalar giderek artmaktadır. Ayrıca, dünyada ve ülkemizde yapı malzemesi üretiminde bağlayıcı olarak bor ve kil minerallerinin kullanıldığı bir çok çalışma tespit edilmiştir. Bu çalışmalardan bazıları aşağıda kısaca özetlenmiştir.

Frederic ve Stevens (1978), yaptıkları araştırmalarda borun bilinen ve seramik ve cam sanayinde de uygulanan ergime sıcaklığını düşürücü ve kaynaştırıcı özelliğinin dayanım artışına neden olduğunu belirlemişlerdir.

Attenborough (1983), duvar paneli üretim çalışmalarında ağırlıkça %27 perlit, %3 fiberglas ve %70 kil kullanmıştır. Üretilen panellerin basınç dayanım değerleri 3,2 Mpa, birim hacim ağırlık değeri 950kg/m3, porozite oranı %69 ve ısı iletim katsayısı 0,21 W/mK olarak belirlemişlerdir. Köktürk (1993), perlit ve bor katkılı betonların en belirgin özellikleri hafifliği ve düşük ısı iletkenliği değeridir. Perlit betonun birim ağırlığı 320-640 kg/m^3 ve ısı iletkenlik değeri 0.07–0.12 W/mK arasında olduğunu bulmuşlardır. Çobanlı (1993), genleştirilmiş perlit, kil ve %10 bor atığı kullanarak üretilen panellerin yüksek ısı yalıtımları ile hafif yapı malzemeleri olmaları yanında kuruma sırasında rötre ve yoğunluk artışı olmaması, yangına ve dona dayanımının yüksek oluşu, kolay üretilmesi gibi olumlu özelliklerinin olduğu belirtilmiştir. Sönmez ve Yorulmaz (1995), kırka boraks işletmesi tesislerinden oluşan kil atıklarının tuğla hammaddesi olarak kullanılabilirliğini araştırmışlardır. Yapılan çalışmaların sonucunda, kırka atık killeri ile tuğla yapımında kullanılan hammaddenin uygun oranda karışımlarının, tuğla yapımında kullanılabileceğini belirlemişlerdir. Targan (2002), kolemanit ve tinkal atıklarının uçucu kül, doğal puzolan ve taban külü ile birlikte çimentoya katıldığında çimento priz süresinin geciktiğini bulmuşlardır. Boncukoğlu ve ark. (2003), tinkal üretimi sırasında ortaya çıkan atıkların çimentoya %1 oranında katılmasıyla yüksek basınç dayanımı elde edildiği, birincil atığın %5, ikincil atığın %10 oranında katılması durumunda ise çimento norm dayanımlarından daha yüksek dayanımlar elde edildiğini bulmuşlardır. BOREN ve TÇMB (2004), ortak yürüttüğü projede kolemanitin klinkere (%10 civarında) katılmasıyla üretilen çimentonun belit tipi(erken dayanımı düşük, geç dayanımı yüksek) olduğu, mekanik mukavemetinin kür süresinin artmasıyla arttığı, hidratasyon ısısının düşük ve radyoaktivite tutma özelliğinin yüksek olduğu belirlenmiştir. 54 saat süren endüstriyel üretim sonrasında elde edilen klinkerler üzerinde yapılan mineralojik analizler sonucunda, Borlu Klinkerin, % 6,5 Kolemanit (% 1,8 B_2O_3) ihtiva eden hammaddenin fırına girmesinden itibaren elde edildiği görülmüştür. Optimum koşullara % 8,9-9,2 kolemanit (% 2.6 B_2O_3) ihtiva eden hammadde ile ulaşılmıştır. Topçu ve ark. (2006), bor minerallerinin belirli oranlarda çimento ve beton içerisine katılması sonucunda çimento ve betonun mekanik özeliklerinde olumlu etkilerinin olduğu görülmüştür. Kavas (2006), bor atıklarını kil ve ince atık şeklinde ayrı ayrı %5, %10 ve %15 oranlarında kırmızı tuğlaya katkı maddesi olarak karıştırarak tuğla dayanımını incelemiştir. En iyi dayanımın %15 oranında sağlandığı sonucuna ulaşılmıştır.

2. Bor katkılı inşaat malzemeleri

Bu bölümde, bor mineralleri ve türevlerinin katkı malzemesi olarak kullanımına yönelik üretilmiş ürünler; sektörel kullanım alanları olacak şekilde belirlenmiş ve bor katkısının inşaat malzemeleri üretimindeki yeri kısaca değerlendirilmiştir. Bor katkısı yapı malzemesi üretiminde enerji tasarrufu, mukavemeti arttırmak, bakteri ve mantar oluşumunu engellemek, aleve karşı dayanıklılık sağlamak, zararlı gaz emisyonunu azaltmak gibi etkiler göstermektedir.

2.1. Tuğla üretimi

2.1.1. Borlu pomza tuğla

Ülkemizde üretilen pomza hammaddesi ile çimento yerine tinkal minerali kullanılarak ısıl işlem sonunda hafif ve yalıtkan tuğla ürünleri üretilmektedir . Pomza blok adı verilen ürünlerin üretimi ile bağlayıcı olarak çimento yerine bor kullanıldığından ısı yalıtımı daha iyi ürünler geliştirilmiştir. Geliştirilen ürünler filtrasyon, atık su arıtımı gibi farklı alanlarda da kullanılmaktadır. Bu ürün “boron pumice brick and production method 201, 2018 kodu ile tarafımdan patentlenmiştir.

2.2.2. Borlu gazbeton üretimi

Bor katkısı ile gaz beton ürünlerde daha çok küçük ve homojen gözenek oluşmaktadır. Bu sayede gazbetonun ısı iletim katsayısı düşmekte, yalıtım özelliği iyileşmekte ve yapıların enerji verimliliği artmaktadır. Ayrıca, bor katkısı ile gazbetonun aleve karşı direnci artmaktadır. Yangın esnasında zararlı gaz ve duman çıkması engellenmektedir.

2.3.3. Borlu perlit tuğla

Perlit ve bor etkileşimi çok iyi bir ısı izolasyonu sağlamaktadır. Yüksek ısı yalıtımı sayesinde yapılara daha küçük kazan ve daha az kalorifer dilimi konulabilmekte, ayrıca bu tür yalıtımlı konutlarda oturanlarında önemli ölçülerde yakıt tasarrufu yapması sağlanabilecektir. Hafifliği, yüksek elastisitesi ve direnci sayesinde özellikle depreme karşı güvenli yapılar inşa edilmesinde vazgeçilmez bir malzemedir. Tuğlanın ses yalıtım değerleri, yüksek değerlerde olması sebebiyle, binaların iç mekanlarını dış ortam gürültüsünden korumaktadır. Akustiğin önemli olduğu yapılarda kullanıldığı taktirde, ses emme özelliği sayesinde eko olayını ortadan kaldırmaktadır. Tuğla kolayca ve dağılmadan kesilip oyulabilmektedir. Bu işlemler için özel bir alet veya techizata gereksinim duyulmamaktadır. Duvar yapımında işçiliği kolaylaştıran bu özellik ayni zamanda kullanımdada çivi çakılması, dübel yerleştirilmesi gibi operasyonların kolayca yapılmasını sağlamaktadır. Bu ürün "boron doped perlite brick and production method" TR 2011 04274 B, 2011 kodu ile tarafımdan patentlenmiştir.

2.2. Alçı

Alçı ürünlerinde katkı olarak kullanılan bor bileşikleri, alçının fizikomekanik özelliklerini iyileştirmektedir. Bor katkısı alçının mukavemetini arttırmaktadır, su emilimini azaltarak neme karşı alçıyı korumakta, antibakteriyel özellik kazandırmakta ve ürün ağırlığını %20 oranında azaltmaktadır.

2.3. Çimento

Borlu Klinkerin, % 6.5 Kolemanit (% 1.8 B_2O_3) ihtiva eden hammaddenin fırına girmesinden itibaren elde edildiği görülmüştür. Optimum koşullara % 8.9-9.2 kolemanit (% 2.6 B_2O_3) ihtiva eden hammadde ile ulaşılmıştır. Klinker yapısında C2S (ana faz) ve C3A ile C4AF fazlarının oluştuğu gözlenmiştir. Erken dayanımı(7 günlük) düşük geç dayanımları yüksek çimentodur. Basınç dayanımı değerleri rapor tablosunda verilmiştir (Mpa) olarak. Bu tür çimentolara belit türü çimento denir. Çok düşük hidratasyon ısılı(very low heat cement) çimentodur. Hidratasyon ısısı sonuçları laboratuvar ölçekli ve endüstriyel ölçekli çalışmalarda borlu çimentoların karakteri olan çok düşük hidratasyon ısılı çimento (VLH Cement EN 14216) sınıfına girdiğini göstermiştir. Döner fırında pişme sırasında kullanılan kömür miktarının yaklaşık 11.6 ton/saat'den 10.3 ton/saat'e düştüğü ve sinterleşmenin 1300 ^oC'de gerçekleştiği kaydedilmiştir. Klinkerin fırında pişmesi sırasında daha az yakıt (kömür) kullanılarak litre ağırlığı (LTW) daha yüksek olan klinker elde edilmiştir (LTW değeri 1377 g/litre). Böylece fırındaki toz klinker üretimi granüler yapıya dönüşmüştür. Elde edilen ürünlerin nötron tutma özelliği oldukça yüksektir. Bu ürün "boron doped perlite brick and production method" TR 2011 04274 B, 2011 kodu ile tarafımdan patentlenmiştir. Bu ürün "colemanite doped portland cement and production method (turkish type cement)" TR 2006 07669, TS 13353, 2006 kodu ile tarafımdan patentlenmiştir.

2.4. Cam yünü

Cam yünü binalarda yalıtım sağlaması bakımından kullanılan bir çeşit izolasyon malzemesidir. Ülkemiz'de bor kullanımının en yaygın olduğu alanlardan birisi cam yünü üretimidir. Bor ve türevleri kullanımı ile cam yünü üretiminde ergime sıcaklığı düşürülerek enerji tasarrufu sağlanmakta, eriyik malzemenin akışkanlığı arttırılmakta, flaksların bünyeden uzaklaştırılması sağlanmakta ve yeniden kristalleşme önlenmektedir.

2.5. Taş yünü

Taş yünü inşaat sektöründe yalıtım amaçlı kullanılmaktadır. Taş yününde bor kullanımı ile ergime sıcaklığı düşürülerek enerji tasarrufu sağlanmakta ve antibakteriyel özellik kazanmasına olanak sağlamaktadır.

2.6. Selülozik izolasyon

Selülozik izolasyon malzemesi atık kağıtlarının geri kazanılması, işlenmesi ve ürün haline getirilmesiyle elde edilen izolasyon tipidir. Malzemenin üretiminde borik asit ve boraks pentahidrat kullanılmaktadır. Malzeme üretimi püskürtme (selüloz yünü) ve plaka şeklinde yapılmaktadır. Püskürtme malzemesinin, plaka ve şilte şeklinde üretilmektedir. Plaka malzemesinin ısı iletim katsayısı 0.58 W/mK dir. Bor kullanımı ile yangına karşı dayanımı yüksek, mükemmel koruyucudur (zararlı haşere ve organizmalara karşı), küflenmeye karşı yüksek direnç ve iyi bir ses izolasyonu sağlar.

2.7. Cam

Bor minerallerinin inşaat sektöründe en fazla kullanıldığı alanlardan biriside cam sektörüdür. Bor katkısı, camın akışkanlığını arttırmakta, ergime sıcaklığını düşürmekte, antimikrobiyal ve kimyasal kararlılık gibi özelliklerini iyileştirmekte ve elektriksel iletkenliğini düşürmektedir. Bor özellikle; borosilikat cam, tekstil ve izolasyon tipi cam elyaflarında yoğun olarak kullanılmaktadır.

2.8. Seramik

Bor katkısı, seramik sektöründe kil çamuru, sır ve fritlerde kullanılmaktadır. Sırlarda borun temel fonksiyonu cam ve malzeme arasında ısıl denge sağlayarak, sırrın ısıl genleşme katsayısını düzenlemektir. Ayrıca, bor ilavesi ergimenin ilk aşamalarında cam oluşumunu sağlamaktır. Bor ve türevleri ayni zamanda seramik malzemenin refrakter özelliğini arttırarak görünümünü de iyileştirmektedir.

2.9. Ahşap

Bor ve türevleri ahşap malzemelerde emprenye olarak kullanılmaktadır. Emprenye, ahşabı dış etkilerden korumak ve kullanım ömrünü uzatmak amacıyla çeşitli yöntemlerle ahşabın bünyesine kimyasal maddelerin emdirilmesi işlemidir. Borik asit, boraks, disodyum oktaborat tetrahidrat gibi borlu bileşikler, ahşap malzemeyi tahrip eden böcek ve mantarlara hem fungisit hemde insektisit özelliği göstermektedir. Ayrıca, çevre için minimum toksisiteye sahip olması, renksiz ve kokusuz olması, odun içine kolay difüze olması, alev geciktirici etki sağlaması gibi özelliklerinde dolayı emprenye kimyasal bileşiklerinde yaygın olarak kullanılmaktadır.

3. Sonuçlar

- Yapı ve inşaat sektöründe ana hammadde olarak değerlendirilmeye başlanmış olan hafif kayaçların kendilerine has bazı özellikleri dikkate alınarak sektörde komfor amaçlı ana malzeme olarak sıkça kullanılmaya başlamıştır. Bu amaçla, ülkemizde inşaat endüstrisinde hafif yapı malzemeleri üretimi üzerine yapılan bilimsel çalışmalar ve araştırmalar giderek artmaktadır.
- Bor ve türevleri kullanıldığında, dayanım açısından sağladığı avantaj ile sektörde öne çıkabilecek bir potansiyele sahip olmaktadır. Borlu Klinkerin, % 6.5 Kolemanit (% 1.8 B_2O_3) ihtiva eden hammaddenin fırına girmesinden itibaren elde edildiği görülmüştür. Optimum koşullara % 8.9-9.2 kolemanit (% 2.6 B_2O_3) ihtiva eden hammadde ile ulaşılmıştır. Klinker yapısında C_2S (ana faz) ve C_3A ile C_4AF fazlarının oluştuğu gözlenmiştir. Erken dayanımı (7 günlük) düşük geç dayanımları yüksek çimentodur. Bu tür çimentolara belit türü çimento denir. Çok düşük hidratasyon ısılı çimentodur.

- Seramik, alçı, tuğla vb sektörlerde bor mineralinin farklı özellikleri bakımından kullanılabileceği görülmektedir. Seramik sektöründe, sır bünyesinde kullanıldığında özellikle yüzey sertliğini arttırarak malzemeye mukavemet kazandırması ve malzemenin kullanım ömrünün artması, bu sektörde bor kullanımını teşvik edecek niteliktedir. Bor ve türevleri ahşap kullanımında ise emprenye malzemesi olarak kullanılmaktadır.
- Yapı sektöründe bor ve türevlerinin en çok kullanıldığı alanların başında cam ve fiberglas sektörleri gelmektedir. Bor katkısı, camın akışkanlığını arttırmakta, ergime sıcaklığını düşürmekte, antimikrobiyal ve kimyasal kararlılık gibi özelliklerini iyileştirmekte ve elektriksel iletkenliğini düşürmektedir

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Beton Üretiminde Atık Agrega Kullanımının Araştırılması

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ÖZET

İnşaat sektöründe kullanılan agregalar, kum, çakıl, kırma taş, geri dönüştürülmüş beton, geri dönüştürülmüş asfalt, cüruf gibi granüler malzemelerdir. Geri dönüştürülmüş agrega örnekleri arasında inşaat ve yıkım atıklarından geri dönüştürülmüş beton (GDA) malzemeler yer almaktadır. Ülkemiz deprem kuşağında bulunmaktadır. Deprem atıklarının kullanılması, çevresel problemlerin ve ekonomik kayıpların azalmasını sağlayacaktır. Bu çalışma kapsamında hazırlanan numunelerde iri boyuttaki geri dönüştürülmüş beton agregası (%10, 15, 20 ve 25) oranlarında doğal agrega ile yer değiştirilmiştir. Hazırlanan numunelerin fiziksel ve mekanik özellikleri bakımından beton üretiminde kullanılabilirliği araştırılmıştır. Genel olarak kontrol numunesine GDA miktarındaki artış, su emme oranlarında artışa neden olurken birim hacim ağırlık değerlerinde azalmaya neden olmuştur. Numunelerde GDA miktarının artması 28 günlük basınç dayanım sonuçlarını olumsuz etkilemiştir. Deneysel araştırmalara göre; GDA' nın belirli miktarlarda beton üretiminde kullanılabilirliğinin uygun olduğu tespit edilmiştir.

Anahtar Kelimeler: Agrega, Geri dönüştürülmüş agrega, Beton, Yoğunluk, Dayanım

Research Of the Development Processes of High Performance Mortars

ABSTRACT

Aggregates used in the construction sector are granular materials such as sand, gravel, crushed stone, recycled concrete, recycled asphalt, slag. Examples of recycled aggregates include recycled concrete (RCW) materials from construction and demolition waste. Our country is located in an earthquake zone. The use of earthquake waste will reduce environmental problems and economic losses. In the samples prepared within the scope of this study, large-sized recycled concrete aggregate was replaced with natural aggregate at rates of (10, 15, 20 and 25%). The usability of the prepared samples in concrete production was investigated in terms of their physical and mechanical properties. In general, the increase in the amount of GDA in the control sample caused an increase in water absorption rates and a decrease in unit volume weight values. The increase in the amount of GDA in the samples negatively affected the 28-day compressive strength results. According to experimental research; It has been determined that the usability of GDA in certain amounts of concrete production is suitable.

Keywords: Aggregate, Recycled aggregate, Concrete, Density, Strength

1.Giriş

Geri kazanılmış yapı malzemelerinin beton üretiminde kullanılabilirliğinin fiziksel, kimyasal ve mekanik özellikleri bakımından araştırılması ve yaygınlaştırılması, ülke ekonomisine katkıda bulunmanın yanı sıra mevcut kaynakların korunması ve çevresel sürdürülebilirliğin sağlanması bakımından son derece önemlidir. İnşaat sektörü de dünyadaki teknolojik değişim ve dönüşümden ciddi şekilde etkilenmiştir. Özellikle gelişmekte olan ülkelerin birçoğunda olduğu gibi Türkiye'de de inşaat sektörü ekonominin lokomotifi olmuştur. Boş arazilere yeni şehirler kurulduğu gibi kullanım ömrünü tamamlamış binalar yerlerini kendinden daha işlevsel, daha nitelikli binalara bırakmış ve bırakmaya devam etmektedir. Geri dönüştürülen yapı malzemelerinin büyük bölümünü de agregalar oluşturmaktadır. Geri kazanılmış beton agregasının yeniden yapı işlerinde kullanılması mümkündür. Bu tezde geri dönüştürülmüş beton agregası kullanımı sırasında meydana gelebilecek olumsuzlukları bertaraf edebilmek için bu agregaları beton üretiminde kullanarak geri dönüştürülmüş beton agregasının oluşturabileceği olumsuzlukları ortadan

kaldırmak ya da minimuma indirmek istenmiştir. Agrega sektörü ülke ekonomisinin vazgeçilmez sektörlerindendir. Yıllık 290 milyon ton gibi yüksek üretim kapasitesi ve yaklaşık 1.5-2 milyar $ gibi bir değer ve 35.000 kişilik doğrudan istihdam imkanları ile giderek artan öneme sahip bir madencilik koludur [1]. Agrega üretim potansiyelinin bu denli yüksek oluşu kaliteli agrega kaynaklarının da hızla azalış eğilimde olduğunun bir göstergesidir. Geleneksel beton üretiminde genellikle doğal, kırma ve geri kazanılmış olmak üzere üç tip agrega kullanılmaktadır [2]. Demirel ve Şimşek yaptıkları çalışmada; erken yaştaki atık betonların geri dönüşüm agregası olarak beton üretiminde kullanılabilirliği araştırılmıştır. Çalışmada, Kalker kökenli kırma taş agregası ve 7 günlük C30 atık betonundan elde edilen geri dönüşüm agregası kullanılmıştır. Geri dönüştürülmüş agregalar, karışım içerisinde iri agrega ve ince agrega olarak ağırlıkça % 0, 10, 20, 30, 40, 50 oranlarında kullanılmış ve geri dönüştürülmüş agregaların betonda kullanılabileceği sonucu vurgulanmıştır (3). Topçu beton kırıklarının agrega olarak kullanılabilirliği üzerine bir çalışma gerçekleştirmiştir. Bu çalışmanın temel amacı, Beton sınıfı (BS) 16 olan beton kırığı agregaları kullanılarak, BS 16 ve BS 20 beton kaliteleri elde edilmeye çalışılmıştır. , beton kırığı kullanılarak üretilen betonların sertleşmiş birim ağırlıkları normal betonlara göre daha düşük olduğu, silindir ve küp basınç mukavemetleri eski beton kırığı agregası miktarı arttıkça azaldığı ve genel olarak değerlendirildiğinde eski beton kırığı kullanılarak istenilen mukavemette betonlar üretilebileceği sonucuna ulaşılmıştır [4]. Savaş yaptığı çalışmada; Isparta İlindeki mevcut ocaklardan elde edilen doğal agrega, İzmit depremi sonucunda yıkılan binalardan elde edilen beton atıkları ve Isparta merkezde yıkılan binalardan elde edilen beton atıkları kullanılarak beton numuneleri hazırlamıştır. Deprem nedeniyle ve imar nedeniyle yıkılan binalara ait atıkların taşıyıcı beton agregası olarak kullanılamayacağı, fakat taşıyıcı olmayan betonlarda, grobetonlarda koşu, bisiklet yolu betonlarında ve stabilize yol dolgularında kullanılabileceği belirtilmiştir (5). Qasrawi'nin yaptığı çalışmada; betonda iri agrega olarak geri dönüştürülmüş beton yıkıntılarının kullanılması araştırılmıştır. Karışım içerisinde atık kullanımının, basınç dayanımını çekme dayanımına göre daha fazla etkilediği, Atık kullanımının, betonun işlenebilirliği üzerinde etkisi olduğu, bu tür malzemelerin kullanılmadan önce ilave denemeler yapılması gerektiği belirtilmiştir (6). Khaloo yaptığı çalışmada; portland çimentolu betonda kaba agrega olarak tuğla kırığı kullanmıştır. Normal agregalarla üretilen betonlar ile karşılaştırdığında basınç dayanımında %7 kayıp olduğunu belirtmiştir. Dayanımdaki azalmaya ek olarak tuğla kırıklı betonların birim ağırlıkların da %9.5 azalma olduğunu saptamıştır (7). Yapılan çalışmalara göre, atık beton agregalarının beton numunelerinin mekanik özelliklerini olumsuz yönde etkilediği şeklinde olsa da uygun oranlarla kullanımının uygun olacağı yönündedir (8).

Bu çalışmada, farklı oranlarda geri dönüştürülmüş agreganın beton üretiminde kullanılması ile ortaya çıkan avantaj ve dezavantajları araştırılmıştır.

2. Malzeme ve Yöntem

2.1. Malzeme

2.1.1. Agrega

Bu çalışmada kullanılan Agrega Giresun Kovanlık ilçesinde yer alan büyükşehir kum-çakıl ocağından temin edilmiştir. Geri dönüştürülmüş agrega olarak geri dönüştürülmüş beton agregası (GDBA) kullanılmıştır.

2.1.2. Çimento

Beton karışımlarında CEM I 42.5 R tipi çimento kullanılmıştır. CEM I 42.5 R tipi çimentonun kimyasal özellikleri aşağıdaki tabloda verilmiştir.

2.1.3. Karışım Suyu

Çalışmada karışım suyu olarak Giresun ili şehir şebeke suyu kullanılmıştır. Kullanılan suyun ilgili standartlarda yer alan özellikleri sağlamasına dikkat edilmiştir.

2.1.4. Kullanılan Gereçler

Laboratuvar çalışmasında kullanılan araçlar ve gereçler, TS 706 'da belirtilen kare gözlü elekler, duyarlı terazi, etüv, plastik küp beton numune kalıpları, kür havuzu, tek eksenli basınç aleti, fırça, gres yağı, mala, plastik tokmak ve şişleme çubuğudur.

2.2. Yöntem

Söz konusu materyaller kullanarak farklı gruplarda beton numuneleri hazırlanmıştır. %10, %15, %20 ve %25 oranlarında iri boyuttaki (4mm göz açıklı elek üzerinde kalan agrega) agrega ile iri boyuttaki GDBA'nın yer değiştirilmesi ile hazırlanan numuneler sırasıyla GDBA10, GDBA15, GDBA20 ve GDBA25 olarak isimlendirilmişlerdir.

2.2.1. Beton numunelerinin hazırlanması

Her bir numune grubu için gerekli olan agrega, GDA ve çimento hassas terazide tartıldıktan sonra homojen olarak karıştırılması sağlanmıştır. Şekil 1' de GDBA katkılı beton harcı görülmektedir.

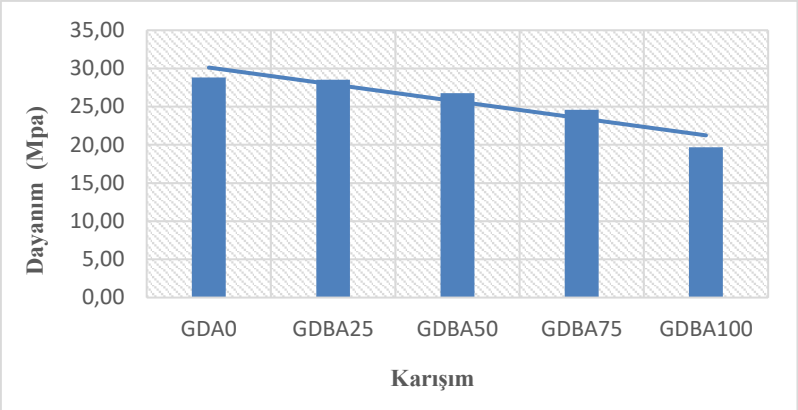
Şekil 1. GDBA katkılı beton harcı

Daha sonra 0.5 su/çimento oranı sağlayacak şekilde su ilave edilmiştir. Elde edilen harç homojen şekilde karıştırıldıktan sonra TS EN 12350-1'e [9] uygun olarak numune kalıplarına yerleştirilmiştir.

3.Araştırma Bulguları

3.1. Basınç dayanımı sonuçları

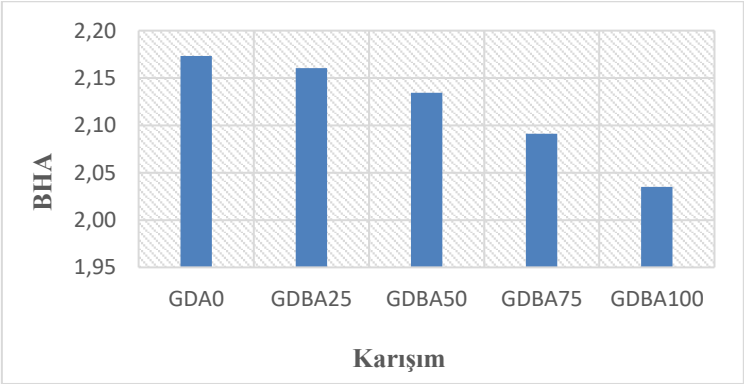
Kontrol numunesi ve GDBA katkılı beton gruplarına ait numuneler kür havuzunda 28 gün bekletildikten sonra tek eksenli basınç testine tabi tutulmuştur. Her bir karışım grubu için ortalama basınç dayanım değerlerine ait grafik Şekil 2.'de verilmiştir. Farklı oranlarda geri dönüştürülmüş tuğla agregaları kullanılarak hazırlanan betonların 28 günlük basınç dayanım değerleri kıyaslandığında kontrol numunesine en yakın dayanım değerini veren numune grubu GDTA25 dir. Kontrol numunesine göre GDTA10, GDTA15, GDTA20 ve GDTA25 numune gruplarının 28 günlük ortalama basınç dayanım değerleri kıyaslandığında sırasıyla %9.61, %19.82, %23.92 ve %28,15 azalma olduğu tespit edilmiştir.



Şekil 2. GDBA katkılı numunelerin basınç dayanım değerleri

3.2. Birim hacim ağırlık deneyi sonuçları

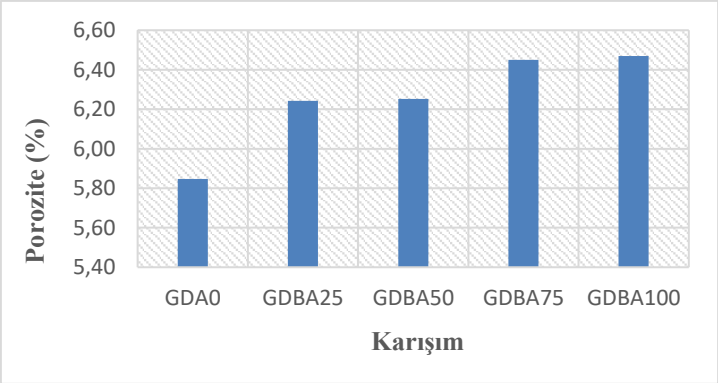
Kontrol numunesi ve GDBA katkılı beton grupları için ortalama birim hacim ağırlık değerlerine ilişkin grafik Şekil 3'de verilmiştir. GDBA ile hazırlanan numuneler arasında kontrol numunesine en yakın birim hacim ağırlık değerine sahip beton grubu GDBA10 kodlu beton grubudur. Kontrol numunesine göre birim hacim ağırlık değerindeki azalış, GDBA10, GDBA15, GDBA20 ve GDBA25 beton grupları için sırasıyla %0.46, %1.84, %3.69 ve %5.99 olarak hesaplanmıştır



Şekil 3. GDBA katkılı numunelerin BHA değerleri

3.3. Porozite deneyi sonuçları

Kontrol numunesi ve GDBA katkılı beton grupları için ortalama porozite yüzdelerine ilişkin grafik şekil 4'de verilmiştir. GDBA ile hazırlanan numuneler arasında kontrol numunesine en yakın porozite değerine sahip beton grubu GDBA25 kodlu beton grubudur. Kontrol numunesine göre porozite değerindeki artış, GDBA10, GDBA15, GDBA20 ve GDBA25 beton grupları için sırasıyla %6.67, %6.84, %10.26 ve %10.60 olarak hesaplanmıştır.



Şekil 3. GDBA katkılı numunelerin porozite değerleri

4. Sonuçlar

- GDA0 kodlu beton grubunun en yüksek dayanım değerine sahip olduğu tespit edilmiştir. Her iki farklı GDA grupları ile hazırlanan numunelerde GDA miktarındaki artış, basınç dayanımı, birim hacim ağırlık değerlerinde azalışa neden olurken su emme ve porozite değerlerinde artışa neden olmuştur.
- Birim hacim ağırlık sonuçları incelendiğinde kontrol numunesine göre ortalama birim hacim hacim ağırlık sonuçlarındaki azalış, tüm ikame oranları için GDBA katkılı numunelerde daha fazladır.
- Kontrol numunesine kıyasla tüm numune grupları için porozite miktarındaki artış GDTA katkılı numunelerde daha fazladır.
- Atıkların geri dönüştürülmesi ile elde edilen agregaların beton üretiminde belirli oranda kullanılabileceği ancak geri dönüştürülmüş beton agregalı harçların su emme eğiliminin fazla olacağı gözlenmiştir.

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Hafif Beton Üretimi ve Mühendislik Özellikleri

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ÖZET

Bu çalışmada, sektörde yaygın olarak kullanılan köpük betona ait fiziksel ve mekanik özellikler incelenmiştir. Üretilen numuneler için 7. Ve 28. günde elde edilen değerler kaydedildi. Araştırma sonuçları ile hafif betona göre yoğunluğu çok daha fazla olan normal betonunun basınç dayanımının daha yüksek olduğu gözlendi. Yüksek yoğunluklu betonlar daha yüksek basınç dayanımı sergiledi. Diğer yandan, yoğunluğun azalmasıyla porozitenin arttığı görülmüştür. Daha hafif betonlar daha yüksek porozite değerlerine sahiptir. Bu sonuçlar, yapısal uygulamalarda daha yüksek basınç dayanımı gerektiren durumlarda normal betonun tercih edilebileceğini ve daha iyi izolasyon sağlayan uygulamalarda hafif betonların tercih edilebileceğini göstermektedir. Araştırma sonuçları, beton karışımlarının yoğunluğunun hem dayanıklılık hem de izolasyon açısından önemli bir faktör olduğunu göstermiştir. Bu bulgular, yapı malzemelerinin tasarımında ve seçiminde mühendislerin ve mimarların bilinçli kararlar almasına yardımcı olabilecek önemli bilgiler sunmaktadır.

Anahtar Kelimeler: Hafif beton, Pomza agregalı beton, Yoğunluk, Mukavemet

Lightweight Concrete Production And Engineering Properties

ABSTRACT

In this study, the physical and mechanical properties of foam concrete, which is widely used in the sector, were investigated. The values obtained for the samples produced on the 7th and 28th days were recorded. According to the research results, it was observed that Portland concrete, which has a much higher density than lightweight concrete, also has a higher compressive strength. High-density concretes exhibited higher compressive strength. On the other hand, it was seen that porosity increased with decreasing density. Lighter concretes had higher porosity values. These results show that Portland concrete can be preferred in cases requiring higher compressive strength in structural applications and that lightweight concretes can be preferred in applications providing better insulation. The research results showed that the density of concrete mixtures is an important factor in terms of both durability and insulation. These findings provide important information that can help engineers and architects make informed decisions in the design and selection of building materials.

Keywords: Lightweight concrete, Pumice aggregate concrete, Density, Strength

1.Giriş

Beton, inşaat sektöründe yaygın olarak kullanılan dayanıklı ve sağlam bir yapı malzemesidir. Geleneksel olarak, çimento, kum, çakıl ve su gibi ana bileşenlerden oluşan normal beton, yüksek mukavemet ve dayanıklılık sağlayarak geniş bir uygulama alanına sahiptir. Çimento üretimi sırasında ortaya çıkan büyük miktardaki CO^2 emisyonu ve diğer sektörlerin atık ve artıklarının bertaraf edilme güçlüğü ve maliyeti, dünya genelinde önemli bir sorun olarak devam etmektedir (1). Bunun yanı sıra, yapıların iyi bir ısı yalıtımına veya depreme dayanıklı olması gerekliliği, yapı malzemeleri üzerinde sürdürülebilir hammaddelerin kullanımına yönelik ilginin artmasına neden olmuştur. Son yıllarda, atık malzemelerin, bağlayıcı malzemelerin veya farklı agrega türlerinin kullanılmasıyla elde edilen betonlar üzerine yapılan araştırmalar artmıştır (2). Bu araştırmaların bir sonucu olarak, çeşitli atık malzemeler ve alternatif bileşenlerin kullanılmasıyla hafif betonlar elde edilebilmektedir. Örneğin, granül-fırın cürufu,

kömür UK, silis dumanı, cam, kağıt çamuru, kauçuk, mikronize lastik lifi, öğütülmüş elektrik kablosu atığı, EPS (genleştirilmiş polistiren), genleştirilmiş perlit ve tarımsal atıklar gibi malzemeler kullanılarak hafif betonlar üretilebilir (3). Hafif betonlar, gaz veya köpük uygulanması, düşük ağırlıkta agregat kullanımı ve bazı bileşenlerin düşük maliyetli malzemelerle değiştirilmesi gibi yöntemlerle elde edilebilir. Gaz beton, ince agregasız beton ve hafif agregalı beton gibi farklı tipleri bulunmaktadır. Bu betonların ortak özellikleri, normal betona göre daha düşük yoğunluğa, daha yüksek mukavemet/ağırlık oranına, daha düşük ısıl iletim katsayısına ve ses yalıtımı özelliklerine sahip olmalarıdır (4). Geleneksel hafif agregatlar (pomza, perlit, kil, UK vb.), gözenekli yapıları nedeniyle daha fazla su talebi ve emme gücü sergilerken, EPS (genleştirilmiş polistiren), su emmeyen, hidrofobik ve kapalı hücre yapısıyla farklılık göstermektedir (5). Bu tür hafif betonlar, yapısal ve yapısal olmayan uygulamalarda kullanılabilmektedir. Hafif betonlar, enerji tasarrufu sağlayan yapılar, ses yalıtımı gerektiren projeler, hafif yapılar ve diğer uygulamalar için tercih edilebilir (6).

Bu çalışmada, normal beton, pomza agregalı Portland betonu ve köpük betonun karşılaştırıldığı bir araştırma sunulmaktadır. Bu üç beton tipinin mekanik özelliklerini, yoğunluklarını, termal performanslarını ve porozitelerini karşılaştırarak avantajları ve dezavantajları belirlenmiştir. Her beton tipinin farklı uygulama alanlarında nasıl performans gösterebileceği değerlendirilmiştir.

2.Hafif Beton Özelliklerinin Belirlenmesi

2.1. Deneylerde kullanılan malzemeler

Deneyde kullanılan malzemeler arasında, Portland CEM 1 52,5 R çimento bulunmaktadır. Bu çimento normal beton ve köpük beton numunelerinde kullanılmıştır. Ayrıca, hafif beton numuneleri için Nevşehir'de üretilen pomza agregası kullanılmıştır (şekil 1). Pomza agrega olarak 3-8 mm'lik agregalar kullanıldı. Agrega hacmi %70, çimento hacmi %30 olarak oluşturuldu. Köpük beton numunelerinin üretiminde ise köpürtücü ajan olarak Foamin C adı verilen sentetik bir köpürme ajanı kullanılmıştır. Numunelerin hazırlanması için karışıma su ilave edilerek amaçlanan uygun yoğunluğu elde etmek amaçlanmıştır. Pomza agregalı hafif beton numunelerinde ise silis kumu kullanılmıştır. Köpük beton numunelerinin üretimi için ise köpük jeneratörü adı verilen bir cihaz kullanılmıştır. Bu malzemeler, deneyin amaçlarına ve numunelerin özelliklerine uygun bir şekilde seçilmiş ve kullanılmıştır. Su/çimento oranları ve yoğunluklarına ilişkin veriler tablo 1'de belirtilmiştir.

Şekil 1. Deneylerde kullanılan pomza agregası

Tablo 1. Kullanılan malzemeler ve reçete

Çimento tipi		Kuru Yoğunluk (kg/m^3)	Çimento (kg/m^3)	(Su+köpük) / çimento
CEM 1 52,5 R	Foamin C	608	536	0.46
CEM 1 52,5 R	Foamin C	783	727	0.37
				Su / Çim.
CEM 1 52,5 R	Pomza agregası	1090	350	0.41

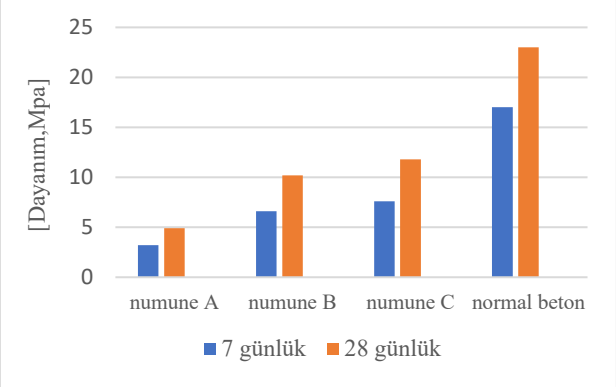
2.2. Deney yöntemleri ve işleyişi

Bu çalışmada, üç farklı beton numunesi kullanılarak deneyler gerçekleştirilmiştir. İlk olarak, pomza agregası kullanılarak hafif beton oluşturulmuştur. İkinci ve üçüncü olarak, köpürtücü ajan olan Foamin C kullanılarak köpük beton numuneleri üretilmiştir. Köpük beton için hedeflenen kuru yoğunluk değeri 600 ve 800 kg/m³ olarak belirlenmiştir. Her iki hedef yoğunluk için ayrı numuneler hazırlanmıştır (şekil 1). Numune hazırlama süreci, su ve çimento karışımının dikey bir karıştırıcıda homojen bir harç elde edilene kadar karıştırılmasıyla başlamıştır. Daha sonra önceden şekillendirilmiş köpük uygun bir köpük jeneratörü kullanılarak çimento hamuruna entegre edilmiştir. Köpük+çimento hamuru karışımı, köpüğün homojen bir şekilde dağılana kadar en az 2 dakika boyunca karıştırılmıştır. Elde edilen kuru yoğunluk değeri takip edilmiştir. Yoğunluğu 800 kg/m³ yakın olan beton için su ve köpük oranı çimentoya göre 0.37 olarak belirlenirken, yoğunluğu 600 kg/m³ yakın olan beton için su ve köpük oranı çimentoya göre 0.46 olarak belirlenmiştir. Pomza agregalı hafif beton için ise öncelikle agregalar yıkanmış ve su ile arındırılmıştır. 3-8 mm pomza agregası kullanılmış ve boyutu ince taneli seçilmiştir. Çimento miktarı 350 kg/m³ ve su-çimento oranı 0.41 olarak belirlenmiştir. Pomza agregalı hafif betonun yoğunluğu, kullanılan agregatın türü, boyutları ve yoğunluğu, çimento-agraga oranı, hava içeriği ve diğer karışım bileşenlerine bağlı olarak değişmektedir. Deneyler sonucunda toplam 3 numune için 7. ve 28. günlerde elde edilen değerler kaydedilmiştir.

Şekil 1. Deneylerde kullanılan numuneler

2.3. Basınç dayanımı deneyleri (Mpa)

Küp numuneler (5 cm kenar uzunluğu), ASTM C109(7) standartlarına göre basınç altında test edildi. 250kN yük kapasiteli CONTROLS marka pres cihazı kullanıldı. Basınç deneyi sırasında, numunelere kontrollü bir şekilde yük uygulanmış ve kırılma noktası belirlenmiştir. Sonuçlar şekil 2'de verilmektedir.



Şekil 2. Basınç dayanımı (A: 608 kg/m³ köpük beton, B: 783 kg/m³ köpük beton, C: ponza beton)

Dayanım sonuçları değerlendirildiğinde, yoğunluğun arttıkça basınç dayanımının da arttığını gösterdi. Kuru Yoğunluğu: 608 kg/m³ olan köpük beton 4.9 MPa basınç dayanımı, kuru yoğunluğu: 783 kg/m³ olan köpük beton 10.2 MPa basınç dayanımı, kuru yoğunluğu: 1092 kg/m³ olan ponza agregalı hafif beton 11.8 MPa basınç dayanımı göstermiştir. Daha yüksek yoğunluğa sahip betonlar daha yüksek basınç dayanımı

sergiledi. Portland 52.5 betona göre yoğunluğu düşük fakat basınç dayanımlarının yaklaşık %80 daha düşük olduğu görüldü. Ayrıca Portland çimento ile elde edilen yaklaşık yoğunluk köpük betona göre yaklaşık %175 daha fazladır. Sonuçlar ayrıca ponza agregalı betonların köpük betonlara göre daha fazla dayanım sergilediğini göstermiştir.

2.4. Birim hacim ağırlık (kg/cm^3)

Numuneler deneyden sonra numunenin 120 °C' lik bir fırında kurutulmasıyla elde edilen yoğunluklar listelendi. Testten sonra, numune en az 48 saat fırında kurutulur. Kurutma süreci boyunca numunenin ağırlığı düzenli aralıklarla kontrol edilmelidir. Ağırlık değişimi durduğunda, numune sabit ağırlık durumuna ulaşmış demektir. Numunelerin kuru birim ağırlığı aşağıdaki formül yardımı ile hesaplanmıştır. Numunelerin ortalama birim hacim ağırlık değerleri (A : 608 kg/m^3, B : 783 kg/m^3, C : 1092 kg/m^3) olarak hesaplanmıştır.

2.5. Su emme oranı (%)

Küp numunelerin (3 farklı) etüv kurusu ağırlıkları tartıldı. Kuru ağırlıkları belirlenen numuneler kür havuzundaki suda 24 saat bekletildikten sonra da şekildeki gibi suya doygun halleriyle tartıldılar. Bu durumda ortalama su emme değerleri ; A : %13,8, B: %12,2, C: %10,6 olarak hesaplanmıştır.

2.6. Porozite oranı (%)

Görünen porozite numunedeki boşluk hacminin numune hacmine oranına denir. Hesaplama sonucunda numune A için : % 66, Numune B için: % 56,5 , Numune C için: % 24,5 değerlerine ulaşılmıştır. Cem 1 portland betona göre porozite oranı oldukça yüksektir. Yüksek porozite, betonun içerisinde daha fazla boşluk veya gözenek olduğunu gösterir. Bu da betonun daha fazla su emme eğilimine sahip olduğu anlamına gelir. Yüksek poroziteli betonlar, suyun içerisine nüfuz edebilmesi için daha fazla alan sağlar.

3.Sonuçlar

- Yoğunluğun arttıkça basınç dayanımının da arttığını gösterdi. Kuru Yoğunluğu: 608 kg/m^3 olan köpük beton 4.9 MPa basınç dayanımı, kuru yoğunluğu: 783 kg/m^3 olan köpük beton 10.2 MPa basınç dayanımı, kuru yoğunluğu: 1092 kg/m^3 olan ponza agregalı hafif beton 11.8 MPa basınç dayanımı göstermiştir.
- Daha yüksek yoğunluğa sahip betonlar daha yüksek basınç dayanımı sergiledi. Portland 52.5 betona göre yoğunluğu düşük fakat basınç dayanımlarının yaklaşık %80 daha düşük olduğu görüldü. Ayrıca Portland çimento ile elde edilen yaklaşık yoğunluk köpük betona göre yaklaşık %175 daha fazladır. Ayrıca ponza agregalı betonların köpük betonlara göre daha fazla dayanım sergilediğini göstermiştir. Köpük betonda yoğunluğun arttırılması dayanımın da artmasını sağlamıştır.
- Su emme değerleri kuru yoğunluğu 608 kg/m3 olan köpük beton için %13.8, kuru yoğunluğu 783 kg/m3 olan köpük beton için %12.2 , kuru yoğunluğu 1092 kg/m3 olan ponza agregalı hafif beton için %10,6 olarak hesaplanmıştır.
- Porozite değerleri kuru yoğunluğu 608 kg/m3 olan köpük beton için % 66, kuru yoğunluğu: 783 kg/m3 olan köpük beton için % 56,5 , Ponza agregalı hafif beton için: % 24,5 değerlerine ulaşılmıştır. Cem 1 portland betona göre porozite oranı oldukça yüksektir.

- Yoğunluk azaldıkça porozitenin arttığı gözlendi. Daha hafif betonlar daha yüksek porozite değerlerine sahipti. Ayrıca porozite artışının su emme değerinin de artışını etkilediği gözlendi.

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Torsional Dynamics of Nonlocal Embedded Rods Using Differential Transformation Method

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ABSTRACT

This study investigates a numerical solution for atomic size dependent torsional vibration of circular nanorods embedded in elastic medium. According to this, the equation of motion and boundary conditions of the relevant nanorod model are transformed with the help of conventional functions by using the differential transformation method. The nonlocal torsional frequencies of different modes of embedded nanorods are compared with the analytical results. Additionally, numerical studies are discussed and the general conclusions obtained from the discussion are shared.

Keywords : Differential transformation method, Embedded nanorod, Nonlocal elasticity, Torsional vibration.

1. Introduction

Nanostructures are known as important components for nano- and micro-scaled electromechanical systems (NEMS/MEMS) technology. Materials such as carbon nanotubes, silica carbide nanotubes, boron nitride nanotubes, nanowires, and nanosheets are examples of various classes of nanostructures. These structures can participate in systems such as biosensors, gas sensors, nanocircuits, and microprocessors.

The stability of nano- and microstructures within their respective systems is of paramount importance to ensure their proper functionality. Therefore, it is essential to develop designs that can withstand the external loads to which such structures may be exposed within the system. The mechanical behaviour must also be known for the design. Mechanical behaviour of nanostructures can be investigated by using semi-experimental methods such as molecular dynamics simulation. Because the simulations require high cost, time-consuming processes, and specialized knowledge, researchers have performed investigation of mechanical behaviour through the theoretical approaches. Eringen's theory of nonlocal elasticity is a popular approach worldwide for the determination of mechanical behaviour of atomic structures [1,2].

According to classical elasticity theory, value of the strain energy of a nanostructure is infinity. Therefore, classical theory cannot provide a valid solution. Nonlocal theory eliminates this deficiency by utilizing the atomic size effect of the nanostructure. In the nonlocal theory, one-dimensional nanomaterials are modelled as one-dimensional continuum mechanical models such as nanobeams [3-11] and nanorods [12-19].

On the other hand, analytical solutions are often insufficient for nonlocal mechanical analyses of nanostructures because atomic parameters and nano scaled environmental factors (such as elastic medium, thermal environment) complicate the governing equation. Therefore, approximated (numerical) solutions are preferred to solve the governing equations. The finite element method, finite difference method, differential quadrature method, differential transformation method are some examples of approximated methods. Since the differential transformation method (DTM) includes the subject of this study, a brief literature review is provided below on selected studies focusing on this method for nonlocal mechanical analyses of nanostructures:

Jena and Chakraverty [20] presented the vibration of Euler-Bernoulli nanobeams. Ebrahimi et al. [21] formulated the vibration of Timoshenko nanobeams. Applications of the differential transformation method have also been carried out on the vibration of functionally graded nanobeams [22,23]. The buckling analyses of Euler-Bernoulli [24,25] and Timoshenko [26] nanobeams have also been investigated. Pradhan and Reddy [27] examined the buckling analysis of nanobeams resting on Winkler foundations. In addition to these, thermal effects on the vibration of Euler-Bernoulli nanobeams have also been studied [28]. The vibration of nanobeams resting on Winkler foundation was investigated by Demir [29]. Moreover, the flapwise bending of double-tapered nanobeams was given based on the Euler-Bernoulli beam theory by Kurt and Kaya [30].

Determining the torsional behaviour of NEMS/MEMS organizations containing the circular cross-sectional nanomaterials is essential to understand the mechanical characteristics of nanostructures. With this motivation, the nonlocal free torsional vibration of nanorods embedded in a fully elastic medium is examined in this study with the differential transformation method. According to this, the nonlocal free torsional vibration is introduced in Section 2. Then, the differential transformation solution for the nonlocal free vibration is developed in Section 3. For the applications of formulation, nonlocal nondimensional frequencies and the accuracy of method are presented and numerical findings are discussed in detail in Section 4. Finally, conclusions summarized from the numerical discussion are given in Section 5.

2. Nonlocal Torsional Vibration

Figure 1 shows the free body diagram of a torsional nanorod embedded in an elastic medium. Where x is longitudinal position and t is time. $\vartheta = \vartheta(x, t)$ is the torsional motion. Also, the cross-section axes of nanorod are given as y and z. According to this, the rotational equilibrium can be written as follows:

$$-M\left(x,t\right)+\left[M\left(x,t\right)+\mathrm{d}M\left(x,t\right)\right]+m\mathrm{d}x-k_t\theta\mathrm{d}x=\rho I_p\frac{\partial^2\theta}{\partial t^2}\mathrm{d}x \tag{1}$$

where $M = M(x, t)$ is the internal torsional moment, $m = m(x, t)$ is the external distributed torsional excitation, k_t is the elastic medium stiffness, ρ is the unit weight, and I_p is the polar moment of inertia. After both sides of the equation are divided by dx, by using the Taylor series for the torsional moment:

$$\frac{\partial M}{\partial x}+m-k_t\theta=\rho I_p\frac{\partial^2\theta}{\partial t^2} \tag{2}$$

To derive the nonlocal equation of motion, we need to know the constitutive relation for the torsional moment:

$$\left(1-\left(e_0a\right)^2\frac{\partial^2}{\partial x^2}\right)M=M_{cl}=GI_p\frac{\partial\theta}{\partial x} \tag{3}$$

where M_{cl} means the classical (local) torsional moment and is calculated as in the following equation. If both sides of this equation are derived according to position and Equation (2) is used, the nonlocal equation of motion is obtained as follows:

$$GI_p\frac{\partial^2\theta}{\partial x^2}-\rho I_p\frac{\partial^2\theta}{\partial t^2}+\left(e_0a\right)^2\rho I_p\frac{\partial^4\theta}{\partial x^2\partial t^2}+m-\left(e_0a\right)^2\frac{\partial^2 m}{\partial x^2}-k_t\theta+\left(e_0a\right)^2k_t\frac{\partial^2\theta}{\partial x^2}=0 \tag{4}$$

On the other hand, the torsional moment that is a mechanical boundary condition should also be obtained. After using Equation (2) into Equation (3) yields the nonlocal torsional moment as follows:

$$M = GI_p \frac{\partial \theta}{\partial x} - (e_0 a)^2 \rho I_p \frac{\partial^3 \theta}{\partial x \partial t^2} - (e_0 a)^2 \frac{\partial m}{\partial x} + (e_0 a)^2 k_t \frac{\partial \theta}{\partial x} = 0 \tag{5}$$

The following expression is required for the analytical solution of equation of motion:

$$\theta(x,t) = \phi(x) e^{i\omega t} \tag{6}$$

where ϕ is the static mode shape and ω is the natural frequency. The mode shape is obtained analytically through a series of mathematical operations by applying Equation (6) into Equations (4) and (5). Details of the analytical solution is not expressed in this study. First, m = 0 is used for free vibration in Equations (4) and (5). It should also be noted that two types of boundary conditions are considered for the mechanical structure:

$$\text{Clamped-clamped: } \phi(0) = 0,\ \phi(L) = 0,$$
$$\text{Clamped-free: } \phi(0) = 0,\ M(L) = \left[GI_p + \omega^2 (e_0 a)^2 \rho I_p - (e_0 a)^2 k_t \right] \phi'(L) = 0 \tag{7}$$

By applying these boundary conditions into the analytical solution of Equation (4), the frequency equations are reached as follows [7]:

$$\omega = \sqrt{\frac{\left[GI_p + (e_0 a)^2 k_t \right] R^2 + k_t}{\rho I_p \left[1 + (e_0 a)^2 R^2 \right]}} \tag{8}$$

Here the following definitions for the boundary conditions should be given:

$$\text{Clamped-clamped: } R = \frac{n\pi}{L}, \text{ Clamped-free: } R = \frac{(2n-1)\pi}{2L} \tag{9}$$

3. Differential Transformation Method

The differential transformation method (DTM) is an approximate solution method based on the Taylor series. The solution is explained by using power series. It is a quite useful method to solve boundary value problems in linear and nonlinear differential equations.

According to this solution method, the solution of differential equation is introduced by the following series:

$$x(t) = \sum_{n=0}^{\infty} \frac{(t - t_i)^n}{n!} \left(\frac{\mathrm{d}^n x(t)}{\mathrm{d}t^n} \right)\Bigg|_{t=t_i} \tag{10}$$

Here, t_i is known as any point in the field where t variable is taken part. The differential transformation of solution function is defined as:

$$F(n) = \sum_{n=0}^{\infty} \frac{H^n}{n!} \left(\frac{\mathrm{d}^n f(t)}{\mathrm{d}t^n} \right)\Bigg|_{t=0} \tag{11}$$

where F denotes the transformed function and f explains the original function. H is a constant value. Also, the inverse differential transformation is written as:

$$f(t)=\sum_{n=0}^{\infty}\left(\frac{t}{H}\right)^{n}F(n) \tag{12}$$

In DTM method, the equation whose solution is searched should be nondimensionalized. This study focuses on the free vibration frequencies of nonlocal torsional vibration and to obtain the frequencies depends on the solution of differential equation given by Equation (4). Therefore, nondimensionalization should be written after Equation (6) is used into Equation (5):

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}\xi^2}+\alpha^2K_t\frac{\mathrm{d}^2\phi}{\mathrm{d}\xi^2}-\alpha^2\bar{\omega}^2\frac{\mathrm{d}^2\phi}{\mathrm{d}\xi^2}-K_t\phi+\bar{\omega}^2\phi=0 \tag{13}$$

The following definitions are given here:

$$\xi=\frac{x}{L},\ \bar{\omega}=\omega L\sqrt{\frac{\rho}{G}},\ \alpha=\frac{e_0a}{L},\ K_t=\frac{k_tL^2}{GI_p}. \tag{14}$$

In addition to this, nondimensionalized boundary conditions can be expressed as:

$$\text{Clamped-free: } \phi(0)=0,\ \phi(1)=0,\ \text{Clamped-free: } \phi(0)=0,\ B\phi'(1)=0 \text{ or } \phi'(1)=0 \tag{15}$$

Where,

$$B=\frac{1}{L}\left[GI_p+\omega^2(e_0a)^2\rho I_p-(e_0a)^2k_t\right] \tag{16}$$

In the solution of differential equations with the DTM, transformation equivalents of the original functions are available [27,29]. According to this, the transformed functions for different original functions are written below in the arrangement of Equation (12):

$$\text{Original: } f(t)=\alpha x(t)+\beta y(t)\text{, Transformed: } F(n)=\alpha X(n)+\beta Y(n) \tag{17}$$

$$\text{Original: } f(t)=\frac{\mathrm{d}^m x(t)}{\mathrm{d}t^m}\text{, Transformed: } F(n)=\frac{(n+m)!X(n+m)}{n!} \tag{18}$$

Based on the DTM solution, the transformed equation of motion is firstly attained. By applying Equations (16) and (17) into Equation (12), the following expression can be obtained:

$$X(n+2)=\frac{-\bar{\omega}^2+K_t}{1+\alpha^2\omega^2\rho I_p-\alpha^2k_t}\times\frac{X(n)}{(n+2)(n+1)} \tag{19}$$

On the other hand, the boundary conditions are transformed as follows for the clamped-free [27,29]:

$$X(0)=0,\ \sum_{n=0}^{n}nX(n)=0 \tag{20}$$

A critical issue in the DTM solution is the number of terms used. A higher number of terms can increase the accuracy of the results. The number of terms used here affects the second boundary condition. However, to apply this boundary condition, the transformed mode shape for $n=1$ should also be formulated due to Equation (19):

$$X(1)=a \tag{21}$$

As a result of the values of mode shape in the transformation function for n = 0 and n = 1, the second boundary condition in Equation (20) is used according to the number of terms selected and the roots of the equation obtained yield the nondimensional frequency values.

On the other hand, for the clamped-clamped boundary condition, the transformed boundary conditions are defined as follows [27,29]:

$$X(0)=0\,,\ \sum_{n=0}^{n} X(n)=0 \tag{22}$$

where an appropriate expression for Equation (21) and the first boundary condition should be used into the second boundary condition.

4. Numerical Results and Discussions

In this section, the numerical findings obtained by using the differential transformation method are presented in tables and graphics for nonlocal torsional vibration of nanorods embedded in elastic medium. Also, numerical findings are also discussed in detail. The mathematical parameters used in the numerical calculations are given in Equation (14). Where $\overline{\omega}$ is the nondimensional frequency, α is the nondimensional atomic parameter, and K_t is the nondimensional stiffness of elastic medium.

Firstly, comparison studies for nondimensional frequencies of nanorods where the effect of the elastic medium is neglected are presented in Tables 1 and 2, respectively, for the first and second modes. According to this, the analytical (exact) results obtained based on Equations (8) and (9) and the nonlocal finite element analysis results given by Numanoğlu and Civalek [7] are compared with the differential transformation results. It should be noted that for nanostructure mechanics, frequencies decrease as the nondimensional atomic parameter increases, and therefore the atomic parameter is an important factor at the nanoscale. Moreover, the nondimensional atomic parameter more reduces the frequencies of clamped-clamped nanorods. On the other hand, approximation studies generally reveal a significant success of the DTM method. Although high deviations from the analytical results are obtained at low term numbers, the results are exactly the same at high term numbers. In the meanwhile, the numerical algorithm does not give a result for some term numbers. This indicates that the number of terms used in the computation should be high.

The nondimensional frequencies of nanorods embedded in elastic medium are listed in Tables 3 and 4 for the first two modes. The elastic medium generally has an enhancing effect on the torsional frequencies of the nanorods. Moreover, the DTM method has provided very successful results. The table results show that DTM is successful than FEM in converging to analytical results.

Table 1. Nondimensional frequencies of fundamental mode for nonlocal torsional vibration of nanorods

Boundary	e_0a/L	Reference Study		Differential Transformation Results (This Study)				
Condition		Analytical	FEM [7]	n = 51	n = 21	n = 11	n = 5	n = 3
C-F	0	1.5708	1.5711	1.5708	1.5708	1.5708	1.5925	1.4142
	0.05	1.5660	1.5662	1.5660	1.5660	1.5660	1.5874	1.4107
	0.1	1.5518	1.5520	1.5518	1.5518	1.5518	1.5726	1.4003
C-C	0	3.1416	3.1437	3.1416	3.1416	3.1411	-	2.4495
	0.05	3.1035	3.1055	3.1035	3.1035	3.1031	-	2.4313
	0.1	2.9972	2.9990	2.9972	2.9972	2.9968	-	2.3792

Table 2. Nondimensional frequencies of second mode for nonlocal torsional vibration of nanorods

Boundary	e_0a/L	Reference Study	Differential Transformation Results (This Study)

Condition		Analytical	FEM [7]	n = 51	n = 21	n = 11	n = 5	n = 3
C-F	0	4.7124	4.7194	4.7124	4.7124	-	3.0764	-
	0.05	4.5868	4.5932	4.5868	4.5868	-	3.0406	-
	0.1	4.2628	4.2680	4.2628	4.2628	-	2.9404	-
C-C	0	6.2832	6.2997	6.2832	6.2831	-	-	-
	0.05	5.9943	6.0087	5.9943	5.9943	-	-	-
	0.1	5.3202	5.3302	5.3202	5.3201	-	-	-

Figure 2 illustrates the deviations (error percentages) of the DTM method for the first three modes of nanorods in response to the increasing of term numbers. Numerical results are not obtained for the regions where the lines cut. Generally, results are not obtained at low term numbers for the higher modes. The results of all modes express that DTM yields very successful results at higher term numbers. On the other hand, DTM results converged slightly faster as the atomic parameter increased in the nonlocal mechanical analysis. Additionally, the findings in Figure 3 indicate that DTM also provides faster convergence performance in the analysis with the elastic medium.

Table 3. Nondimensional frequencies of fundamental mode of nonlocal torsional vibration of embedded nanorods (K_t = 10)

Boundary Condition	e_0a/L	Reference Study		Differential Transformation Results (This Study)				
		Analytical	FEM [7]	n = 51	n = 21	n = 11	n = 5	n = 3
C-F	0	3.5309	3.5310	3.5309	3.5309	3.5309	3.5406	3.4641
	0.05	3.5288	3.5289	3.5288	3.5288	3.5288	3.5384	3.4627
	0.1	3.5225	3.5226	3.5225	3.5225	3.5225	3.5317	3.4584
C-C	0	4.4575	4.4590	4.4575	4.4575	4.4572	-	4.0000
	0.05	4.4308	4.4322	4.4308	4.4308	4.4305	-	3.9889
	0.1	4.3570	4.3582	4.3570	4.3570	4.3567	-	3.9573

Table 4. Nondimensional frequencies of second mode of nonlocal torsional vibration of embedded nanorods (K_t = 10)

Boundary Condition	e_0a/L	Reference Study		Differential Transformation Results (This Study)				
		Analytical	FEM [7]	n = 51	n = 21	n = 11	n = 5	n = 3
C-F	0	5.6751	5.6751	5.6751	5.6751	-	4.4118	-
	0.05	5.5712	5.5765	5.5712	5.5712	-	4.3870	-
	0.1	5.3077	5.3118	5.3077	5.3077	-	4.3181	-
C-C	0	7.0341	7.0489	7.0341	7.0340	-	-	-
	0.05	6.7773	6.7900	6.7773	6.7773	-	-	-
	0.1	6.1890	6.1977	6.1890	6.1890	-	-	-

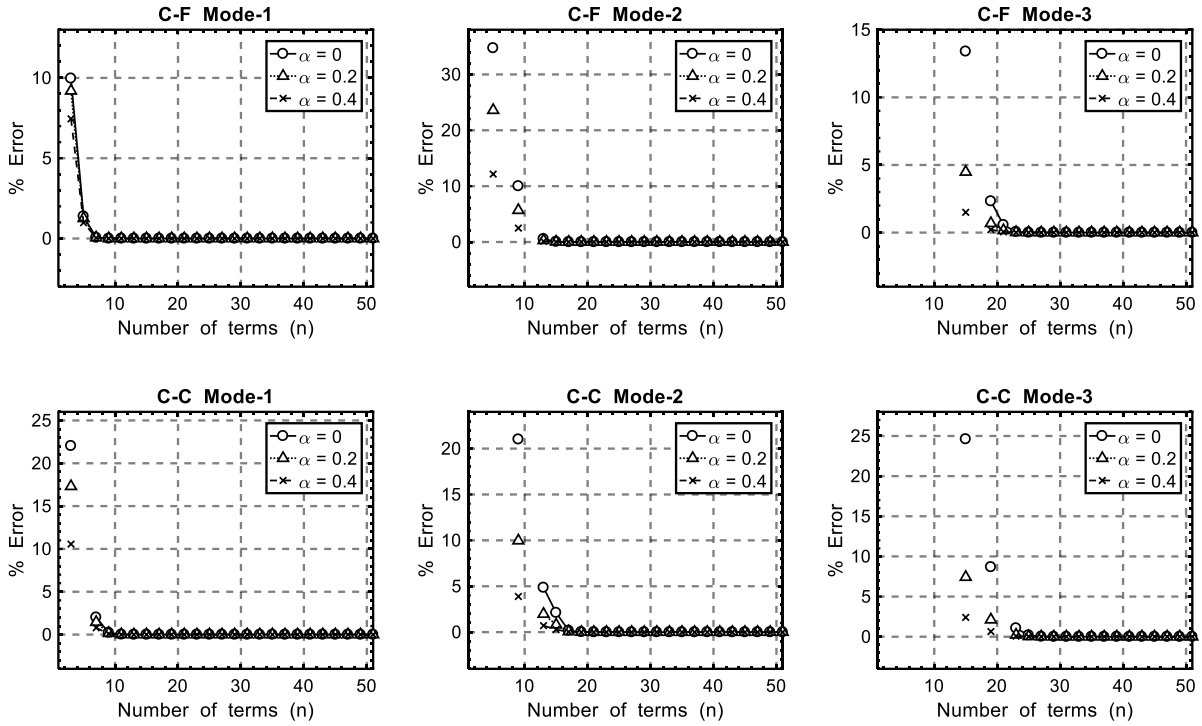

Figure 2. Deviation percentages for first three modes nondimensional frequencies of torsional nanorods

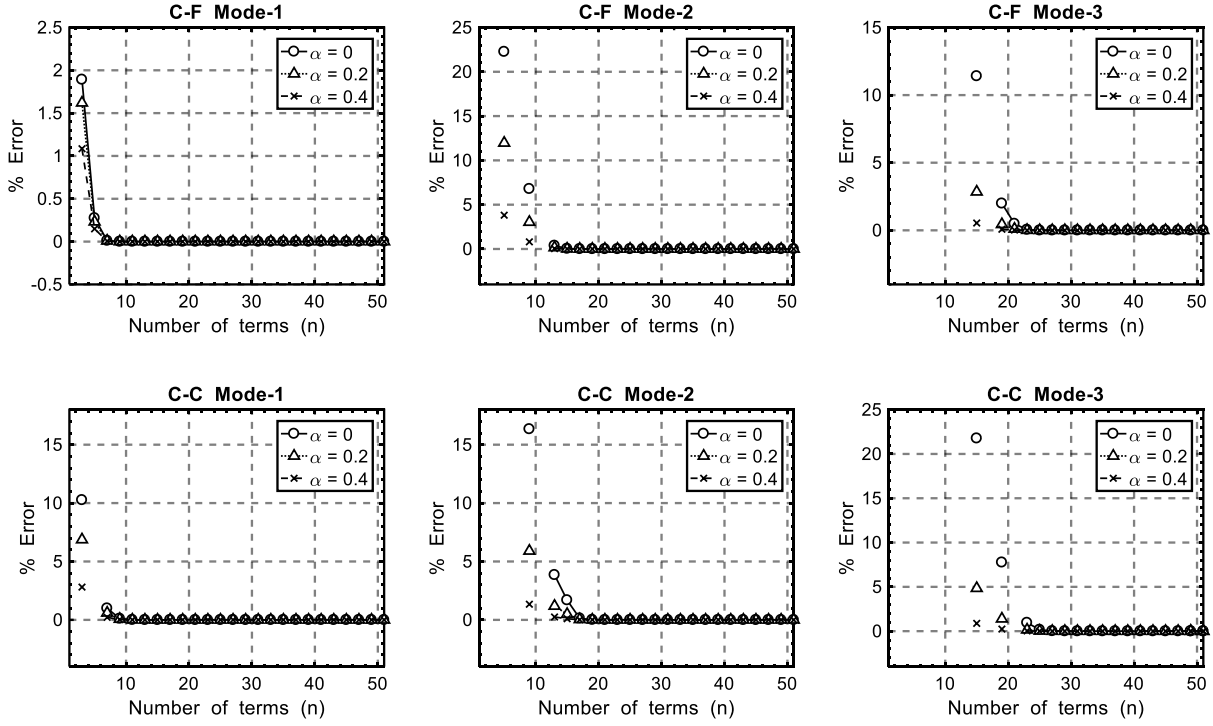

Figure 3. Deviation percentages for first three modes nondimensional frequencies of embedded torsional nanorods (K_t = 10)

The variations of nondimensional frequencies of first three modes of nanorods embedded in an elastic medium with increasing elastic medium stiffness are plotted in Figures 4 and 5. To ensure high accuracy in the calculations, n = 51 terms are used with the DTM. Elastic medium stiffness is seen as a parameter that increases frequencies. The atomic parameter has less effect on the frequencies of nanorods with high elastic medium stiffness.

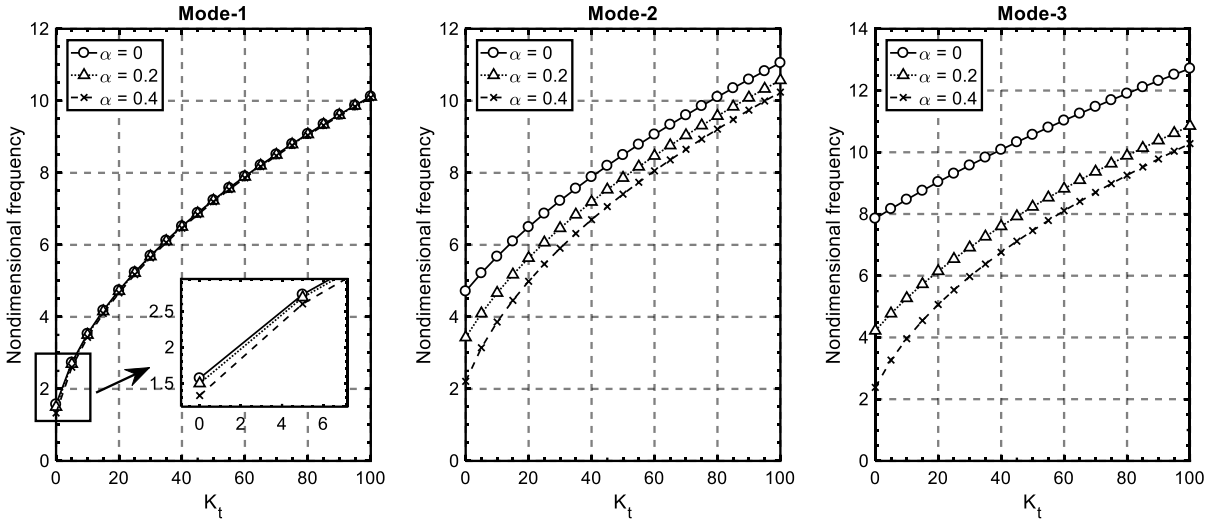

Figure 4. Variations of frequencies of torsional clamped-free embedded in elastic medium with different stiffness according to the increment of nondimensional nonlocal parameter

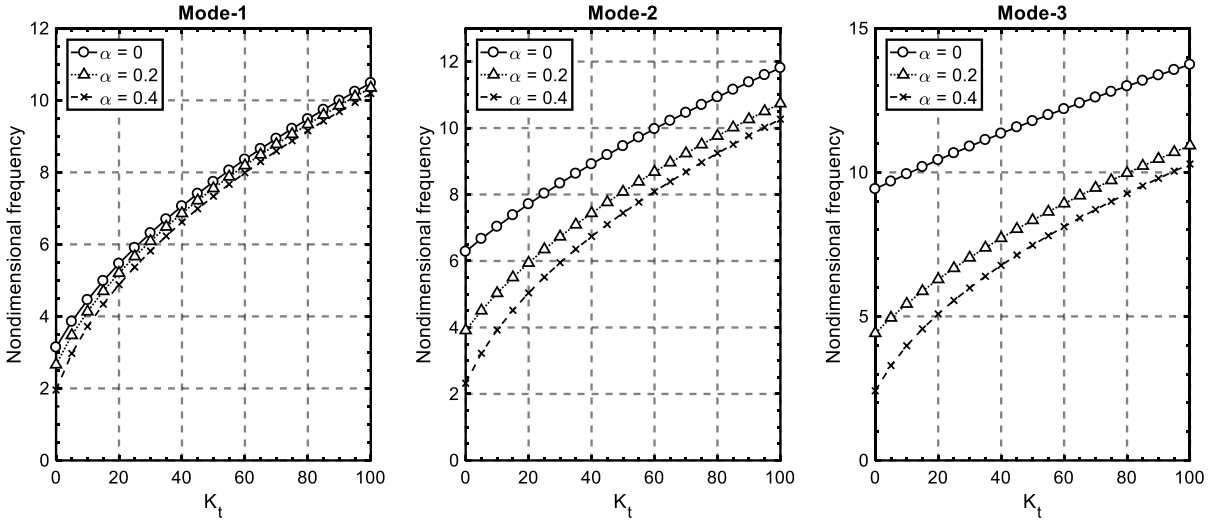

Figure 5. Variations of frequencies of torsional clamped-clamped embedded in elastic medium with different stiffness according to the increment of nondimensional nonlocal parameter

5. Conclusions

In this study, the nonlocal free torsional vibration of nanorods embedded in an elastic medium is investigated by employing the differential transformation method. Firstly, the equation of motion is derived based on the equilibrium approach. Then, the differential transformation solution is obtained by using the transformed functions. Within the scope of the numerical results, the torsional frequencies calculated with the DTM are compared with analytical and finite element results. Also, the numerical results are discussed in detail and the following conclusions are reached:

- The atomic parameter reduces the torsional frequencies. Therefore, the atomic parameter is indispensable for the mechanical analysis of nanostructures.
- The atomic parameter is more effective in the clamped-clamped nanorod that are more rigid than clamped-free nanorod.
- The elastic medium increases the frequencies. In this case, the lowering effect of atomic parameter on the frequencies decreases.
- While the DTM results are not inappropriate for low term numbers, these agree with the analytical results for high term numbers.
- In DTM analysis, the deviation decreases as the nonlocal parameter increases. This conclusion demonstrates that DTM can be useful for nonlocal mechanical analysis problems.

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Temperature-Dependent Luminescence Characteristics of Er-Doped $LiCaBO_3$

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ABSTRACT

This study investigates the synthesis and characterization of pure and Er-doped LiCaBO3 samples, focusing on their structural and photoluminescence properties. Samples were prepared via the conventional solid-state reaction method. Structural characterization was conducted using X-ray Diffraction (XRD) on a Rigaku SmartLab diffractometer, while photoluminescence (PL) measurements employed a 1/4 m monochromator with a liquid nitrogen-cooled InGaAs detector. Temperature-dependent PL measurements were performed from 10K to 300K using a closed-cycle He cryostat.

XRD results confirmed the successful formation of the LiCaBO3 crystal structure in both undoped and Er-doped samples. Er doping in the 1–6% range did not significantly alter the lattice structure. Room temperature PL measurements showed a non-linear dependence on Er concentration, with the highest emission at 5% Er. Interestingly, PL intensity in the 5% Er-doped sample decreased as temperature was lowered, contrary to typical thermal quenching behavior.

In summary, pure and Er-doped LiCaBO3 materials with high structural integrity were synthesized. The unusual temperature-dependent PL behavior observed in the 5% Er-doped sample suggests possible unique energy transfer or thermalization mechanisms, warranting further investigation.

Keywords : Erbium, $LiCaBO_3$, Low temperature photoluminescence, Luminescent materials.

1. Introduction

Phosphor materials are indispensable components in a myriad of advanced technological applications, serving as the cornerstone for innovations in solid-state lighting, high-resolution displays, sophisticated laser systems, and a diverse array of sensors [1], [2]. Their ability to efficiently convert absorbed energy into emitted light makes them critical for modern optoelectronic devices. Among the various activators employed in the development of high-performance phosphors, rare earth (RE) ions stand out due to their unique 4f electronic configurations [3], [4]. These configurations result in sharply defined electronic transitions that facilitate a broad spectrum of light absorption and emission, effectively spanning nearly the entire ultraviolet (UV), visible (VIS), and near-infrared (NIR) regions [5]. The intrinsic shielding of the 4f electrons by the outer 5s and 5p orbitals renders these transitions largely impervious to external environmental influences, leading to narrow emission bands and high quantum efficiencies, which are highly desirable for many applications [6].

Borate compounds have garnered significant attention as host matrix materials for RE^{3+} ions, primarily owing to their exceptional physicochemical and optical properties [7]. The structural versatility of borates is remarkable; they can form a wide variety of crystal lattices through boron-oxygen polyhedra, which are typically composed of trigonal BO_3 and tetrahedral BO_4 units [8]. This structural flexibility allows for the incorporation of various dopant ions, including rare earths, into different crystallographic sites, thereby enabling the tuning of their optical properties. Within the borate family, lithium borates are particularly noteworthy for their low melting points, high thermal stability, wide band gaps, and low phonon energies [9]. These characteristics are crucial for minimizing non-radiative relaxation processes, which can quench luminescence, and for ensuring the stability of the phosphor under high operating temperatures. Calcium

borates, on the other hand, contribute additional structural rigidity and mechanical stability to the host matrix, making them particularly well-suited for high-temperature and demanding photonic applications [9]. The combination of lithium and calcium in a borate matrix, such as $LiCaBO_3$, thus offers a promising platform for developing robust and efficient luminescent materials

Erbium (Er^{3+}) ions are among the most extensively investigated rare earth activators, particularly for their distinctive luminescence properties [10]. A key feature of Er^{3+} is its prominent $^4I_{13/2} \rightarrow {}^4I_{15/2}$ electronic transition, which emits light around 1.53 µm [11]. This specific wavelength is of immense technological importance as it coincides with the third telecommunication window (C-band), a region where optical losses in silica-based optical fibers are minimal [12]. Consequently, this wavelength plays a pivotal role in long-distance optical communication systems, enabling high-speed and efficient data transmission over vast networks. Er^{3+} ions are therefore widely employed in the fabrication of light sources, optical sensors, and all-optical amplifiers that operate within this critical spectral range [13]. Beyond telecommunications, Er^{3+}-doped phosphor materials are also intensely explored for medical imaging applications. The low absorption of 1.53 µm light by living tissues allows for deeper penetration and reduced scattering, making Er^{3+}-doped materials ideal for in vivo imaging and diagnostics [14]. Furthermore, Er^{3+} ions are extensively studied in upconversion photoluminescence research, where they convert lower-energy photons into higher-energy visible light emissions, offering potential for advanced displays, bio-imaging, and solar energy conversion [15]. The visible transitions, in addition to the 1.53 µm transition, further broaden the applicability of Er^{3+} ions in various photonic devices

This study focuses on the synthesis, structural characterization, and luminescence properties of Er^{3+}-doped $LiCaBO_3$ phosphors, with a particular emphasis on their temperature-dependent photoluminescence behavior. Understanding how temperature influences the luminescence characteristics is crucial for optimizing these materials for practical applications, especially in environments where temperature fluctuations are common. The conventional solid-state reaction method was employed for sample preparation. The subsequent sections detail the experimental methodology, present the results from X-ray diffraction and photoluminescence measurements, and discuss the implications of these findings for the development of advanced photonic devices. The aim is to provide a comprehensive analysis of Er^{3+}-doped $LiCaBO_3$, contributing to the broader knowledge base of rare-earth-activated borate phosphors and their potential in cutting-edge technologies.

2. Materials and Methods

2.1. Sample Preparation

Pure and Erbium (Er^{3+})-doped lithium calcium borate ($LiCaBO_3$) samples were synthesized using the conventional solid-state reaction method, a widely recognized and cost-effective technique for producing crystalline inorganic compounds. This method is favored for its simplicity, scalability, and ability to yield highly crystalline materials with good homogeneity when appropriate synthesis parameters are maintained. The starting materials, all of analytical reagent grade, included lithium carbonate (Li_2CO_3), calcium carbonate ($CaCO_3$), boric acid (H_3BO_3), and erbium oxide (Er_2O_3). These precursors were carefully weighed in stoichiometric ratios to achieve the desired chemical composition of $LiCaBO_3$ and varying concentrations of Er^{3+} doping. The precise control over stoichiometry is crucial to ensure the formation of a single-phase material and to accurately control the dopant concentration, which directly influences the luminescence properties

Initially, the weighed starting materials were thoroughly mixed in an agate mortar for approximately 30 minutes to ensure a homogeneous distribution of the constituent powders. This mechanical mixing step is critical for facilitating solid-state diffusion during subsequent heat treatments. The resulting powder mixtures were then subjected to a two-step thermal treatment process. The first step involved pre-calcination at 450 °C for 1 hour in a high-temperature muffle furnace. After the initial calcination, the powder mixture was removed from the furnace, allowed to cool to room temperature, and then re-

ground and re-mixed in the agate mortar. This intermediate grinding step is essential for breaking down agglomerates formed during calcination and for further enhancing the homogeneity of the mixture, thereby promoting more complete solid-state reactions in the subsequent high-temperature step

The final thermal treatment involved heating the powders at 800 °C for 8 hours in the same muffle furnace. This high-temperature sintering step is crucial for the complete formation of the crystalline $LiCaBO_3$ host lattice and for the effective incorporation of Er^{3+} ions into the host structure. After the sintering process, the furnace was allowed to cool naturally to room temperature, and the obtained solid samples were then collected for further characterization. The entire synthesis process was carried out in an atmospheric environment.

2.2. Characterization Techniques

Structural analysis of the synthesized $LiCaBO_3:Er^{3+}$ materials was performed using X-ray Diffraction (XRD) at room temperature. A Rigaku SmartLab diffractometer, equipped with a Cu Kα radiation source (operating at 40 kV and 30 mA, with a characteristic X-ray wavelength λ = 1.54051 Å), was utilized for this purpose. The samples were scanned over a 2θ angular range from 15° to 90°, with a step size of 0.01° and a scanning speed of 0.02°/s. The collected diffraction patterns were then compared with the reported XRD peaks for the $LiCaBO_3$ crystal, first synthesized and reported by Wu et al. [16], to confirm the formation of the $LiCaBO_3$ phase and to assess the presence of any secondary phases. The sharpness and intensity of the diffraction peaks provide insights into the crystallinity and crystallite size of the synthesized materials

Photoluminescence (PL) measurements were conducted to investigate the optical emission properties of the Er^{3+}-doped $LiCaBO_3$ samples. The PL spectra were recorded using a specialized setup that included a 1/4 m monochromator coupled with a liquid nitrogen-cooled InGaAs detector. The InGaAs detector is particularly suitable for detecting emissions in the near-infrared (NIR) region, where the characteristic Er^{3+} emission at 1.53 µm is observed. For excitation, a 532 nm Nd:YAG solid-state laser was employed, providing an output power of 60 mW. The choice of a 532 nm excitation wavelength is strategic, as it efficiently pumps Er^{3+} ions to higher energy levels, leading to subsequent radiative transitions and luminescence. The laser power was carefully controlled to avoid saturation effects and sample damage. Temperature-dependent PL measurements were also performed by placing the samples in a cryostat, allowing for precise temperature control from 10 K to 300 K.

3. Results and Discussion

3.1. XRD Results and Structural Analysis

Figure 1 illustrates the X-ray Diffraction (XRD) measurement results for the synthesized pure and Er^{3+}-doped $LiCaBO_3$ samples. A critical observation from these patterns is the presence of sharp and well-defined diffraction peaks across all samples, which is a clear indication of their excellent crystallinity. High crystallinity is a desirable characteristic for phosphors, as it generally correlates with enhanced luminescence efficiency due to reduced scattering and non-radiative recombination centers

Crucially, the observed diffraction peaks for all samples are in full agreement with the reference diffraction patterns for the $LiCaBO_3$ phase as reported by Wu et al. [16]. This confirms that the conventional solid-state reaction method successfully yielded the desired $LiCaBO_3$ crystal structure without the formation of any significant secondary phases.

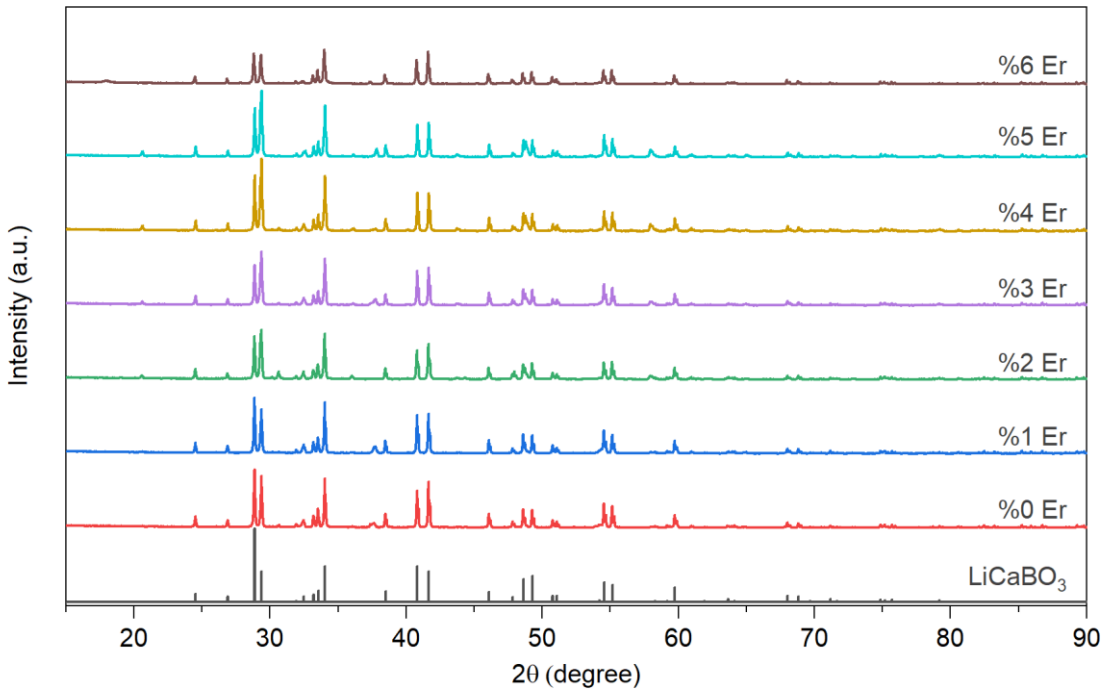

Figure 1. XRD results of samples

Upon closer inspection, it was noted that the diffraction peak intensity of the sample doped with 6% Er^{3+} was discernibly lower compared to the other samples (e.g., 1-5% Er^{3+} doping). This reduction in peak intensity, while still maintaining the $LiCaBO_3$ phase, suggests a decrease in the overall crystallinity or an increase in structural disorder for the higher Er^{3+} concentration. Excessive doping of rare earth ions into a host lattice can lead to lattice distortion or formation of defects. In this case, the lower peak intensity for the 6% Er^{3+} sample implies that the incorporation of a higher concentration of Er^{3+} ions might have introduced more lattice strain or defects, slightly compromising the long-range order of the crystal structure. This observation is particularly important as it provides a structural basis for understanding the subsequent photoluminescence results, where a similar trend in luminescence intensity is expected.

3.2. Effect of Er^{3+} Concentration on Photoluminescence Characteristics

Figure 2 presents the photoluminescence (PL) measurement results obtained at room temperature for $LiCaBO_3$ samples doped with varying concentrations of Er^{3+}. The most prominent feature in these spectra is a highly intense emission peak observed in the near-infrared (NIR) region, specifically spanning the wavelength range of 1520-1550 nm. This characteristic emission band is unequivocally attributed to the intra-4f electronic transition of Er^{3+} ions, specifically the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition [11].

The investigation into the effect of Er^{3+} concentration revealed a clear trend: the luminescence intensity systematically increased as the Er^{3+} concentration was raised from 1% up to 5%. This phenomenon is typically observed in rare-earth-doped phosphors at lower dopant concentrations, where an increase in the number of active luminescent centers (Er^{3+} ions) directly leads to a higher probability of light emission. The maximum luminescence intensity was recorded for the 5% Er^{3+}-doped sample, indicating an optimal doping concentration for this specific host material and synthesis conditions. At this concentration, the balance between the number of active Er^{3+} ions and the potential for concentration quenching mechanisms is achieved.

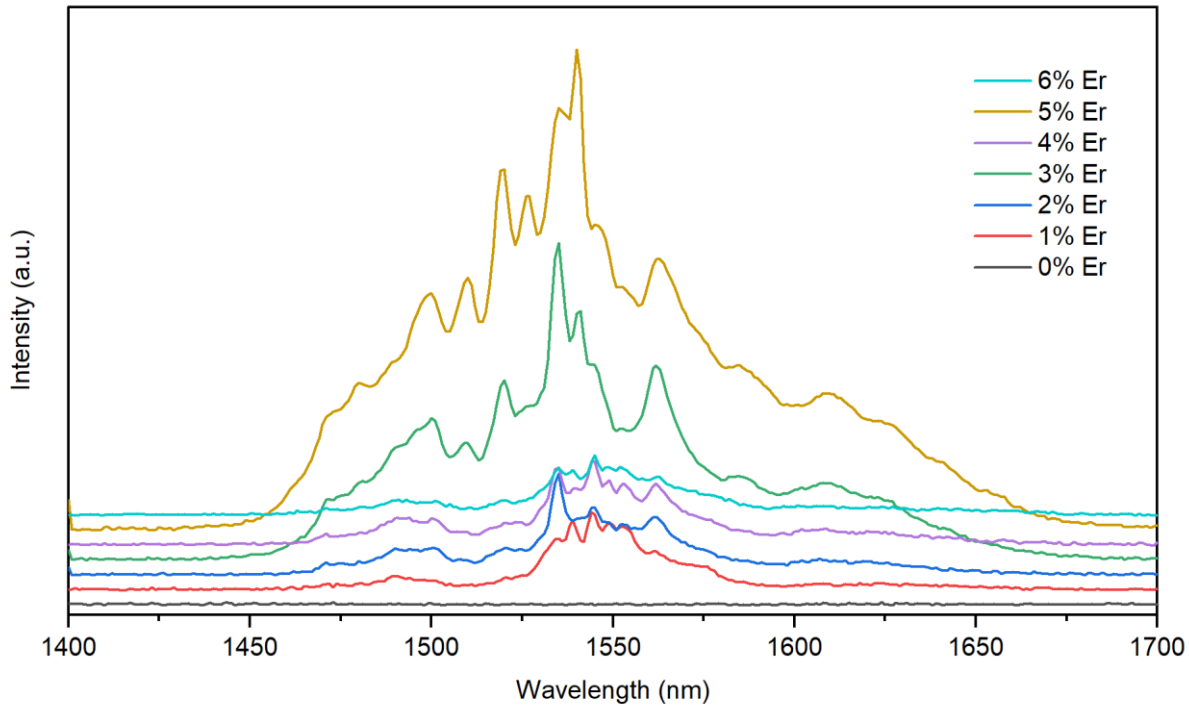

Figure 2. Room temperature PL results of samples as a function of Er concentration

However, a significant decrease in luminescence intensity was observed for the 6% Er^{3+}-doped sample. This reduction in PL intensity at higher dopant concentrations is a well-known phenomenon in luminescent materials, commonly referred to as concentration quenching [17]. Concentration quenching occurs when the distance between neighboring activator ions becomes sufficiently small, leading to non-radiative energy transfer processes between them. The observed decrease in PL intensity for the 6% Er^{3+} sample aligns perfectly with the XRD results, which indicated a lower crystallinity for this sample. The degradation of the crystal structure, as suggested by the XRD data, likely creates more defects and non-radiative pathways, exacerbating the concentration quenching effect and leading to a substantial reduction in luminescence efficiency.

3.3. Temperature-Dependent Photoluminescence Characteristics

Figure 3 illustrates the temperature-dependent photoluminescence behavior of the 5% Er^{3+}-doped $LiCaBO_3$ sample, which exhibited the highest luminescence intensity at room temperature. The measurements were conducted over a broad temperature range, from 10 K to 300 K, providing comprehensive insights into the thermal stability and performance of the phosphor. A general trend observed was that the luminescence intensity decreased as the temperature was lowered towards 10 K. This behavior is somewhat counterintuitive compared to many conventional phosphors where luminescence often increases at lower temperatures due to reduced thermal quenching [18]. However, in certain systems, particularly those involving complex energy transfer dynamics or specific thermal activation processes, different temperature dependencies can arise.

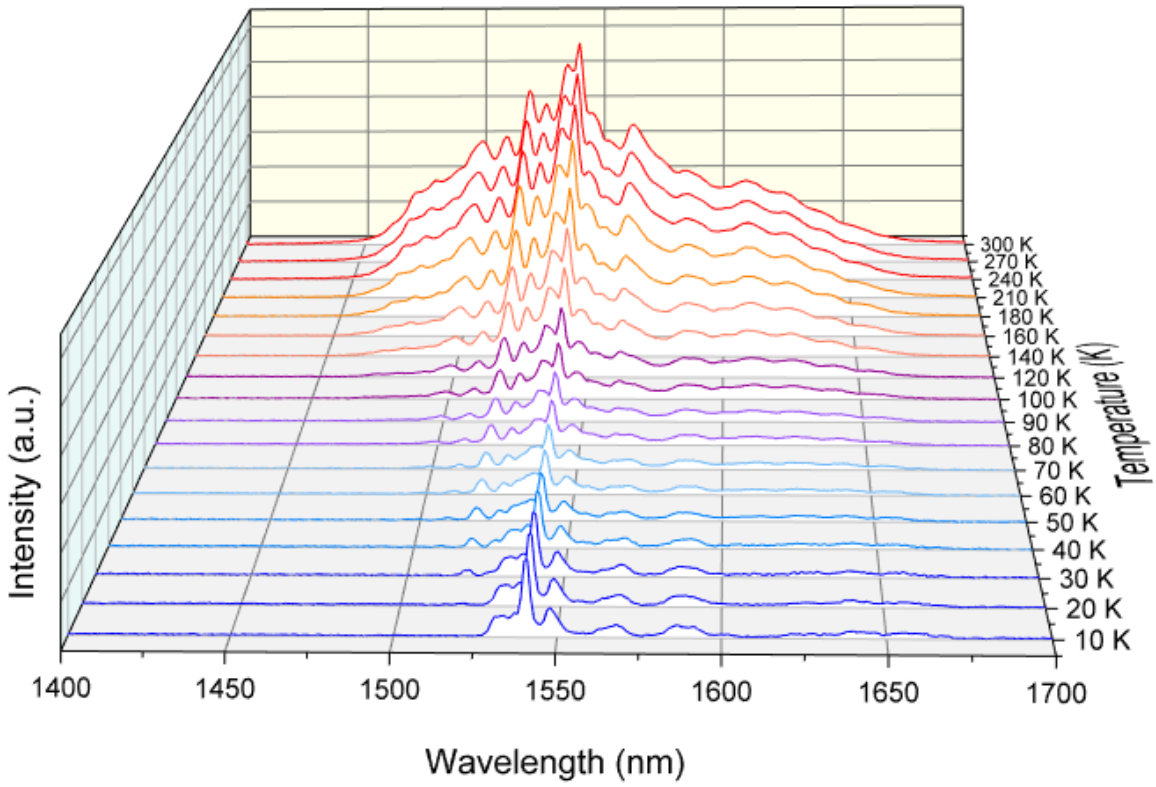

Figure 3. Low temperature PL results of the 5% Er-doped sample in the 10 K – 300 K temperature range

At the lowest temperature investigated, 10 K, a notable spectral change occurred: emissions at wavelengths shorter than 1530 nm (corresponding to relatively higher energy transitions) completely disappeared. Concurrently, the intensity of longer wavelength emissions (lower energy transitions) decreased but remained detectable. The PL luminescence observed at low temperatures is primarily attributed to the electron transitions between the $^4I_{13/2}$ and $^4I_{15/2}$ energy levels of the Er^{3+} ions. The disappearance of higher-energy components at very low temperatures suggests that certain thermally activated processes, which contribute to these emissions at higher temperatures, are frozen out. This could involve phonon-assisted transitions or energy transfer mechanisms that require a certain amount of thermal energy to be efficient

Interestingly, as the temperature approached room temperature (300 K), the luminescence intensity increased, and new splittings emerged on the high-energy side of the PL peak. This increase in luminescence intensity with rising temperature up to room temperature, coupled with the appearance of new spectral features, is a significant finding. It suggests a complex interplay between the Er^{3+} ions and the $LiCaBO_3$ crystal lattice. The interaction between the Er^{3+} ions and the host crystal field can lead to Stark splitting of the energy levels, and these splittings can become more pronounced or new transitions can be activated as thermal energy increases, populating higher Stark sublevels [19]. This phenomenon indicates that the $LiCaBO_3$ host matrix provides a favorable environment for Er^{3+} luminescence at ambient temperatures, potentially due to efficient energy transfer from the host to the Er^{3+} ions or a reduction in certain non-radiative pathways that are dominant at very low temperatures

Crucially, the stability of the peak position in the 1530 nm - 1550 nm range, despite the variations in intensity and spectral fine structure with temperature, highlights the robustness of the primary Er^{3+} emission. This thermal stability of the emission wavelength is a highly desirable property for practical

applications, as it ensures consistent performance across varying operating temperatures. The observed increase in PL luminescence intensity as temperature rises towards room temperature, combined with the stable emission wavelength, strongly suggests that Er^{3+}-doped $LiCaBO_3$ materials are highly suitable for a range of photonic applications. These include solid-state lasers, where stable and efficient emission is critical; optical amplifiers, which require consistent gain characteristics; and biomedical imaging systems, where reliable signal generation across physiological temperature ranges is essential. The unique temperature-dependent behavior observed in this study further enhances the understanding of these materials and their potential for advanced optoelectronic devices.

4. Conclusion

In this study, Erbium (Er^{3+})-doped lithium calcium borate ($LiCaBO_3$:Er^{3+}) materials were successfully synthesized using the conventional solid-state reaction method. The structural integrity and phase purity of the synthesized samples were confirmed through X-ray Diffraction (XRD) analyses. These analyses demonstrated that all prepared samples crystallized in the desired $LiCaBO_3$ phase. Er^{3+} doping within the concentration range of 1-5% did not induce any significant detrimental effects on the host crystal structure.

Photoluminescence (PL) measurements conducted at room temperature provided critical insights into the optical properties of these materials. An emission peak was observed in the near-infrared (NIR) region, centered around 1520-1550 nm. This characteristic emission is directly attributable to the well-known $^4I_{13/2} \rightarrow {}^4I_{15/2}$ electronic transition of the Er^{3+} ions. The effect of Er^{3+} concentration revealed an optimal doping level: the luminescence intensity progressively increased as the Er^{3+} concentration was raised from 1% to 5%. However, beyond this optimal concentration, specifically at 6% Er^{3+} doping, a noticeable decrease in luminescence intensity was observed. This quenching effect is attributed to the slight reduction in crystallinity observed in the XRD data for the higher doping concentration

The temperature-dependent PL measurements were showed that as the temperature decreased from 300 K to 10 K, a general reduction in PL luminescence intensity was observed. More specifically, at 10 K, the shorter wavelength emissions below 1530 nm completely vanished, while longer wavelength emissions persisted with reduced intensity. Conversely, as the temperature increased towards room temperature, the PL luminescence intensity increased, and new spectral splittings appeared on the high-energy side of the main emission peak. This indicates a complex interaction between the Er^{3+} ions and the $LiCaBO_3$ host lattice.

Despite these temperature-induced spectral changes, a key finding was the remarkable stability of the main emission peak's position in the 1530 nm - 1550 nm range. This wavelength stability, coupled with the observed increase in luminescence intensity as the temperature approaches room temperature, highlights the robust performance of these materials under varying thermal conditions. Consequently, this study strongly supports the potential utility of Er^{3+}-doped $LiCaBO_3$ materials in a diverse array of advanced photonic applications.

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Control of Porous Titania Membrane Properties via Sintering: Microstructure and Filtration Performance

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ABSTRACT

This study investigates how sintering conditions influence the microstructure and water permeability of porous titania membranes fabricated by tape casting. To increase membrane thickness, two approaches were tested: lamination of three green tapes and sequential tape casting of up to three layers. Sequential tape casting produced mechanically stable membranes, whereas lamination resulted in weak interfacial bonding and sudden failure during filtration. Green tapes were sintered at 500–1100 °C for 1–3 h, and the effects on pore structure and filtration performance were evaluated. Increasing the sintering temperature from 1000 to 1100 °C enlarged the average pore size (170–264 nm) but reduced porosity, while extending the sintering time at 1000 °C increased porosity without significantly altering pore size. Water permeability correlated with both pore size and porosity, underscoring the importance of microstructural tailoring for membrane optimization.

Keywords: Titania, Tape casting, Porous membranes, Microstructure, Water permeability.

1. Introduction

Porous ceramics exhibit excellent chemical, thermal, and mechanical stability, making them suitable for a wide range of applications, including catalyst supports, filtration, and energy-related devices [1-3]. Their functional performance is strongly governed by structural parameters such as pore size, porosity, and connectivity, which in turn influence properties such as permeability, strength, and selectivity [1, 4]. Among these applications, filtration is particularly critical, as pore size distribution and porosity directly determine flux and separation efficiency in porous ceramic membranes [5, 6].

The pore characteristics of ceramics can be tailored through several factors, including raw material properties, the use of additives, fabrication methods, and sintering conditions [7]. Tape casting has emerged as a versatile technique for fabricating flat, thin, and multilayer ceramic membranes with thicknesses ranging from tens to hundreds of micrometers [8, 9]. In this method, slurry composition, drying behavior, and subsequent thermal treatment play decisive roles in defining the microstructure and final membrane performance.

Titania (TiO_2) is particularly attractive for porous membrane applications due to its chemical stability, photocatalytic activity, and potential for separation and purification processes [10, 11]. The sintering process plays a central role in tailoring the microstructure of titania membranes, as both temperature and duration influence pore size, porosity, and mechanical integrity. However, increasing membrane thickness remains a challenge: lamination may introduce interfacial weaknesses, whereas sequential tape casting provides a promising alternative for producing mechanically stable multilayer membranes [12, 13].

In this study, we investigate the fabrication of porous titania membranes by tape casting, with emphasis on increasing thickness through two approaches: lamination of multiple green tapes and sequential tape casting of dried tape layers. The effects of sintering temperature and time on pore structure and filtration behavior are systematically analyzed, and the correlation between microstructural

features and water permeability is discussed. The findings highlight the importance of microstructural tailoring for optimizing the performance of titania membranes in filtration applications.

2. Materials and Method

2.1. Starting material

Commercial TiO_2 powder (Kronos 1171, Germany; mean particle size 0.26 µm; specific surface area 9.0 $m^2.g^{-1}$) was used. Polyvinyl butyral (PVB, Mowital B60H) and polyethylene glycol (PEG 600) served as binder and plasticizer, respectively. An azeotropic ethanol/toluene mixture (50/50 vol%) was used as the tape-casting solvent.

2.2. Fabrication of porous titania membrane

TiO_2 was dispersed in the solvent and ball-milled (zirconia media) for ~2 h. Binder was added and milled for 24 h, followed by plasticizer addition and a further 24 h of mixing. The slurry was tape-cast on Mylar using a stainless-steel doctor blade (~30 cm min^{-1}) and dried.

To increase thickness, two approaches were applied: (i) Lamination: three individual green tapes were stacked and laminated; (ii) Sequential tape casting: three successive layers were cast sequentially onto previously dried green tapes. Green sheets were cut to size and sintered at 500–1100 °C (1 h) and at 1000 °C for 1 and 3 h.

2.3. Characterization and permeability testing

Final microstructure and thickness were examined by FESEM (Zeiss SIGMA VP). Average pore size was obtained from FESEM images using ImageJ. Open porosity was measured by the Archimedes immersion method in deionized water. Phase composition was determined by XRD (Philips X'Pert PRO PW1730, Cu K_α, λ = 1.5406 Å, 40 kV, 30 mA). Water permeability was evaluated in a dead-end stirred cell (Amicon 8010) connected to compressed N_2 (Figure 1). The feed side was held at constant pressure, the permeate at atmospheric pressure, at 25 °C and transmembrane pressure (TMP) up to 0.4 bar. Permeation flux was calculated as

$$j = \Delta V/(t.A) \quad (1)$$

where ΔV is the collected permeate volume, t the filtration time, and A the membrane area.

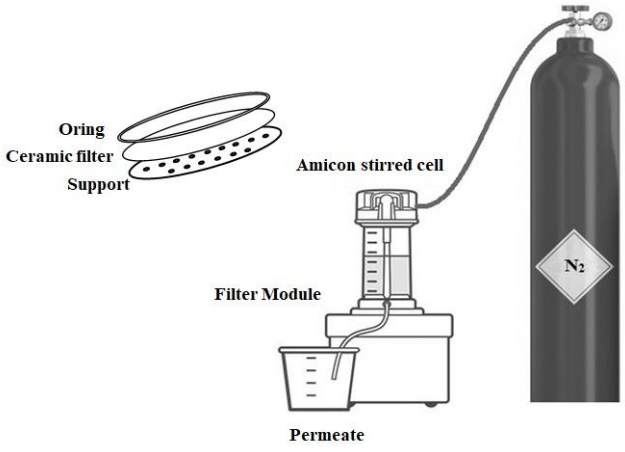

Figure 35:schematic of water permeability test under nitrogen gas pressure.

3. Results and Discussion

3.1. Influence of layering techniques

Figure 2 shows scanning electron microscopy images of the fractured cross-sections of the membranes after pressure-induced failure in the pressure cell, highlighting the distinct differences in interfacial bonding between the two fabrication strategies. In the sequential tape casting approach (Figure 2a), the interfaces between the layers were well integrated, resulting in a dense and homogeneous cross-section with no visible separation. This indicates that during sequential deposition, the subsequent slurry layer adheres effectively to the previously dried green tape, forming a consolidated structure upon sintering. In contrast, the laminated membranes (Figure 2b) exhibited clear debonding at the interfaces of the stacked layers. The weak interfacial bonding resulted in pronounced separation lines within the fracture surface, which compromised the structural integrity of the membrane. The top-view SEM image of the laminated sample (Figure 2c) further confirms this observation, showing the three layers distinctly separated at the fracture site.

The mechanical stability of the membranes was further assessed under hydrostatic nitrogen pressure (Figure 1). The laminated membranes failed at pressures below 0.2 bar, indicating premature delamination under stress. By comparison, the membranes prepared through sequential tape casting withstood pressures up to 0.4 bar before failure, demonstrating their superior resistance to pressurization. These results clearly show that sequential tape casting provides stronger interfacial bonding and higher mechanical reliability compared to lamination, making it a more effective strategy for fabricating multilayer porous titania membranes intended for filtration applications.

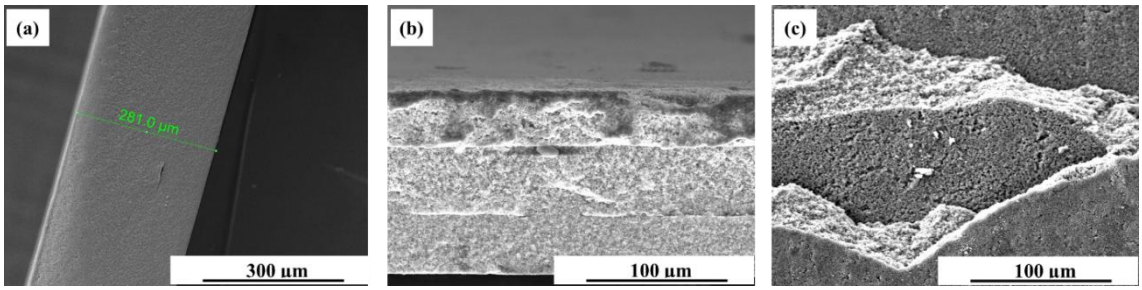

Figure 36: FESEM micrographs of samples prepared by sequential tape casting (a) and lamination, showing cross-sectional (b) and top (c) views.

3.2. Crystalline structure and microstructural analysis

Figure 3 presents the XRD patterns of porous titania sheets sintered at different temperatures (500–1100 °C for 1 h) and at 1000 °C for different durations (1 and 3 h). At sintering temperatures below 1000 °C, the samples predominantly exhibited the anatase phase. However, when the sintering temperature increased to 1100 °C, anatase was completely transformed into rutile. This anatase-to-rutile transformation is a well-known thermally driven phase transition in titania, and the results clearly demonstrate that temperature is the dominant factor controlling the crystalline phase. Sintering time also influenced phase transformation: extending sintering time at 1000 °C from 1 h to 3 h enhanced the conversion of anatase to rutile, confirming the time-dependent nature of the process.

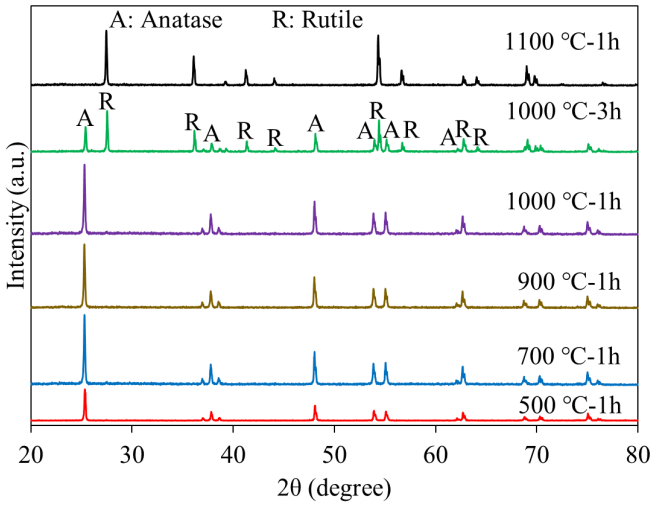

Figure 37: XRD patterns of titania sheets sintered at 500 to 1100 ℃ for 1h and 1000 ℃ for 3 h.

The corresponding microstructures of the sintered sheets are shown in Figure 4. With increasing sintering temperature, grains coalesced and grew significantly, leading to a denser structure. A marked increase in average grain size was observed as the temperature rose from 1000 °C to 1100 °C, indicating accelerated grain growth in this range. Prolonged sintering time also promotes grain coarsening, as shown in Figures 4b and 4d, which can be attributed to grain boundary migration processes that are strongly time dependent.

Interestingly, the effect of sintering time on porosity differed from that of temperature. While higher temperatures tended to densify the structure and reduce porosity, increasing the sintering time slightly increased the open porosity (Table 1). This phenomenon can be explained by the anatase-to-rutile phase transformation. Since rutile has a higher density than anatase, the formation of rutile grains alongside remaining anatase induced localized shrinkage and structural rearrangement, thereby increasing the fraction of open pores [14]. Thus, partial phase transformation significantly influenced the porosity of the sheets, even under constant sintering temperature.

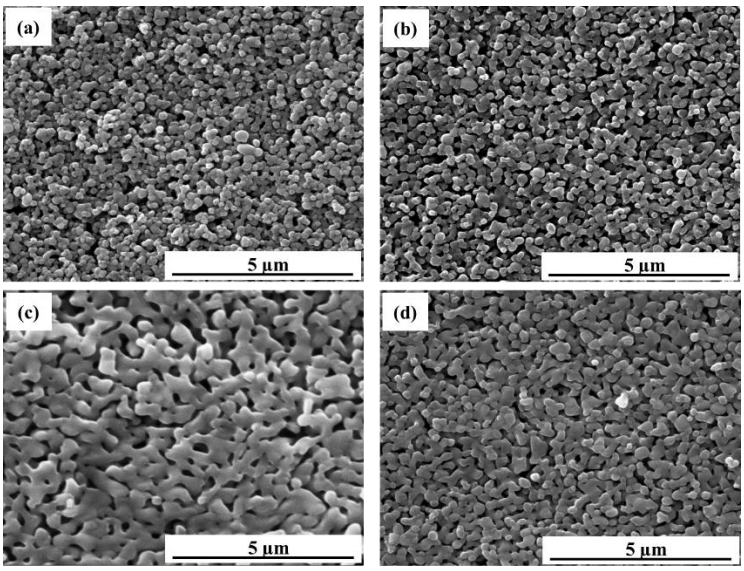

Figure 38: FESEM images of porous titania sheets sintered at 900 (a), 1000 (b), 1100 (c) for 1 h and 1000 ℃ for 3 h (d).

3.3. Permeability study

The results of water permeability measurements are summarized in Table 1. No data were obtained for membranes sintered below 900 °C, as these samples exhibited insufficient mechanical strength and failed even under pressures lower than 0.2 bar. With increasing sintering temperature from 900 °C to 1100 °C, the water permeability of the membranes progressively improved. This trend can be explained by changes in pore structure: although the total porosity decreased, the fraction of open pores increased, and the average pore size rose markedly from 170 nm at 1000 °C to 264 nm at 1100 °C. At 1000 °C, prolonging the sintering time from 1 h to 3 h also resulted in higher permeability. This improvement is attributed to microstructural rearrangements induced by the partial anatase-to-rutile transformation, which facilitated the formation of additional open pores.

The maximum operating pressure showed a comparable dependence on sintering conditions. Membranes sintered at 1000–1100 °C exhibited enhanced structural stability, withstanding pressures up to 0.4 bar. These results emphasize the close relationship between sintering parameters, microstructural evolution, and filtration behavior, highlighting the importance of carefully optimizing processing conditions to achieve mechanically robust and highly permeable porous titania membranes.

Table 8: Permeability performance of porous titania sheets in the Amicon stirred cell

Sintering temperature (°C)	Sintering time (h)	Open porosity (%)	Pore size (nm)	Permeability ($L/m^2.h.bar$)	Maximum operating pressure (bar)
900	1	52	165	335	0.2
1000	1	50	170	348	0.3
1100	1	43	264	589	0.4
1000	3	57	173	432	0.3

4. Conclusions

This study demonstrates that sequential tape casting is a more effective strategy than lamination for fabricating multilayer porous titania membranes, due to its stronger interfacial bonding and higher mechanical stability. Sintering strongly influences the microstructure: raising the temperature from 1000 °C to 1100 °C enlarged the average pore size from about 170 nm to 260 nm and increased water flux accordingly, while extending the dwell time from 1 h to 3 h at 1000 °C mainly increased open porosity (from 50% to 57%) without significantly changing pore size, due to partial anatase-to-rutile transformation. Overall, the results highlight the tight link between processing, structure, and performance, emphasizing that precise control of both sintering temperature and time is essential for producing robust, high-permeability titania membranes for filtration applications.

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Durability Assessments of Lime and Brick Powder-Based Grouts

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ABSTRACT

Historic structures are subject to various forms of damage and deterioration over time. Recent research indicates that injections are among the most widely employed methods for their consolidation. Despite being an irreversible process, grouting is favored for its effectiveness in restoring structural continuity. It is evident that the injection material must exhibit resistance to environmental exposure. In this study, the durability properties of three grout formulations were evaluated and compared: an air lime-based grout (AG1), a natural hydraulic lime-based grout (HG1), and a hydraulic lime grout incorporating a pozzolanic brick powder additive (HG3). The compressive strengths of the grouts were first compared, followed by chemical and mineralogical analyses (XRF, XRD, FTIR) to examine their compositions. To evaluate durability, hardened grouts were subjected to freeze-thaw cycles and sulfate exposure. While the hydraulic lime-based grouts (HG1 and HG3) showed significantly higher compressive strength and freeze-thaw resistance than the air lime grout (AG1), a critical finding emerged from the sulfate resistance tests. The pozzolan-modified grout (HG3) demonstrated lower resistance to sulfate attack compared to the plain hydraulic lime grout (HG1). Microstructural analysis (SEM-EDS) revealed that this vulnerability was caused by the formation of expansive gypsum and thaumasite, whose precursors were made available by the pozzolanic addition. It was concluded that while hydraulic lime is essential for durable grouts, the inclusion of pozzolanic additives requires careful consideration of the specific environmental conditions. For balanced performance, particularly in sulfate-rich environments, a plain natural hydraulic lime grout may offer a more reliable and durable solution.

Keywords: Brick Powder, Consolidation, Durability, Grout, Historic Structures, Lime.

1. Introduction

Historic structures are invaluable assets that reflect the cultural, architectural, and technological heritage of civilizations. However, these structures are continuously exposed to various detrimental factors over their lifespan, including environmental conditions, geotechnical challenges, natural hazards such as earthquakes, and usage-related stresses. This prolonged exposure inevitably leads to damage and deterioration, compromising their structural integrity and long-term survival. Consequently, the development and application of effective conservation and strengthening techniques are of vital importance in the field of cultural heritage preservation.

Among the various intervention methods, grout injection is one of the most widely employed techniques for the consolidation and preservation of historic masonry structures. Despite being an irreversible application, grouting is frequently preferred due to its high effectiveness in restoring the load-bearing capacity, ensuring the continuity of damaged structural elements, and improving overall durability. The primary goal of a grouting intervention is to fill cracks and voids within the masonry, thereby rebuilding monolithic structural behavior.

The success of a consolidation treatment via injection is critically dependent on the properties of the grout material used. The physical, chemical, and mechanical compatibility of the repair material with the original material is crucial to avoid introducing new forms of damage, such as rigid inclusions or harmful chemical reactions within the historic building parts. Furthermore, the injection grout must exhibit sufficient resistance to the same environmental factors that caused the initial deterioration, including freeze-thaw cycles and salt crystallization, particularly sulfate attack, which is a common cause of degradation in porous building materials.

This study focuses on the durability assessment of lime-based grouts, which are often considered more compatible with historic materials than cement-based alternatives. Specifically, three different grout formulations were designed and evaluated: An air lime-based grout (AG1), a natural hydraulic lime-based grout (HG1), and a hydraulic lime grout incorporating a pozzolanic brick powder additive (HG3). The research aims to compare their performance not only in terms of injectability and mechanical strength but, more critically, their durability under aggressive environmental conditions. By subjecting the hardened grouts to freeze-thaw cycles and sulfate exposure, this paper investigates the influence of the binder type (air vs. hydraulic lime) and the pozzolanic addition (brick powder) on long-term performance. By employing a comprehensive set of chemical, mineralogical, and microstructural analyses, this work seeks to provide a scientific basis for designing durable and compatible injection grouts for the conservation of historic structures.

Therefore, this study provides a comprehensive durability assessment of three distinct lime-based grout formulations: air lime, natural hydraulic lime, and hydraulic lime modified with a pozzolanic brick powder. The objective is not only to compare their fundamental mechanical and chemical properties but also to critically evaluate their performance under different aggressive environmental conditions, namely freeze-thaw cycles and sulfate attack. By doing so, this research investigates the complex and potentially conflicting role of pozzolanic additives, aiming to elucidate the critical trade-offs between mechanical strength and chemical resistance. The goal is to provide a more nuanced, scientific basis for designing compatible and genuinely durable injection grouts for the conservation of historic structures.

1.1. A Review on the Durability of Lime and Brick Powder-Based Grouts

The development of compatible and durable injection grouts is a central theme in the conservation of historic masonry. A successful grout formulation must balance several competing requirements: adequate fluidity for injection, long-term volumetric stability, and appropriate mechanical properties that do not create rigid inclusions within the historic fabric. The scientific literature reflects a broad consensus on these fundamentals, with numerous studies dedicated to optimizing grout performance through material characterization and performance evaluation (Gökyiğit-Arpaci et al., 2019).

A primary focus of research has been the enhancement of lime-based grouts through additives. Natural hydraulic lime (NHL) is often favored, but its properties can be tailored. Similarly, research on grouts derived directly from natural resources, such as those produced from argillaceous (clay-bearing) limestone, underscores the importance of the binder's inherent chemical and mineralogical composition for achieving suitable consolidation properties (Oktay et al., 2020). For instance, the addition of approximately 10% white cement by weight has been shown to effectively enhance early-age strength, with mechanical properties continuing to improve for up to 180 days (Pachta et al., 2020). Conversely, advanced nanomaterials like fumed nano-silica can improve shrinkage and mechanical characteristics, but their application is often constrained by high cost and the need for significant dosages of superplasticizers to maintain workability (Papayianni et al., 2012).

The use of pozzolanic materials, particularly those from traditional sources like brick powder, is a well-established strategy for improving lime-based binders. The processing of these pozzolans is critical; Miriello et al. (2009) demonstrated that prolonged milling of clay brick powder alters its mineralogy and reactivity, directly influencing the grout's final properties and potential durability. However, the

proportion of such additives is paramount. In a study using demolition residues in lime-soil blocks, Figueiredo et al. (Figueiredo et al., 2012) observed that durability significantly decreased when the replacement level of lime exceeded a 50% threshold.

The ultimate measure of a grout's success is its long-term durability against environmental stressors, which remains a critical and complex area of investigation. Comprehensive reviews confirm that the durability of lime-based mortars is a multifaceted issue dependent on binder composition, curing, and carbonation, with lime-pozzolan formulations generally showing robust performance (Alvarez et al., 2021; Veiga et al., 2019). Experimental studies provide more direct evidence. Miltiadou-Fezans et al. (2021) conducted a crucial comparative study showing that an NHL grout with a 10% pozzolan addition exhibited the best resistance to sodium sulfate attack. In stark contrast, a ternary grout (composed of white cement, pozzolan, and hydrated lime) failed after only nine cycles at 50°C, highlighting the risks of using cementitious blends in high-salt environments. Further demonstrating the inherent resilience of lime-based binders, Fares et al. (2022)reported that a lime matrix used in a stainless steel reinforced grout system maintained excellent mechanical and bond characteristics even after aggressive salt and alkali aging cycles.

Despite these advances, the literature reveals a clear need for more integrated studies that connect grout composition directly to performance under multiple, realistic exposure conditions. While many studies evaluate mechanical properties, fewer conduct rigorous and parallel durability testing (e.g., freeze-thaw and sulfate attack) on the same set of well-characterized formulations. Furthermore, there is a gap in research that uses microstructural analyses like SEM-EDS to explicitly document the degradation mechanisms or the beneficial role of pozzolans after durability exposure. This review solidifies the scientific basis for the present study, which is designed to address these specific gaps.

2. Materials and Method

This section details the materials, formulations, and experimental procedures employed to evaluate the performance and durability of the developed injection grouts.

2.1. Materials

The grout formulations developed for this study were based on three primary binder components: an air lime, a natural hydraulic lime, and a pozzolanic brick powder. The chemical compositions of these materials, determined by X-Ray Fluorescence (XRF), are presented in Table 1.

Binders: Two types of lime were used as the main binders. The first was a high-calcium air lime of class CL 80-S, conforming to the BS EN 459-1 (2010) standard. The second was a natural hydraulic lime of class NHL 3.5, also conforming to BS EN 459-1(2010). The CL 80-S was characterized by a high CaO content (69.0%), while NHL 3.5 contained a significant amount of silica (11.4%) and had a hydraulic index of 0.2, indicating its inherent setting properties.

Pozzolanic Additive (Brick Powder): A reactive pozzolan was produced in the laboratory. Clay was ground, calcined at 850°C for 3 hours, and rapidly cooled. The resulting material was sieved through a 0.063 mm (No. 230) sieve, and the passing part was used. The produced brick powder exhibits high pozzolanicity, characterized by high contents of SiO_2 (57.2%) and Al_2O_3 (17.1%).

Admixtures and water: Two types of chemical admixtures were used to control the fresh properties of the grouts. A polycarboxylic ether-based superplasticizer (SP) with a density of 1.08-1.14 g/cm³ was used to achieve the required fluidity. Additionally, a synthetic copolymer-based viscosity modifying admixture (VMA) with a density of 1.0-1.02 g/cm³ was employed in the hydraulic lime-based series. Both admixtures had a chloride content of less than 0.1%. Standard tap water was used for all mixtures.

Table 1. Chemical composition of the raw materials (wt. %).

Component (%)	CL 80-S	NHL 3.5	Brick Powder (850°C)
SiO_2	0.80	11.40	57.20
Al_2O_3	0.30	0.40	17.10
Fe_2O_3	1.20	2.60	8.00
MgO	1.30	0.56	3.10
CaO	69.00	66.10	0.70
K_2O	0.10	0.10	3.10
TiO_2	<0.1	<0.1	0.90
Cr_2O_3	0.50	1.30	0.80
P_2O_5	<0.1	<0.1	0.20
MnO	<0.1	<0.1	0.10
Loss on Ignition (LOI)	26.60	17.20	6.60

2.2. Grout Formulations and Sample Preparation

Three distinct grout series were designed for this study, as detailed in Table 2. The series were designated as:

AG1: A grout based on solely air lime (CL 80-S).

HG1: A grout based solely on natural hydraulic lime (NHL 3.5).

HG3: A grout based on natural hydraulic lime (NHL 3.5) blended with brick powder. For the HG3 formulation, brick powder was added as 30% of the total binder weight. The water-to-binder (w/b) ratio and superplasticizer (SP) dosage were adjusted for each series to achieve a comparable level of fluidity suitable for injection.

Table 2. Mix proportions of the grout formulations

Series ID	Binder System	Water/Binder Ratio (w/b)	SP[1] (%)	VMA[**] (%)
AG1	100% Air Lime (CL 80-S)	1.40	1.40	-
HG1	100% Hydraulic Lime (NHL 3.5)	0.85	1.50	0.40
HG3	70% NHL 3.5 + 30% Brick Powder	0.80	1.50	0.50

Grouts were prepared with a high turbulence mixer, and the mixer blade had a helicoidal shape. As the first step of the mixing procedure, dry binders were hand-mixed to avoid agglomeration. Afterwards, the whole lime is added to 90% of total mix water and mixed for 10 minutes. The remaining water (with diluted chemical admixture) is added within 30 seconds without stopping the mixer. After all materials had been added, the mixture was maintained for an additional 3 minutes. The mixing speed was kept constant at 800 rpm during mixing procedure. Prismatic specimens with dimensions of 40 x 40 x 160 mm were cast for all subsequent tests. Specimens were stored at 20±2°C and relative humidity of 95±5% for 7 days (CEN 1999a). After 7 days, the specimens were demolded and stored at 20±2°C and relative humidity of 65±5% until the testing day.

SP: Superplasticizer, dosage as a percentage of total binder weight.[1]

** VMA: Viscosity Modifying Admixture, dosage as a percentage of total binder weight.

2.3. Test Methods

A comprehensive testing program was conducted to evaluate the mechanical, chemical, mineralogical, and durability properties of the hardened grouts.

2.3.1. Compressive Strength

The 28-day compressive strength of the hardened grouts was determined in accordance with the TS EN 1015-11 (2007) standard. The test was performed on the broken halves of 40 x 40 x 160 mm prismatic specimens previously subjected to flexural strength testing.

2.3.2. Chemical and Mineralogical Characterization

To investigate the composition of the hardened grouts, a suite of analytical techniques was employed on powdered samples (<90 µm) obtained from 28-day-old specimens.

X-Ray Fluorescence (XRF) was determined using a Bruker S8 Tiger model XRF spectrometer. X-Ray Diffraction (XRD of the samples were qualitatively identified using a Bruker D8 Advance model diffractometer. Fourier-Transform Infrared Spectroscopy (FTIR) were analyzed to complement the XRD results using a Perkin Elmer Spectrum 100 model spectrophotometer.

2.3.3. Durability Assessment

The resistance of the hardened grouts to environmental stressors was evaluated through freeze-thaw and sulfate attack tests on prismatic specimens.

Freeze-thaw resistance: The resistance to freeze-thaw was evaluated based on a procedure adapted from ASTM D560 (2012). Prismatic specimens (40x40x160 mm) were saturated in water for at least 24 hours before the test. A single cycle consisted of 24 hours of freezing at -23°C followed by 23 hours of thawing at 21°C in a 100% relative humidity environment. The test was concluded after 12 cycles or when the specimen disintegrated. Mass loss and visual appearance were recorded after each cycle.

Sulfate attack resistance: The resistance to salt crystallization was assessed using a method adapted from TS EN 12370 (2001). Cubic specimens (50x50x50 mm) were dried to a constant mass at 60°C and then subjected to repeated cycles. A single cycle consisted of 2 hours of immersion in a 14% (by weight) Na_2SO_4 solution at 20°C, followed by 20 hours of drying in an oven at 60°C, and finally 2 hours of cooling at ambient temperature. The test was terminated after 15 cycles or upon sample failure. Mass change and visual deterioration were documented after each cycle.

2.3.4. Microstructural Analysis

To investigate the deterioration mechanisms in samples subjected to sulfate attack, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) was performed. The analyses were conducted on fragments taken from the inner surface of the cycled HG1 and HG3 specimens to identify the morphology of the hydration products and the presence of degradation products like gypsum and thaumasite.

3. Results

This section presents the experimental results obtained from the characterization and durability tests performed on the three-grout series, which are air lime-based (AG1), hydraulic lime-based (HG1), and hydraulic lime with brick powder (HG3).

3.1. Compressive Strength Development

The compressive strength of the grout series was evaluated at 28 and 90 days to understand their mechanical performance over time. The results, including standard deviations, are presented in Figure 1.

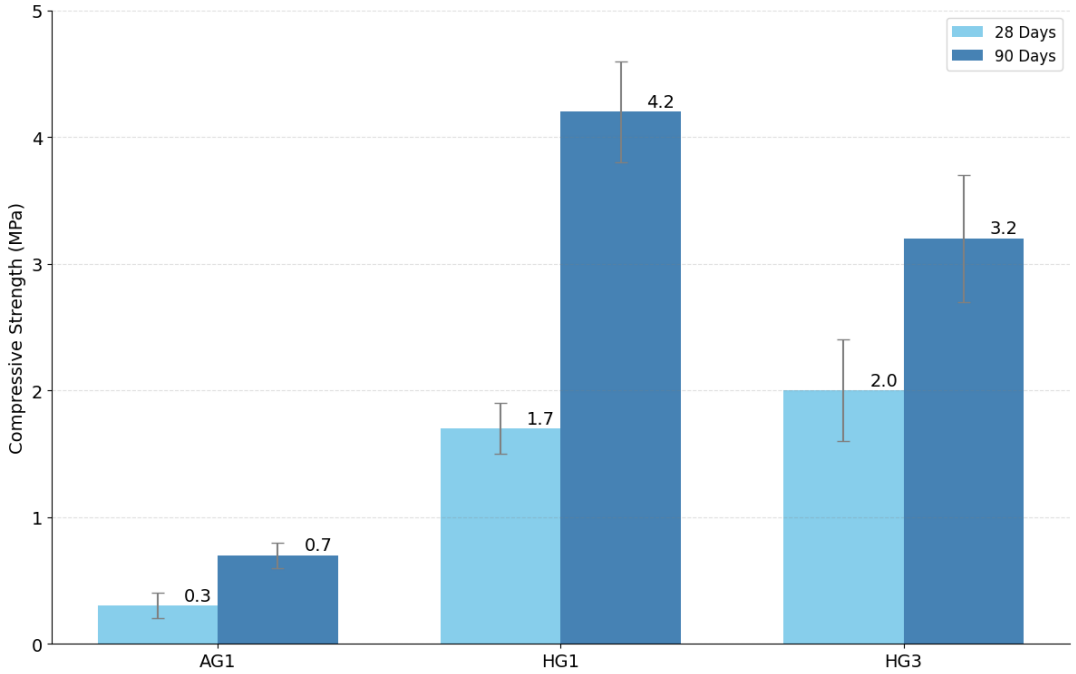

Figure 1. Comparison of 28- and 90-day compressive strength for the AG1, HG1, and HG3 grout series,

As shown in Figure 1, the binder type significantly influenced the mechanical performance. At 28 days, the highest compressive strength was achieved by the HG3 series (2.0 MPa), which contained both natural hydraulic lime and pozzolanic brick powder. The HG1 series, based solely on hydraulic lime, also developed considerable strength (1.7 MPa). In contrast, the air lime-based AG1 series exhibited a significantly lower compressive strength of only 0.3 MPa.

All series demonstrated an increase in strength between 28 and 90 days. The most substantial gain was observed in the HG1 series, which reached 4.2 MPa, more than doubling its 28-day strength. The HG3 series also showed a notable increase to 3.2 MPa. The AG1 series, while showing a slight increase to 0.7 MPa, confirmed the slow and limited strength development characteristic of non-hydraulic binders.

3.2. Chemical and Mineralogical Composition of Hardened Grouts

The chemical and mineralogical nature of the hardened grouts at 28 days was investigated to understand the relationship between the initial materials and the final products.

3.2.1. XRF Analysis

The bulk chemical compositions of the 28-day hardened grouts, determined by XRF, are presented in Table 3. The results show that the chemical composition of the hardened grouts is directly influenced by their initial binder systems. For the single-binder series (AG1 and HG1), the primary components are CaO and SiO_2, and their oxide percentages closely mirror those of the raw lime binders used in their production (as shown previously in Table 1). For instance, the CaO content in the hardened AG1 and HG1 grouts was 67.7% and 64.3%, respectively, which is very close to the 69.0% and 66.1% found in the raw CL 80-S and NHL 3.5 limes.

Table 3. Chemical composition of hardened grout series at 28 days (wt. %)

Component (%)	AG1	HG1	HG3
SiO_2	0.80	11.20	19.20
Al_2O_3	0.40	0.50	3.90
Fe_2O_3	0.20	0.20	2.10
MgO	1.20	0.50	1.00
CaO	67.70	64.30	53.80
K_2O	0.10	<0.1	0.70
SO_3	0.60	0.70	0.70
Loss on Ignition (LOI)	28.90	22.50	17.90

In contrast, the composition of the HG3 series reflects the significant contribution of the pozzolanic brick powder. Compared to the plain hydraulic grout (HG1), the HG3 grout exhibits substantially higher percentages of SiO_2 (19.2% vs. 11.2%), Al_2O_3 (3.9% vs. 0.5%), and Fe_2O_3 (2.1% vs. 0.2%). This confirms the effective incorporation of the silica- and alumina-rich pozzolan into the final matrix. The low levels of SO_3 detected across all series are likely attributable to the mixing water and the superplasticizer used.

3.2.2. Mineralogical Composition (XRD and FTIR Analysis)

The mineralogical composition of the 28-day hardened grouts was investigated using XRD and FTIR to identify the phases formed. A summary of the key findings, combining semi-quantitative XRD data with characteristic absorption bands from FTIR, is presented in Table 4.

Table 4. Chemical composition of hardened grout series at 28 days (wt. %)

Phase / Chemical Group	Identification Method	AG1	HG1	HG3
Portlandite ($Ca(OH)_2$)	XRD (%)	84.00	46.00	40.00
Calcite ($CaCO_3$)	XRD (%)	10.00	14.00	13.00
Quartz (SiO_2)	XRD (%)	-	-	13.00
Hydraulic Phases (Larnite. etc.)	XRD (%)	-	36.00	29.00
Hydroxyl Group (-OH)	FTIR (cm^{-1})	3643.00	3642.00	3643.00
Carbonate Group (CO_3^{2-})	FTIR (cm^{-1})	1429.00, 887.10	1417. 87, 4712.00	1406. 87, 3712.00
Silicate Group (Si-O)	FTIR (cm^{-1})	-	995.00	798.00

The XRD results reveal significant mineralogical differences driven by the binder system. The air lime grout (AG1) is predominantly composed of portlandite (84%), with limited carbonation (10% calcite). In contrast, the hydraulic lime grout (HG1) contains a lower amount of portlandite (46%) but a significant proportion of hydraulic phases (36%), confirming the formation of cementitious products inherent to the NHL 3.5 binder. The addition of brick powder in the HG3 series resulted in a further decrease in portlandite (40%), suggesting its consumption during pozzolanic reactions, which is supported by the presence of quartz (13%) and a high percentage of hydraulic phases (29%).

The FTIR analysis strongly corroborated these findings. All spectra showed a sharp absorption peak for the O-H group in portlandite (around 3643 cm^{-1}) and characteristic peaks for the C-O group in calcite (around 1420 cm^{-1} and 875 cm^{-1}). Crucially, the spectra for HG1 and HG3 also showed distinct bands for Si-O bonds. The HG1 series exhibited a peak at 995 cm^{-1}, associated with amorphous silica in the hydraulic phases. The HG3 series showed a peak at 798 cm^{-1}, which is characteristic of crystalline quartz from the

brick powder, thus confirming the successful incorporation of the pozzolan and the formation of new silicate structures.

3.3. Durability Performance

The resistance of the grout series to environmental stressors was evaluated through freeze-thaw and sulfate attack tests.

3.3.1. Freeze-Thaw Resistance

The performance of the grout series under freeze-thaw cycling varied significantly depending on the binder type, as visually documented in Figure 2. The air lime-based grout, AG1, failed catastrophically, completely disintegrating during the very first freeze-thaw cycle. This indicates a very low resistance to frost action.

In severe contrast, both hydraulic lime-based series, HG1 and HG3, demonstrated significantly higher durability. These specimens successfully completed all 12 freeze-thaw cycles without disintegration. By the end of the 12th cycle, minor surface cracking was observed on both series, but the specimens maintained their structural integrity and overall dimensions. The final state of all three series after testing is compared in Figure 2.

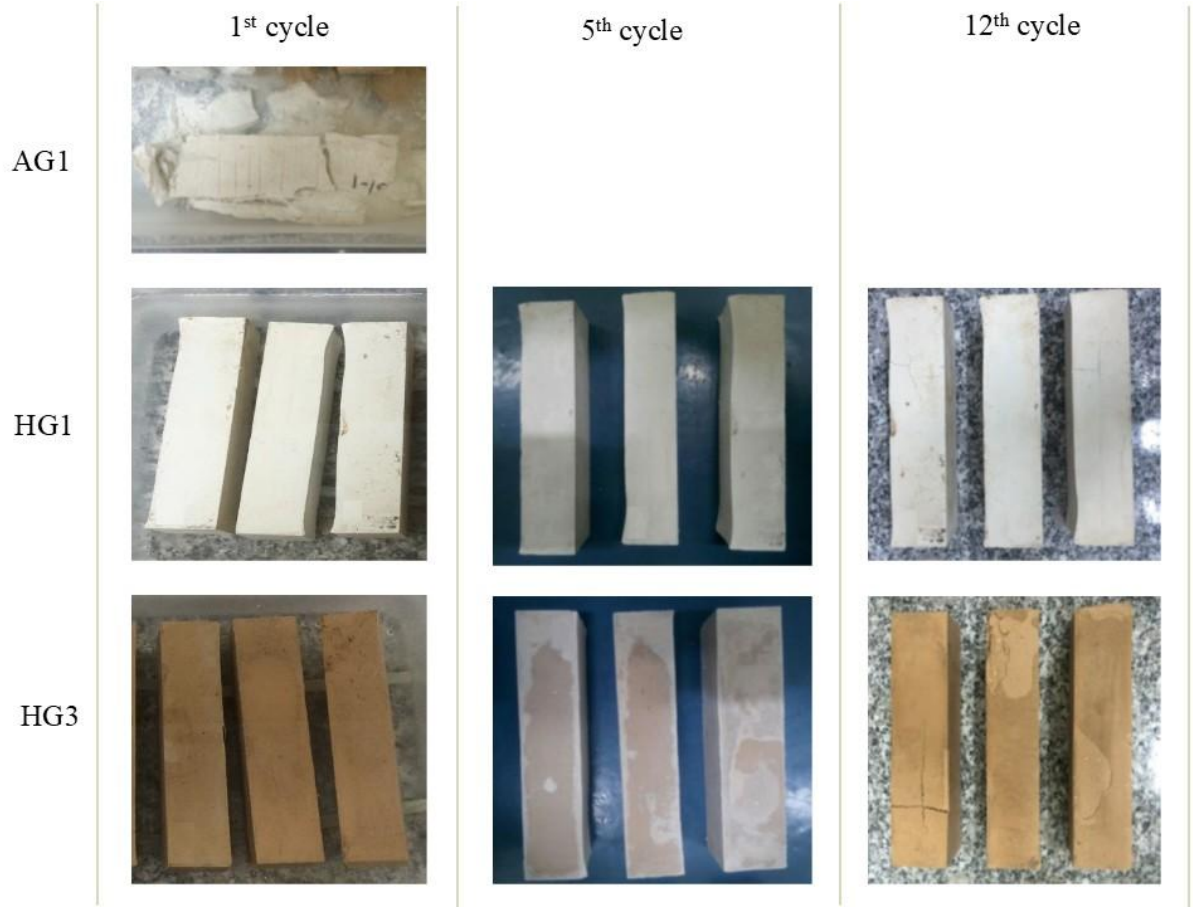

Figure 2. Visual state of the grout specimens after the freeze-thaw durability test.

3.3.2. Sulfate Resistance

The resistance of the grout series to sodium sulfate attack showed notable differences in performance and failure mechanisms, as summarized in Figure 3.

The air lime-based grout, AG1, exhibited the lowest resistance, completely disintegrating after only 5 cycles of exposure.

The hydraulic lime-based grouts demonstrated superior, albeit different, performance. The HG1 series (plain hydraulic lime) completed all 15 cycles, but showed significant deterioration, including erosion and rounding of the specimen's edges, although its core remained intact. In contrast, the HG3 series (hydraulic lime with brick powder) began to show signs of deterioration, such as spalling, after the 7th cycle and ultimately failed by disintegrating during the 14th cycle.

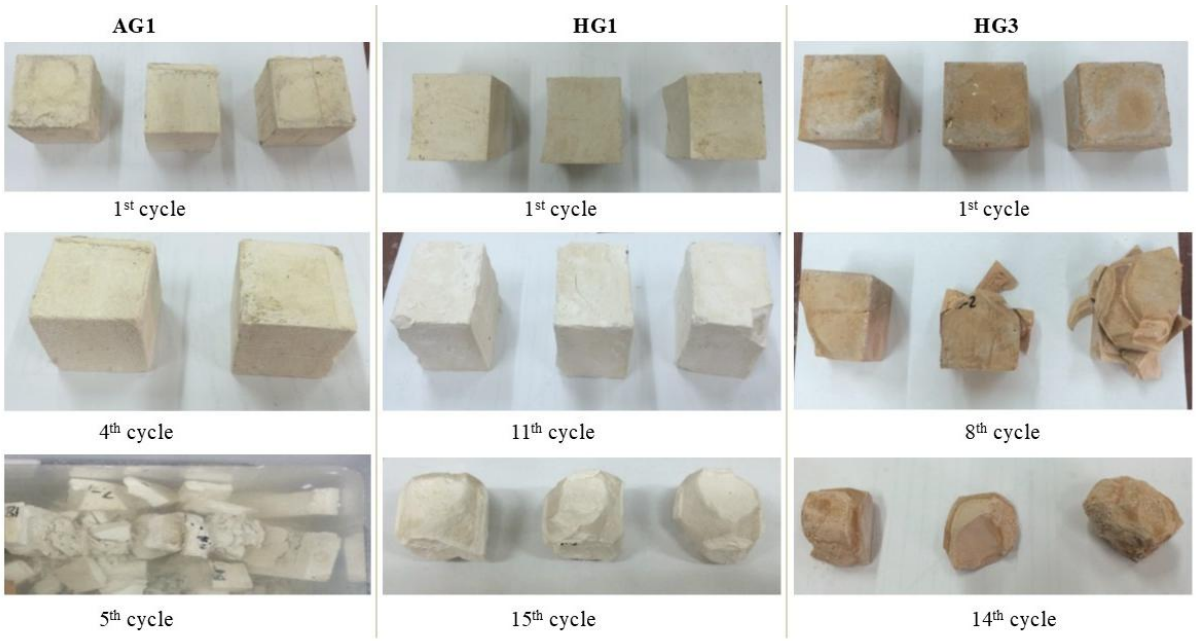

Figure 3. Comparative deterioration of grout specimens after exposure to sodium sulfate attack.

3.4. Microstructural Analysis After Sulfate Attack

To investigate the underlying causes of the observed differences in sulfate resistance, SEM-EDS analyses were conducted on the internal surfaces of the cycled HG1 and HG3 specimens. The key microstructural findings are presented in Figure 4.

In the HG1 specimen, which survived 15 cycles, the microstructure appeared dense. The EDS analysis confirmed that sodium sulfate had not penetrated deep into the matrix, and as a result, deleterious expansive products such as gypsum or thaumasite were not formed. While the typical morphology of calcium-silicate-hydrate (C-S-H) gel was not clearly visible in the SEM images, its presence was confirmed indirectly via EDS. The measured Ca/Si atomic ratio of approximately 1.8 falls within the widely accepted range (0.8–2.1) for C-S-H phases, thus confirming their formation within the HG1 matrix.

In stark contrast, the microstructural analysis of the HG3 specimen revealed the widespread formation of expansive crystalline products. The SEM micrograph in Figure 4 clearly shows the presence of these new phases disrupting the matrix. The accompanying EDS analysis confirmed their identity as gypsum ($CaSO_4 \cdot 2H_2O$) and thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$). The formation of thaumasite was facilitated by the presence of all necessary precursors in the HG3 system: a source of sulfates from the

test solution, calcium carbonate ($CaCO_3$) from the carbonation of free lime, and a source of silica from both the hydraulic lime and the pozzolanic brick powder. The formation of these highly expansive products is the direct cause of the internal stress that led to the cracking and eventual disintegration of the HG3 samples.

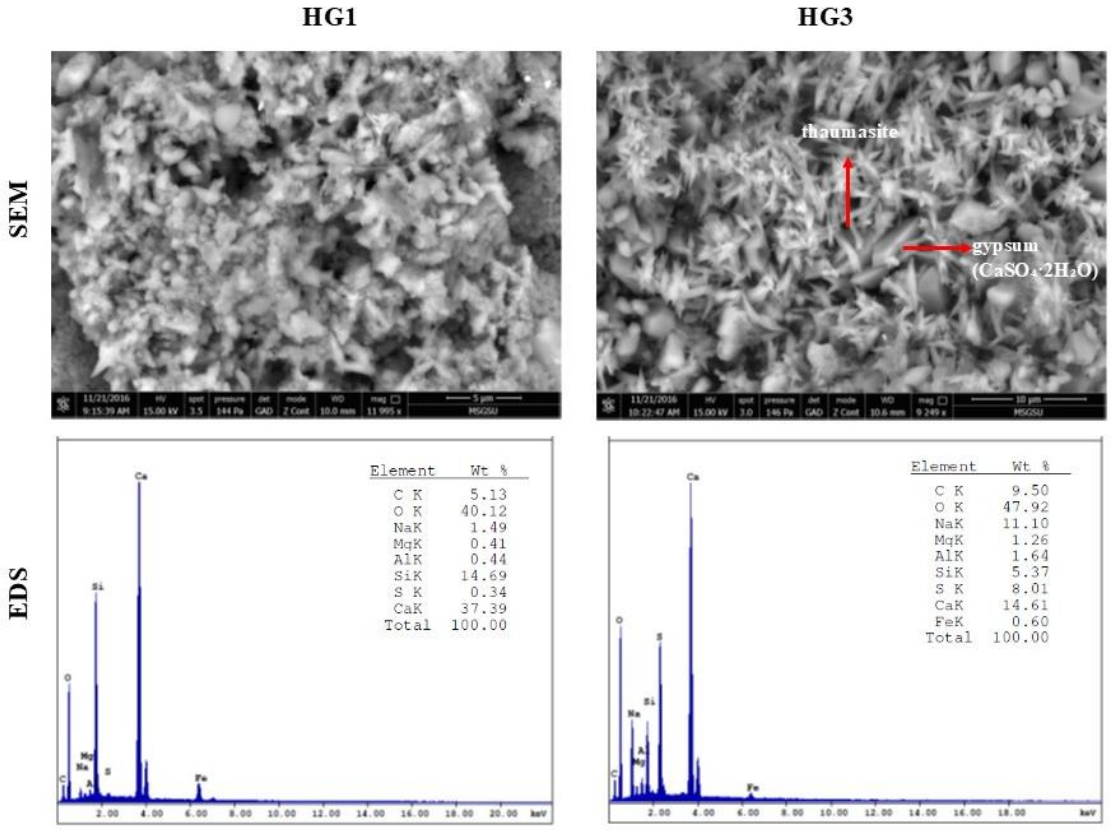

Figure 4. Microstructural analysis of grout specimens after sulfate attack.

4. Discussion

The experimental results of this study offer significant insights into the complex behavior of lime-based injection grouts, particularly concerning the interplay between binder composition, mechanical performance, and long-term durability. The discussion will focus on interpreting the key findings that are the fundamental role of hydraulicity in grout performance, the conflicting effects of pozzolanic additives under different exposure conditions, and the resulting implications for conservation practice.

A primary finding is the obvious superiority of hydraulic lime-based grouts (HG1 and HG3) over the air lime-based formulation (AG1). The rapid failure of AG1 in the freeze-thaw test and its minimal strength gain are attributable to its reliance on slow atmospheric carbonation, which results in a porous microstructure inherently vulnerable to frost-induced environmental effects. In contrast, the hydraulic binders in HG1 and HG3 facilitated the formation of a dense, cementitious matrix rich in calcium-silicate-hydrate (C-S-H) phases, as confirmed by XRD and FTIR. This denser microstructure provided the necessary mechanical strength and lower permeability to resist internal stresses, ensuring robust performance in both compressive strength and freeze-thaw tests.

Perhaps the most critical finding of this study is the dual, and ultimately conflicting, role of the pozzolanic brick powder. The addition of this pozzolan in the HG3 series enhanced 28-day compressive strength and contributed to a durable matrix under freeze-thaw conditions. However, this same

modification rendered the grout more susceptible to sulfate attack than the plain hydraulic lime grout (HG1). The microstructural analysis explains this phenomenon: The pozzolanic reaction, while beneficial for strength, introduced a highly reactive source of alumina and silica. This created an ideal chemical environment for the formation of destructive, expansive phases—namely gypsum and thaumasite—when exposed to an external sulfate source. The HG1 grout, lacking this abundance of reactive alumina and silica, did not facilitate thaumasite formation and thus exhibited greater resilience, failing only by gradual surface erosion rather than catastrophic internal expansion. This highlights a critical principle, which is enhancing one performance characteristic, such as strength, can inadvertently compromise durability under specific chemical attacks.

These findings have profound implications for the formulation of injection grouts for heritage conservation. It is evident that a grout's suitability cannot be determined by a single performance metric. The results demonstrate that a formulation optimized for mechanical strength may be dangerously inappropriate for an environment with aggressive chemical agents, such as sulfate-rich soils or groundwater. Therefore, the design process must be holistic, prioritizing chemical compatibility and long-term durability tailored to the specific threats of a given site. While pozzolanic additives are valuable, their use demands careful consideration and risk assessment, especially in environments with a known potential for sulfate exposure.

5. Conclusions

This study evaluated the durability of three lime-based grouts with different binder systems. Based on the experimental results, the following conclusions can be drawn:

Binder type is the primary determinant of performance. Hydraulic lime-based grouts (HG1 and HG3) significantly outperform air lime-based grout (AG1) in terms of both mechanical strength and freeze-thaw resistance, owing to the formation of a dense, cementitious matrix.

Pozzolanic additives introduce a critical performance conflict. The addition of pozzolanic brick powder (HG3) increased early-age strength but severely compromised the grout's resistance to sulfate attack. This was due to the creation of a chemical environment that facilitated the formation of destructive expansive products like gypsum and thaumasite.

The plain hydraulic lime grout offered the most balanced performance. The HG1 formulation, without pozzolanic additives, demonstrated the most reliable overall durability, showing adequate strength and superior resistance to both freeze-thaw cycling and sulfate exposure.

A holistic, site-specific approach to grout design is essential. The findings underscore that optimizing for a single property (like strength) can be detrimental to long-term durability. Grout selection for historic structures must prioritize chemical compatibility with the specific environmental conditions of the site, especially when a risk of sulfate attack is present.

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Impact of Deposition Parameters on the Properties of SnO_2 Thin Films for Perovskite Solar Cells

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ABSTRACT

Perovskite solar cells (PSCs) are set to transform the energy industry. Their remarkable power conversion efficiencies and cost-effective fabrication processes make them the obvious choice for the future. The electron transport layer (ETL) is a crucial component that significantly influences device performance. Here, tin oxide (SnO_2) has emerged as a highly promising candidate due to its excellent electrical conductivity, wide optical bandgap, and chemical stability. This study systematically investigates the effects of varying deposition pressures (5, 10, and 15 mTorr) and substrate temperatures (150 and 300°C) on the structural, optical, morphological, and electrical properties of SnO_2 thin films deposited with Physical Vapor Deposition (PVD). The SnO_2 films deposited at 300 °C and 15 mTorr performed best in all areas of investigation. They boasted the best combination of morphological uniformity and high optical transmittance. These findings are crucial for optimising SnO_2-based ETLs for high-efficiency PSCs and other optoelectronic devices.

Keywords: SnO_2, Electron Transport Layer, Perovskite Solar Cells.

1. Introduction

The development of perovskite solar cells (PSCs) has been a subject of considerable research interest in recent years due to their high power conversion efficiencies (PCEs), low production costs, and ease of fabrication. One of the key components in PSCs is the electron transport layer (ETL), which facilitates the efficient extraction of electrons from the perovskite absorber layer and directs them toward the electrode (Damgacı &Seyhan, 2023). Among the various materials explored for use as ETLs, tin oxide (SnO_2) has attracted significant attention due to its favorable electrical conductivity, optical transparency, and excellent chemical stability. SnO_2 exhibits a wide optical band gap (≈3.6–4.0 eV), excellent electrical conductivity, and high chemical and thermal stability (Liu et al., 2003).

The deposition method of SnO_2 strongly influences its structural, optical, and electronic properties. While solution processing methods have been widely adopted, physical vapor deposition (PVD) has recently gained significant interest due to its better control over film thickness, uniformity, and reproducibility (Gupta et al., 2004). The performance of SnO_2 as an ETL is influenced by its structural, optical, and electrical properties, which can be tailored by adjusting the deposition parameters during thin film fabrication (Kashyap et al., 2009). In this context, the deposition of SnO_2 films using PVD under varying conditions, such as pressure and temperature, offers a route to optimize these properties for enhanced PSC performance. Tao and the research group investigated the impact of sputtering power on

the performance of SnO_2 ETLs deposited via radio frequency magnetron sputtering at room temperature for PSCs. They found that reducing the sputtering power from 120 W to 60 W lowered the surface roughness of the SnO_2 films, improved the ETL/perovskite interface, and enhanced charge extraction. As a result, the power conversion efficiency increased from 8.19% to 12.58%. This study emphasizes the significance of controlling PVD parameters to maximize ETL quality and device performance (Tao et al., 2019). Another research group investigated the impact of working gas flow rate and oxygen content on the growth of intrinsic SnO_2 (i-SnO_2) layers during RF sputtering. Their findings revealed that the films had an amorphous-like nanocrystalline structure with surface roughness values ranging from 1.715 to 3.936 nm. XPS analysis also indicated the presence of point defects such as tin interstitials and oxygen vacancies, which significantly influence the film's electronic properties and interface quality (Al-Mansoori et al., 2017). Gong et al. (2019) performed a comprehensive investigation into the temperature-dependent optical characteristics of SnO_2 thin films utilizing spectroscopic ellipsometry. The study revealed that modifications in substrate temperature induced substantial variations in the optical transmittance spectra and refractive index dispersion, attributable to temperature-mediated alterations in film densification, lattice ordering, and defect state distribution

In this study, SnO_2 thin films were deposited using the PVD method at two different substrate temperatures (150 °C and 300 °C) and under three distinct chamber pressures (5, 10, and 15 mTorr) to systematically investigate the influence of deposition conditions on the morphological and optical properties of the films for potential use as ETLs in perovskite solar cells.

2. Materials and Method

SnO_2 thin films were deposited onto soda-lime glass substrates sized 2.5 × 2.5 cm^2 and with a thickness of 1.1 mm using a radio frequency (RF) magnetron sputtering system. The sputtering target used was high-purity SnO_2 (99.999%, 5N). The sputtering process was conducted at a target rotation speed of 8 rpm, producing films with an average thickness of approximately 100 nm. The PVD coating method was chosen because it provides precise control over deposition rate and film thickness.

2.1. Thin Film Deposition

To evaluate the influence of ambient pressure on film properties, depositions were performed under three different working pressures: 5, 10, and 15 mTorr. Additionally, the substrate temperature was systematically 150 °C and 300 °C to examine the impact of temperature on the optical and surface morphology properties of the SnO_2 films.

Figure 1. Fabrication of SnO_2 Thin Films Using Physical Vapor Deposition

2.2. Characterization

To evaluate the morphological and optical properties of the SnO_2 thin films, Atomic Force Microscopy (AFM) and UV-Vis spectroscopy analyses were conducted. AFM (Innova, Bruker) was utilized to investigate the surface topography and quantify the root mean square (RMS) roughness of the films with high spatial resolution. Surface roughness plays a crucial role in determining the interface quality of thin films, particularly in optoelectronic device applications. Optical characterization was performed using a UV-Vis spectrometer (Shimadzu 3600i Plus) to determine the optical transmittance and estimate the optical bandgap of the films. These analyses were instrumental in correlating the surface and optical properties of the SnO_2 layers with varying deposition conditions.

3. Results and Discussion

The optical properties of the SnO_2 thin films, as characterized by their UV-Vis transmission spectra, are highly dependent on the deposition parameters, specifically substrate temperature and deposition pressure. Similarly, AFM characterization reveals that deposition parameters, including substrate temperature and pressure, significantly influence the surface morphology and roughness of SnO_2 thin films. Lower roughness values, which are achieved under optimized conditions, encourage the formation of uniform SnO_2 ETLs and reduce interfacial recombination losses.

3.1. Impact of Deposition Parameters on Optical Properties

A definitive correlation exists between the substrate temperature and the optical properties of the deposited SnO_2 thin films, with deposition pressure also playing a significant role (Bin et al., 2021; Nwanna et al., 2022). Films fabricated at an elevated substrate temperature of 300°C exhibit substantially higher average transmittance values across the visible wavelength range compared to those deposited at 150°C, and this improvement is further influenced by the deposition pressure, where coatings performed at 5, 10, and 15 mTorr show notable variations in optical transmission and film quality.

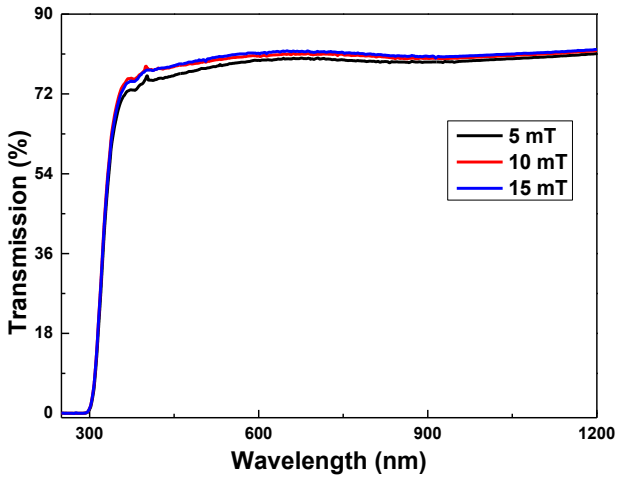

Figure 2. Transmission spectra of SnO_2 thin films at 150 °C under 5, 10, and 15 mTorr

The SnO_2 thin films deposited at 150°C exhibit average transmittance values ranging from 78.28% to 80.18% within the 400-700 nm wavelength region. A gradual increase in optical transmittance is observed with rising deposition pressure, reaching its maximum at 15 mTorr. This finding suggests that, even under relatively low-temperature conditions, the deposition pressure exerts a substantial influence on enhancing the quality of the film by affecting its density and crystallinity. It can thus be concluded that an increase in pressure at 150°C results in enhanced optical transparency and a decrease in defect concentration within the films.

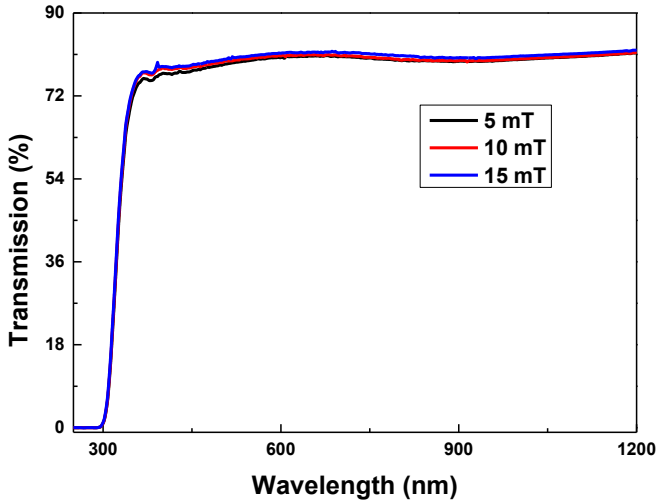

Figure 3. Transmission spectra of SnO_2 thin films at 300 °C under 5, 10, and 15 mTorr

At 300 °C, the SnO_2 films exhibit slightly higher transmittance values, ranging from 79.28% to 80.31%. In a manner analogous to the lower-temperature condition, an incremental increase in transmittance is observed with increasing pressure, reaching a maximum at 15 mTorr. However, the magnitude of this improvement is less pronounced compared to that at 150 °C. This indicates that elevated substrate temperatures already promote enhanced crystallinity and surface ordering, rendering the effect of deposition pressure on optical properties relatively minor.

3.2. Effect of Deposition Parameters on Surface Topography of Thin Films

A comparison of AFM results at 150 °C and 300 °C indicates that higher substrate temperature generally promotes smoother and more uniform films at low (5 mTorr) and high (15 mTorr) pressures in Figure 4. However, at 10 mTorr, both temperatures lead to pronounced roughness, with the effect being more severe at 300 °C. These findings suggest that substrate temperature and deposition pressure must be carefully optimized together to achieve homogeneous SnO_2 thin films suitable for device integration. Overall, the AFM analysis emphasizes that deposition parameters, especially substrate temperature and pressure, critically determine nanoscale roughness, which in turn plays a decisive role in the optoelectronic performance of SnO_2-based electron transport layers.

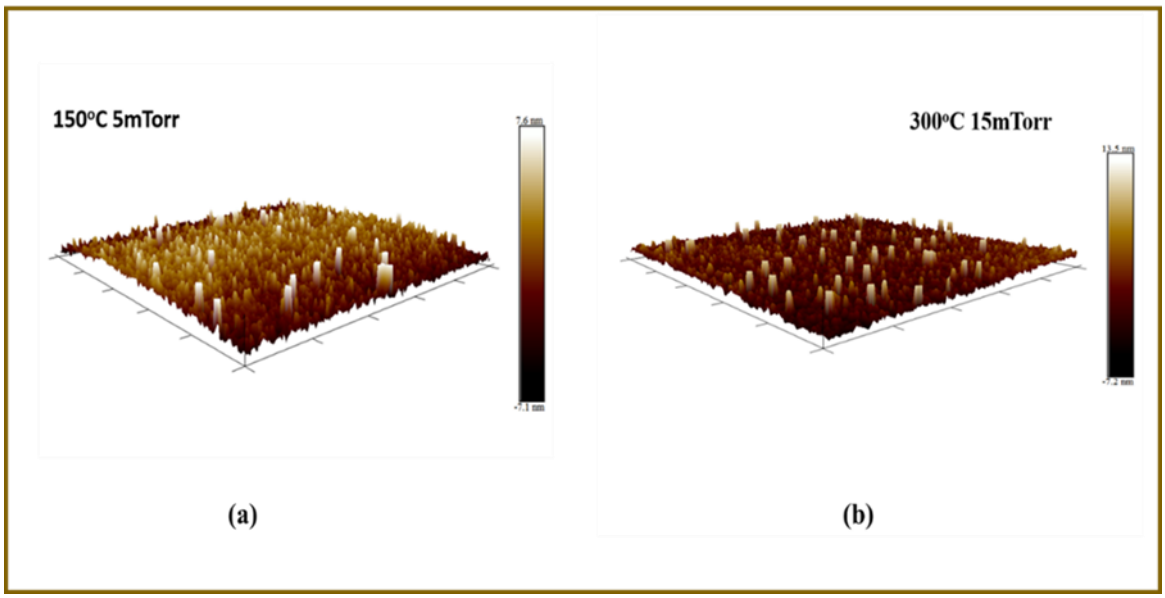

Figure 4. AFM three-dimensional surface morphology images of SnO_2 thin films deposited under different conditions: (a) at 150 °C and 5 mTorr; (b) at 300 °C and 15 mTorr

4. Conclusions

These findings suggest that controlling the deposition temperature and pressure can optimize SnO_2 films for specific optoelectronic and sensing applications. The SnO_2 thin film deposited at 15 mTorr and annealed at 300 °C exhibited the most favorable surface characteristics for photovoltaic applications, offering an optimal combination of morphological uniformity, structural continuity, and interfacial compatibility with the perovskite absorber layer.

Future studies will investigate the role of additional factors, such as doping and film thickness, on the band gap properties of SnO_2.

5. Acknowledge

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Fabrication and investigation of chemical and mechanical stability and self-cleaning properties of superhydrophobic coating on Brass

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ABSTRACT

Water droplets on surfaces, especially in humid and industrial atmosphere, cause reducing efficiency and increasing corrosion damages. Existing methods for dealing with those have limitations due to high costs and environmental incompatibility. As a sustainable alternative, superhydrophobic coatings based on copper oxide have been considered due to their high contact angle. In this study a structure coated on brass substrates and optimized by hydrothermal methods. In this work, brass substrates and copper chloride, and stearic acid as a surface modifier were used. One of the biggest challenges with superhydrophobic surfaces is making sure that coatings stay chemically durable over time. The test's results showed the optimized sample's surface contact angle (SCA) kept its superhydrophobic properties in acidic environments after 1 and 4 days (pH= 4 and 6). However, in alkaline solutions (pH= 8 and 10) after 4 days, the SCA dropped below 150°; in other words, at pH 4.00, 6.00, 8.00, and 10.00 the SCA decreased 22, 14, 25, and 30%, respectively. Abrasion testing is a way for checking surface's mechanical durability. The optimized superhydrophobic sample's SCA stayed within the range of 163.4° to 149.4° after 10 abrasion cycles. Finally, in self-cleaning test, the optimized superhydrophobic sample for its higher surface energy, clean itself completely without any scrubbing or extra effort.

Keywords: Brass, Superhydrophobicity, Self-cleaning, Chemical stability, pH, Abrasion.

1. Introduction

Brass alloys are widely used across many industries, including marine engineering [1], heat exchangers [2], electronics, communications [3], solar energy [4], oil-water separation [5], and even rubber manufacturing [6]. This popularity is largely due to their strong mechanical properties, excellent resistance to corrosion, and good electrical and thermal conductivity. Even though brass is naturally resistant to corrosion, it can still suffer from various forms of chemical or electrochemical damage. Issues like dezincification, pitting, fatigue corrosion, and stress corrosion can form on its surface and eventually degrade its performance [6, 7].

Today, research is focused on finding eco-friendly alternatives, particularly those that modify surface wettability to resist corrosion [8]. Superhydrophobic coatings, which trap a layer of air between water and the surface to repel moisture, have emerged as a promising solution. Several methods have been developed to create these coatings, including chemical vapor deposition, femtosecond laser treatment,

chemical etching, electrodeposition, hydrothermal processing, and spraying, among others [9]. There are two main approaches to creating superhydrophobic surfaces. The first focuses on making the surface rougher, which traps air in the tiny grooves and bumps. This trapped air helps repel water. The second approach involves lowering the surface energy, which stops water molecules and ions from sticking to or damaging the surface in harsh, corrosive environments. To achieve the roughness, various techniques are used, and afterward, the surface is treated with substances like stearic acid or lauric acid to enhance its hydrophobic properties [10].

In some works, Van Han et al. [11] in 2014, explored how to create a superhydrophobic coating on an aluminum surface. They started by etching the aluminum in hot water at 100 °C for a set period. After this, they applied a modifier called octadecyl trichlorosilane. Interestingly, the contact angle actually dropped after etching, but then increased significantly once the modifier was added, greatly improving the surface's water resistance. Baitai et al. [12] in 2005, looked at copper plates and used a chemical etching method to roughen the surface and give it superhydrophobic properties. First, they cleaned the copper with nitric acid for 15 minutes. Then, the copper was soaked in a solution of hydrochloric acid and acetic acid for 8 to 24 hours. After that, it was treated with a methanol-based fluoroalkyl silane solution and water, then dried at 130 °C for an hour to finish the process. Zhibo et al. [13] in 2017 created a superhydrophobic surface on aluminum by etching it with a mix of hydrochloric acid and hydrogen peroxide, then coating it with stearic acid. When they compared water contact angles, raw aluminum had about 66°, and after etching, the surface actually became superhydrophilic. But after applying the stearic acid, the contact angle shot up to 160°, turning the surface superhydrophobic. Jan et al. [14] worked with brass and etched it to create a surface featuring tiny micro- and nanoscale structures coated with a low-energy material. This surface showed a contact angle of 157.5° and a very low residual contact angle of 2.7°, indicating strong hydrophobicity. They also found that this surface had impressive anti-icing properties. The freezing of water droplets was delayed thanks to an "air cushion" layer that reduces heat transfer and boosts insulation.

The hydrothermal method is a flexible and widely used technique for producing nanomaterials [15]. In a study by Zhao et al. [15], this method was applied to grow a composite of copper oxides (CuO and Cu_2O) on a copper surface. By adjusting the heating conditions and chemical concentrations, they were able to create surfaces with either hydrophobic or superhydrophobic characteristics. Under a microscope, the surface structures appeared as reflective octahedral and spherical forms of Cu_2O. In another study, Niu et al. [16] developed a superhydrophobic surface made of Cu_2O on a brass mesh using a simple spray technique. The resulting surface featured nano- and micro-scale structures that resembled coral reefs and achieved an impressive water contact angle of 159.6°, indicating excellent hydrophobicity.

Superhydrophobic coatings made from copper oxide have gained interest thanks to their unique properties and eco-friendly nature. Despite their potential, there's still limited research on how to produce these coatings using methods that are both efficient and sustainable [17]. According to pervious work [18], copper oxide nanostructures were grown on brass surfaces using a hydrothermal technique. Key factors in the synthesis process such as, temperature, reaction time, and precursor concentration were carefully optimized using experimental design and the Taguchi method. Then, the chemical stability through acidic or an alkaline solution (pH=4-10), mechanical durability through abrasion test, and self-cleaning performance were characterized.

2. Materials and Method

2.1. Raw materials

According to pervious work [18], brass (65 wt. % copper, 35 wt. % zinc) with 0.5 mm thickness (Zochen, Iran) was used as the substrate. Hydrofluoric acid (HF, Shadram Shimi, Iran), and hydrocholoric acid (HCl, Mojalali, Iran) as surface roughness generator, and cetyltrimethylammonium bromide (CTAB, Merck, Germany) as a particle disperser were used. In addition, copper chloride (Merck, Germany) for reaching copper oxide (to increase roughness on the micro-nano scale), urea (Neutron, Iran) as pH

adjustment, stearic acid (Merck, Germany) for decreasing surface energy, and 96% pure ethanol solution (Hamon Teb, Iran) for preparing stearic acid were prepared.

2.2. Preparation of the substrate and Synthesis of superhydrophobic coating

According to pervious work [18], brass substrates were carefully prepared and modified to improve their surface properties, particularly wettability. The process began with sanding and cleaning to remove oxides, followed by a series of ultrasonic baths and oven drying. Using a Taguchi experimental design in Minitab, nine different hydrothermal treatments were tested by three factors such as, A (etching time in HF), B (molar ratio of urea to copper chloride), and C (reaction time during synthesis). The brass samples were etched with HF and HCl before being immersed in hot distilled water. A copper-based coating solution was then prepared using copper chloride, CTAB, and varying amounts of urea. The pre-treated brass was suspended in this solution at 90 $^{\circ}$C for specific durations. After coating, the samples were thoroughly rinsed, dried, and finally treated with stearic acid to enhance hydrophobicity. The effectiveness of each treatment was evaluated by measuring the surface contact angle (SCA) to identify optimal surface conditions. Finally, the optimum sample had the SCA of 163.4°.

2.3. Characterization

Contact angle measurements were taken at three different points on each sample for reaching SCAs' pictures (CAG20, Jican Group, Iran). The average value was calculated using Image J software. To examine the surface structure of the synthesized coatings, field emission scanning electron microscopy (FE-SEM, MIRA3, TESCAN, Czech Republic) was employed.

Chemical stability of the optimized superhydrophobic surface was tested by immersing samples in water solutions with pH values ranging from 4 to 10. SCA were measured after 1 day and again after 4 days to assess any changes in wettability. FE-SEM imaging was also used after immersion to check for structural changes or damage on the surface. To test self-cleaning ability, a layer of powder paint was evenly spread over the coated surface. Then, drops of distilled water were gently released while the sample was tilted at an angle of less than 10°, allowing observation of how well the coating shed dirt through rolling water droplets.

Among the various techniques for testing the mechanical durability of superhydrophobic coatings, abrasion testing is widely used [19]. In this work, the coating's resistance to wear was evaluated by placing coated brass samples face-down on sandpaper under a 200 g weight. Each abrasion cycle involved moving the sample 10 cm in a straight line. SCA and DCA were measured after specific intervals, up to a total of 10 abrasion cycles, to track changes in surface properties.

3. Results and Discussion

3.1. Chemical stability

One of the biggest challenges with superhydrophobic surfaces is making sure the coatings stay chemically durable over time that has received a lot of attention. To test this, the optimized sample was soaked in water solutions with different pH levels, ranging from 4.00 to 10.00, as shown in Figure 39. The SCAs were measured after 1 day and again after 4 days. As you can see in Figure 39-a, after just one day, the SCA values barely changed, and the sample kept its superhydrophobic properties in acidic environments. However, in alkaline solutions, the SCA dropped below 150°, with the biggest decrease seen at pH 10.00. Figure 39-b shows that after 4 days, the decline in SCA became more noticeable across all solutions. At pH 4.00, the SCA went down from 152.3° to 119.1°, and at pH 6.00, it dropped from 157.7° to 135.9°. In alkaline conditions, the SCA fell even further—from 149.6° to 111.5° at pH 8.00, and from 137.7° to 96.6° at pH 10.00.

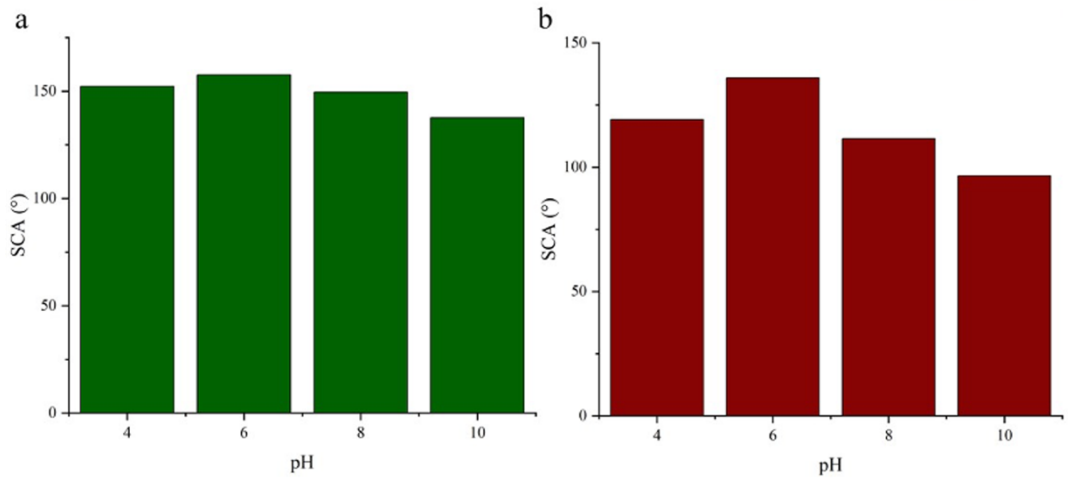

Figure 39- SCA of the optimum sample immersion in the solutions with different pH after a) 1 day, b) 4 days.

Figure 40 presents FE-SEM images of the coated samples after being exposed to acidic conditions at pH 4.00. In Figure 40-a, the sample was exposed for just one day, and the images show that the micro/nano-sheet structure of the CuO coating remains largely intact. This suggests that the acid had only a limited impact in the short term, and the stearic acid layer likely helped protect the surface from corrosion. Figure 40-b shows the same sample after 4 days of exposure to the acidic environment. Here, significant damage to the surface is visible (the orderly sheet structure has broken down, and the surface looks rough, porous, and uneven). This deterioration is due to the gradual breakdown of the CuO coating and the degradation of the protective stearic acid layer. As the coating wears away, the underlying copper substrate becomes exposed, which can lead to corrosion and the formation of secondary oxides or copper hydroxides on the surface. These changes cause polar groups, like hydroxyls, to form, increasing the surface's free energy and, as a result, reducing the SCA.

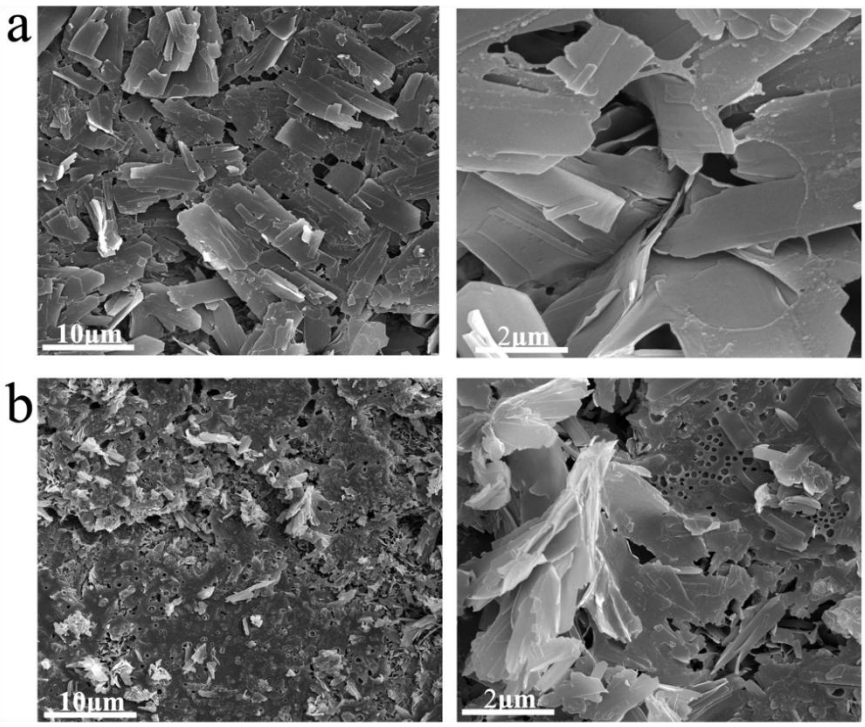

Figure 40- *FESEM images of the optimized sample after being immersed in solutions with pH 4 a)1 day, b)4 days.*

3.2. Mechanical stability

Abrasion testing is a common way to check how mechanically durable a surface is. As shown in Figure 41, the optimized superhydrophobic sample was tested by dragging it across 400-grit sandpaper in two perpendicular directions, with a 200-gram weight pressing down on it. Each pass covered a distance of 10 cm. Figure 42 shows how the SCA changed with the number of abrasion cycles. The SCA stayed within the range of 163.4° to 149.4°, which means the surface kept its superhydrophobic properties even after 10 rounds of abrasion.

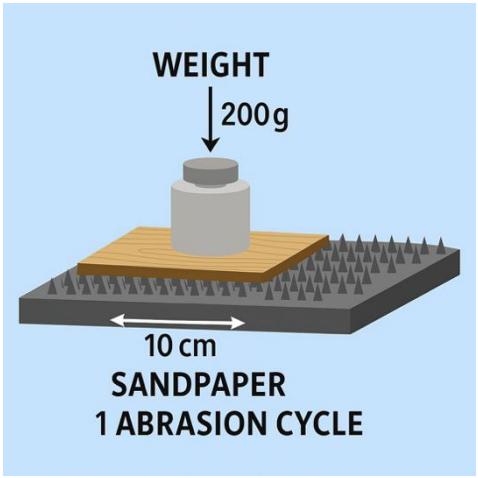

Figure 41- schematic Sandpaper abrasion test

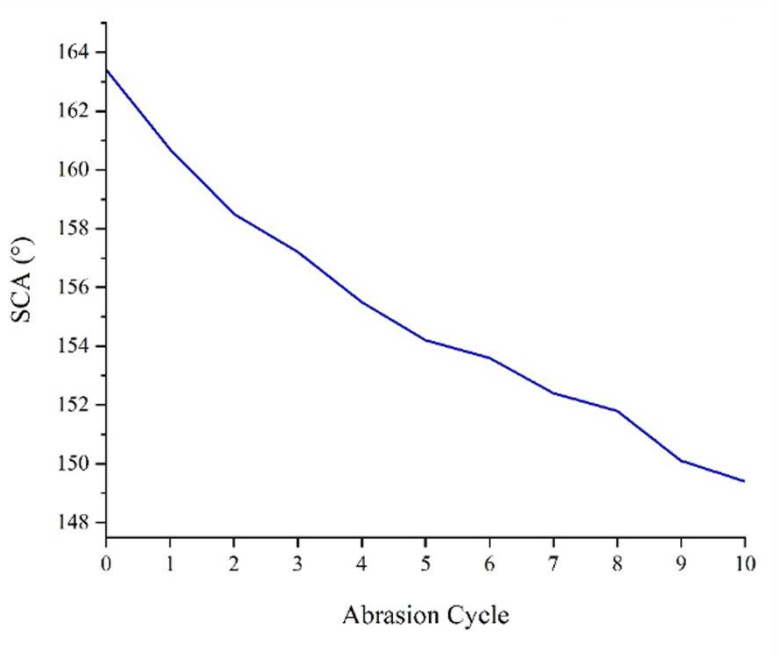

Figure 42- Optimal sample SCA after 10 abrasion cycles.

Figure 43 displays FE-SEM images of the optimized superhydrophobic surface after undergoing 10 abrasion cycles. Although there is some localized wear and tear in certain areas, the overall hierarchical micro/nano-structured roughness is still mostly intact. This suggests that the surface has strong structural stability and can withstand mechanical stress well.

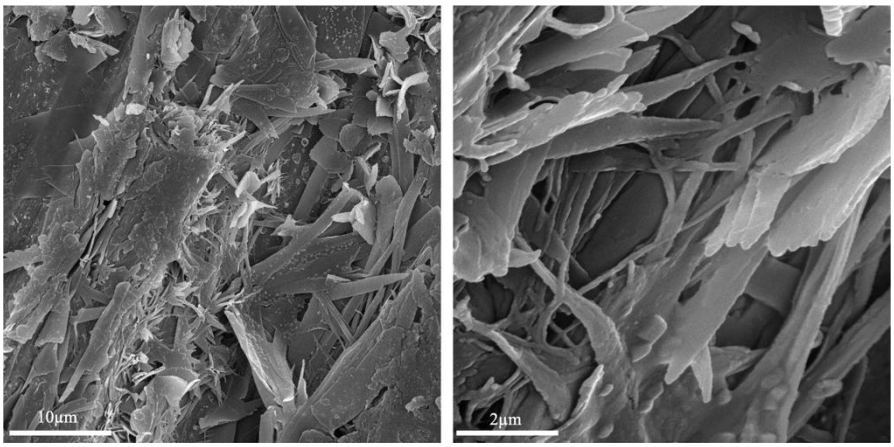

Figure 43- FESEM images after 10 abrasion cycles.

3.3. Self- cleaning properties

A standout feature of superhydrophobic surfaces is their ability to clean themselves. To test this, paint powder was sprinkled evenly over the coated brass surface, which was tilted at less than 10°. On these hydrophobic surfaces, water droplets tend to stick to each other rather than the surface because of its low surface energy. So, when water droplets roll over, they pick up and carry away the dirt thanks to their higher surface energy. This means the surface can clean itself completely without any scrubbing or extra effort. Figure 11 clearly shows this effect, where just a single water droplet leaves a clean path behind on the superhydrophobic surface.

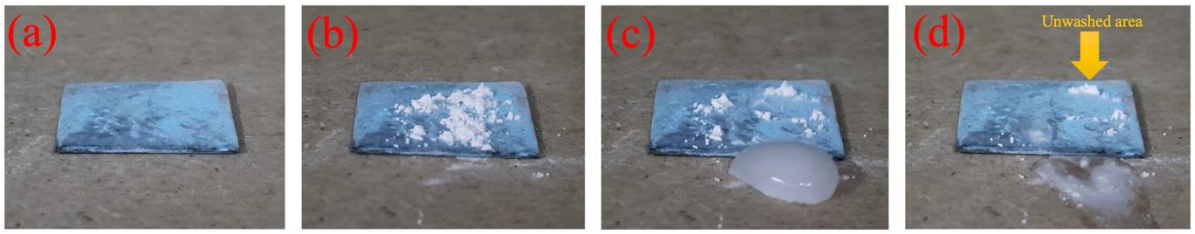

Figure 44- Self-cleaning properties of Optimum sample (a to d).

4. Conclusions

This study provides valuable results from different tests that include, chemical and mechanical durability, and self-cleaning performance. The important results are as follows:

- A crucial aspect addressed in this work is the chemical stability of the coatings, which is a common challenge for superhydrophobic materials. The optimized coating maintained its hydrophobicity properties effectively under acidic conditions (pH=4 and 6) even after several days of exposure, indicating strong chemical stability in such environments. However, under alkaline conditions (pH=8 and 10), a noticeable decline in performance was observed after four days. At pH 4.00, the SCA decreased from 152.3° to 119.1°, at pH 6.00, it declined from 157.7° to 135.9°, at pH 8.00, SCA fell from 149.6° to 111.5°, and at pH 10.00 went down from 137.7° to 96.6°.
- Mechanical durability was also tested through abrasion cycles, where the coating showed remarkable resilience, maintaining a contact angle above 149° after 10 abrasion cycles. This suggests that the coatings can withstand mechanical wear and tear.

- Finally, the coating's self-cleaning ability was confirmed, as the surface could clean itself completely without any additional scrubbing or effort, thanks to its high surface energy and hydrophobicity.

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Experimental and Numerical Study of Dent Damage Effects on the Fitness for Service (FFS) of Gas Pipelines

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ABSTRACT

Mechanical damage is recognized as a critical factor contributing to accidents in pipeline systems. Pipelines, particularly in the oil and gas industry, serve as one of the most essential and widely used methods for transporting fluids over long distances. Due to their operational significance, it is imperative to ensure that these systems function reliably and safely. Maintaining structural integrity throughout their service life requires diligent handling and strict adherence to safety protocols to minimize the risk of damage—especially mechanical damage—that could compromise performance. The primary objective of the present study is to evaluate the pressure-bearing capacity of steel pipes that have sustained dent defects and compare it to the ultimate pressure tolerance of defect-free pipes. This comparison aims to reveal how mechanical properties are altered in the presence of a dent and to determine a safe operational threshold for pipes affected by such damage. Both experimental and numerical methods were utilized to analyze these changes and establish guidelines for the allowable limits of pressure in dented pipeline segments. The experimental phase involved hydrostatic pressure tests on two sets of pipe specimens: one with dent defects and one without. These tests were conducted until each sample reached its failure point. Parallel to this, numerical simulations were carried out using Abaqus engineering software to replicate the experimental conditions and predict failure behavior. To validate the simulation results, data from the experimental tests—such as the residual strength factor and ultimate failure pressure—were compared with numerical outcomes. The findings demonstrated strong correlation between both methodologies, confirming that the numerical model could reliably be extended to other pipeline configurations with varying geometrical dimensions. As a result, the residual strength factor derived from this study can be effectively applied to assess and design pressure equipment exhibiting dent-type mechanical damage.

Keywords: steel pipe, Dent, Burst pressure, Abaqus.

1. Introduction

As industrial pipelines and equipment age, they are increasingly subjected to various forms of degradation due to harsh environmental conditions. These deteriorations lead to defects that pose serious challenges for operating companies, including the need for repair, replacement, or reduction in operating pressure. Implementing repair or replacement strategies typically requires service interruption, often resulting in unplanned shutdowns and significant costs. Moreover, repairing damaged sections demands meticulous planning, procurement of appropriate materials, and acquisition of necessary

permits (such as safety clearances), making the process time-consuming. Consequently, immediate corrective action upon defect detection is generally not feasible.[1-4]

Mechanical damage in transmission systems typically manifests in two primary forms: Dent and Gouge, in some cases, these defects may appear in combination. These anomalies occur on the pipe wall and can ultimately lead to crack initiation and premature equipment failure. Dents generally exhibit a spherical geometry and are commonly located along the pipe body. The progression of such defects induces strain localization and plastic deformation, potentially resulting in cracks of varying dimensions and a reduction in the metal's toughness. These damages are often caused by external impacts from equipment such as drilling rigs, graders, snowplows, or other machinery that disturbs or penetrates the soil surrounding the pipeline.

A dent is defined as a permanent deformation of the pipe's cross-section, resulting in a reduction in diameter and a concave shape from the inside. A simple dent is smooth and not accompanied by cracks, grooves, or other imperfections. While conventional pipelines may experience fatigue failure due to internal pressure fluctuations, dented pipes are more susceptible to such failure due to the high local stresses that develop in the pipe wall. These stresses arise from the combination of the dent and fluctuating internal pressures. In such cases, the fatigue life of a dented pipe depends on the geometry and type of dent.

In the present study, the effect of damage on the mechanical properties of steel pipes is investigated. Two types of specimens are considered: intact (undamaged) pipes and damaged pipes with dent defects. The results will be comparatively analyzed. Initially, standard tensile test specimens will be extracted from the pipes to accurately determine their mechanical behavior, including yield strength, ultimate tensile strength, and elongation at break. The primary objective is to identify the difference in burst pressure between intact and dented pipes

Subsequently, a numerical simulation will be conducted using Abaqus software to model the dent defect in a manner that closely aligns with experimental data. Following the simulation, the influence of dent severity on the performance of pressurized pipes will be evaluated through comparative analysis under both defect-free and dented conditions, experimentally and numerically

Ultimately, the findings of this study may be extended to industrial-scale applications, contributing to improved damage assessment and structural integrity evaluations in pipeline systems.

2. Experimental procedures

In the present study, metallic materials were used to construct the experimental samples, each of which is described in detail. A gas pipe made of plain carbon steel was selected and examined in two conditions: defective and non-defective. The samples were labeled as shown in Table 1.A cap or lens, made of plain carbon steel, was welded to both ends of each pipe sample to seal them, as illustrated in Figure 1. The joining of different components was carried out using welding technology. The fusion welding process involves melting the base materials and adding a filler metal to form a molten layer. In this study, the pipes were first secured with clamps. The caps were then spot-welded to the pipes at the 3, 6, 9, and 12 o'clock positions using a fusion welding machine. Subsequently, chain welding was performed by rotating the pipe. The electrode used for the welding process was the E 6013 Super-Mica electrode. This component is designed to connect various parts to the head of high-pressure pneumatic

devices. In the current study, it was used to link the hydrostatic testing device available in the laboratory to the prepared samples. The coupling used was a high-pressure model (rated at 5000 psi) manufactured by LMC Company, as shown in Figure 2.

Table 1. Dimensions of the samples used in the current investigation

Parameters	Sample without dent (Sample A)	Sample with dent damage (Sample B)
Pipe length	35 cm	35 cm
Thickness	1 mm	1 mm
Diameter	46 mm	46 mm

Figure 1. Cap used in the sample in this current investigation.

Figure 2. Male and female couplings.

The pipe samples were cut to a length of 35 cm, and their end caps (or lenses), made of plain carbon steel, were attached using a welding process. An inlet nozzle was then welded onto each sample to facilitate the hydrostatic test. The coupling assembly was connected to the inlet nozzle on one side (male coupling) and to the hydrostatic testing device on the other side (female coupling). The hydrostatic test was conducted using a high-pressure device, with all safety precautions strictly observed. To ensure consistency, all test conditions were kept identical for both sample types—except for the presence of a defect in the dented sample. For the sample with the indentation defect, a laboratory plunger was used to apply pressure and create the dent. The resulting indentation was measured prior to testing. Subsequently, the hydrostatic test was performed on the dented sample under the same conditions as

the non-defective sample, again observing all safety protocols. An image of the prepared sample is shown in Figure 3, and the dent defect is illustrated in Figure 4.

Figure 3. The prepared sample (no dent defects-Sample A).

Figure 4. Defective sample indentation (sample B).

Hydrostatic pressure testing is a widely recognized method used to assess the strength and detect leaks in gas pipelines. It is universally accepted as a reliable means of verifying the suitability of pressurized components for operational service[5, 6]. Pipeline companies routinely perform hydrostatic pressure tests during the installation of new pipelines to identify defects in material construction, prevent injuries during handling, and detect flaws introduced during installation.

A successful pressure test establishes a safety margin for pipeline performance and determines the Maximum Allowable Operating Pressure (MAOP) [5]. In this study, the primary objective of the hydrostatic test was to determine the ultimate failure pressure of the sample. The test was conducted in a controlled environment within a specialized hydrostatic pressure laboratory. Each sample was placed in a robust, reinforced tank filled with water and sealed with a protective cap to ensure safety during testing. The test tank is shown in Figure 5, and the procedural steps are illustrated in Figure 6.

Figure 5. Hydrostatic pressure testing machine.

Figure 6. Completion of hydrostatic testing of dent defect specimens (sample B).

Upon injecting air pressure into the intact sample, failure occurred at a pressure of 307 bar (30 MPa). The rupture exhibited a characteristic "fish mouth" opening, indicating ductile fracture behavior. In comparison, Sample B—containing a 10% indentation defect relative to its diameter—failed at a pressure approximately 65 Bar lower than the intact sample (Sample A). This significant reduction in failure pressure is attributed to the increased stress concentration at and around the indentation site. The localized deformation intensifies internal pressure distribution, making the material more susceptible to early failure. Additionally, higher residual strains at the indentation point further compromise structural integrity, accelerating the onset of fracture compared to the defect-free sample.

The images of the two damaged samples and the fracture locations of the two samples are shown separately in Figures 7 and 8, respectively.

a

b

Figures 7. Image of two destroyed samples ((a) Sample A, and (b) Sample B).

a

b

Figures 8. The location of the fracture of two samples ((a) Sample A, and (b) Sample B).

The figures clearly illustrate that the fracture site is located near the indentation area of the specimen. This is due to the plastic deformation that occurred at the indentation site, resulting in significant work hardening and strain hardening. The hardened region exhibits increased local resistance compared to the surrounding material, which causes stress concentration to shift toward the adjacent areas.

The highest stress concentration typically occurs at the slopes of the deformation—specifically, the edges of the indentation. These regions represent transition zones between the original geometry of the pipe and the deformed section, making them the most likely sites for failure initiation.

When an indentation is formed, compressive residual stresses develop at its center, while tensile residual stresses persist around the periphery. Since material failure generally initiates in regions under tensile stress, the fracture tends to occur around the indentation rather than at its center [6, 7].

3. Numerical procedures

The defective sample was also simulated using Abaqus engineering software. The dimensional specifications of the sample were entered into the software in a completely similar manner to the experimental sample (Table 2). The results of the hardness and Tensile test were entered as information on the mechanical properties of the sample, and the same test was performed as with the experimental sample. Table 3 shows the characteristics of sample B (with Dent) for the experimental case compared to the simulated one.

Table 2. Mechanical properties of the sample in experimental and simulated mode.

Sample mode B	Poisson's ratio	Yang's Modulus (GPa)	UTS (MPa)[2]	Yield stress (MPa)
Numerical	0.3	200	525	385

Table 3. Sample B characteristics for the experimental mode compared to the simulated one

Sample mode B	Ultimate Destruction Pressure (MPa)	Dent diameter (mm)	Thickness (mm)	Depth of dent (mm)	Diameter (mm)	Percentage of dent relative to diameter
Experimental	24	11	1	4.6	46	10%
Numerical	23	11	1	4.6	46	10%

The hydrostatic pressure test conducted on Sample B was executed in three distinct stages:

- **Stage One:** The indenter was driven into the specimen, resulting in a localized plastic deformation characterized by a depth of 4.6 mm and a diameter of 11 mm.
- **Stage Two:** The indenter was withdrawn, resulting in a permanent indentation that remained from the initial deformation stage.
- **Stage Three:** Internal pressure was gradually applied to the sample until structural failure occurred. The sample ultimately failed at an internal pressure of 23 MPa.

Figure 9 illustrates the extent of indentation in Sample B, captured at the final of stage one. The indenter is shown at its maximum penetration depth, with the light blue coloration indicating the full 4.6 mm indentation. Figure 10 presents a visual comparison between the actual indentation and its corresponding simulated model, highlighting the consistency between experimental and computational results.

Ultimate Tensile Strength[1]

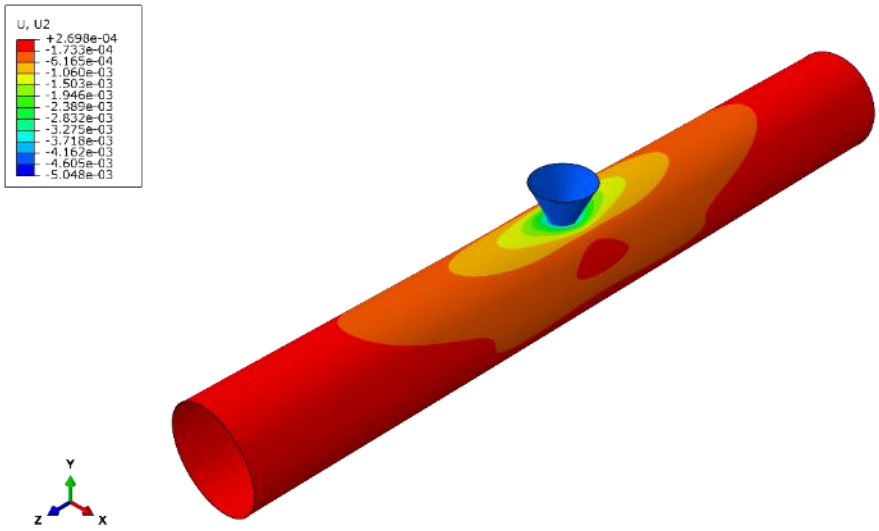

Figure 9. The dent formation in the sample B.

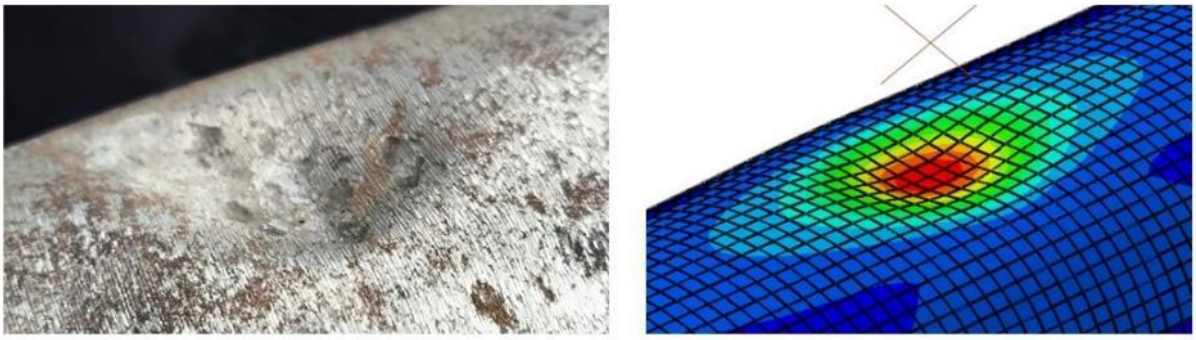

Figure 10. Actual and simulated dent in sample B.

Figure 11 also shows the von Mises stress distribution for sample B when the indenter is indenting (stage 1). The stresses have changed from blue (lowest) to red (highest). The highest stress is concentrated near the connection of the piston to the pipe body at the edges of the indentation.

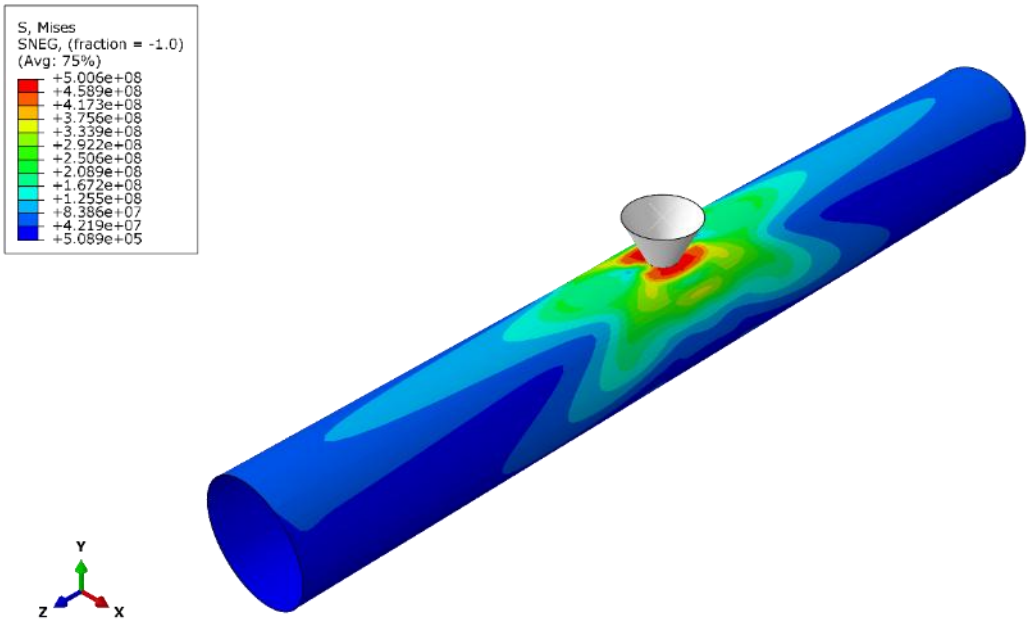

Figure 11. Von Mise stress distribution in the test specimen B.

Figure 12 presents the displacement distribution in Sample B at the conclusion of the second simulation stage. The left panel displays a high-resolution mesh configuration, enabling detailed visualization of element-level deformation. In contrast, the right one depicts the same displacement field without mesh overlays or body elements, offering a clearer view of the overall deformation profile.

The highest displacement is observed at the center of the indentation, indicated by the red region. This red zone not only marks the peak displacement but also corresponds to the diameter of the indentation formed during the initial loading phase. In the meshed view (left panel), the depression appears fully integrated, with a uniform displacement distribution across all mesh elements—demonstrating consistent deformation behavior throughout the indented region.

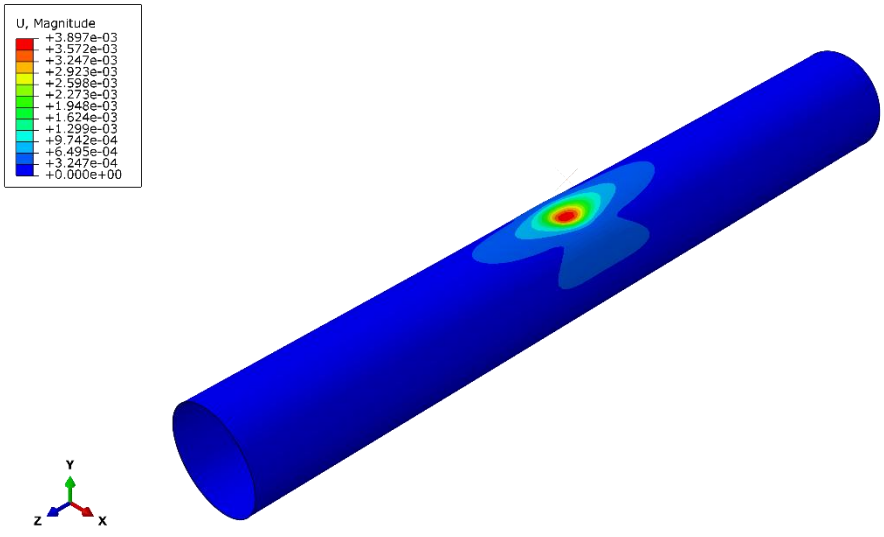

Figure 12. Displacement distribution in sample B

Also, Figure 13 shows the strain distribution in sample B when the plunger is removed (second stage). As can be seen, the maximum strain is about 8 mm (red dot) in the center of the indentation, which is due to the plastic deformation of the tube body, which has reached its maximum at the red dot.

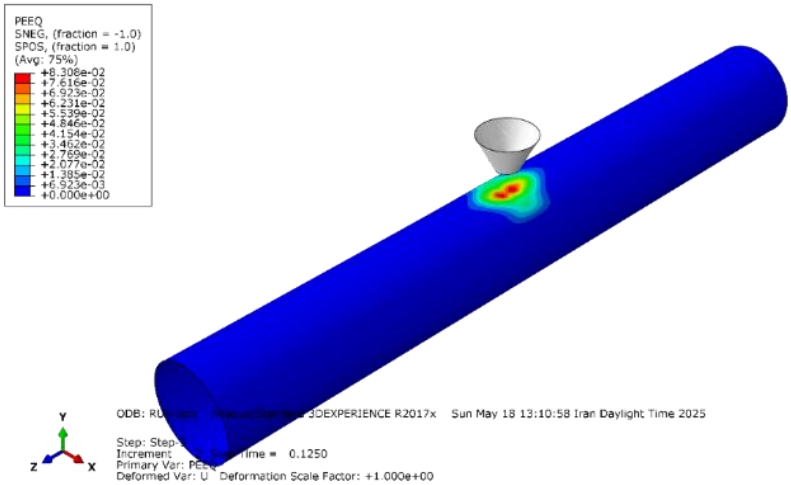

Figure 13. Strain distribution in the test of specimen B (second step)

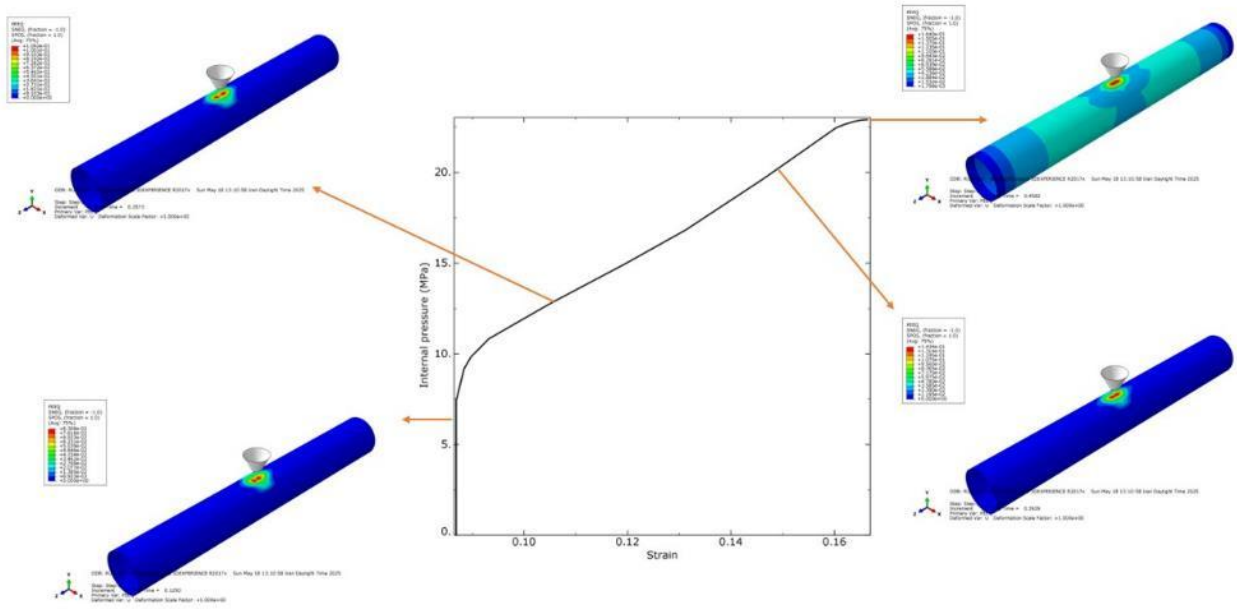

Figure14. Internal pressure strain diagram and strain distribution at different stages for sample B

The above figure (Figure 14) shows a combination of the internal pressure-strain diagram along with the strain distribution. This figure is from the third stage of the simulation experiment. On the lower left of the figure, it can be seen that at a pressure of 6 MPa (elastic region), a very small strain (maximum 0.083) was introduced into the sample, which was concentrated in the depth of the indentation. At 7.5 MPa, the elastic-to-plastic state began to change and the diagram had a steep slope up to 11 MPa. In the

upper left figure, the strain distribution at a pressure of 12.5 MPa can be seen. The maximum strain at this pressure is 0.108.

With the continued injection of pressure, the diagram has progressed with a gentle slope in the plastic state, which can be seen in the lower right image of the figure, the strain distribution for a pressure of 20 MPa. In this case, the maximum strain is 0.143. Also, in the upper right image, the strain distribution shape at the failure state and the ultimate destruction pressure (23 MPa) can be seen. It can be seen that the strain rate for the failure state is 0.164.

As observed, with increasing internal pressure, the maximum strain rate also increases until the moment of failure in different states, with the highest maximum strain rate corresponding to the final destruction moment. For all states, the maximum strain is concentrated in the depth of the indentation, which is due to the effect of the piston loading due to the high strain gradient on the body of the sample, so the curved edges cause the strain to be concentrated in the area of the depth of the indentation and the location of the piston effect[8-10].

4. Analysis of results

In the image below, you can see the pressure-time diagram after the completion of the hydrostatic pressure test for two samples A and B. In sample A, which has no indentation, the ultimate failure pressure is 307 bar, while in sample B, the ultimate failure pressure has decreased to 242 bar. This change is due to the stress concentration caused by the indentation and the areas around it. After the hydrostatic pressure test, a simulation was performed and it was also observed that the ultimate failure pressure for the sample is completely similar to the real (experimental) state of 230 bar. From these results, it can be seen that the test was carried out completely correctly and the simulation results are also consistent with the experimental state, so these results can be generalized and used in the industry.

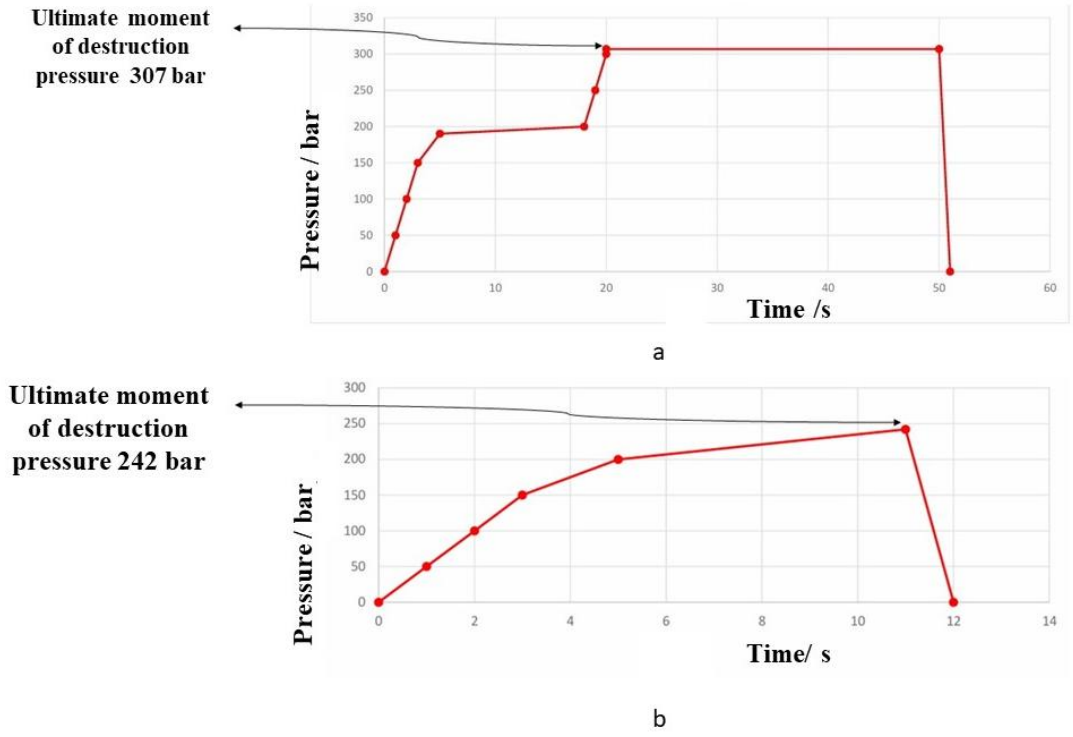

Figure 15. Pressure-time diagram of samples (Sample A (a) Sample B (b))

5. Conclusion

According to the analysis of the results, it can be said that simulation is very useful for preventing financial losses and human losses. It can also be seen that simulation produces results very close to experimental reality, which is very useful in the design of industrial components. Therefore, by using simulation, industrial components can be designed in such a way that they show a sign before failure that prevents sudden failure and its possible dangers, for example, for pipe components, leak before break can be easily designed using the data obtained from simulation. It is also possible to determine and predict the working life of industrial components used in sensitive industries according to the working pressure and even increase it, which will also reduce maintenance costs.

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Thermal Barrier Coatings: A Comprehensive Review of Materials, Deposition Techniques, and Performance

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ABSTRACT

Thermal barrier coatings (TBCs) are advanced protective systems widely applied to gas turbine blades, combustor liners, and other high-temperature components to enhance their service life and efficiency. These coatings typically consist of a ceramic top coat, a metallic bond coat, and an underlying superalloy substrate. Yttria-stabilized zirconia (YSZ) remains the most extensively used top coat material due to its low thermal conductivity and high thermal expansion coefficient [1,2]. However, limitations such as phase instability and sintering at elevated temperatures (>1200 °C) have led to increasing interest in alternative materials, including rare earth zirconates and multi-layer architectures [3,4]. Deposition techniques such as air plasma spray (APS), electron beam physical vapor deposition (EB-PVD), and high-velocity oxy-fuel (HVOF) significantly influence microstructure, porosity, and thermal performance [5,6]. This review highlights the latest developments in TBC materials, deposition methods, degradation mechanisms, and emerging strategies for improved durability. Challenges such as CMAS (calcium–magnesium–alumino–silicate) attack, oxidation of the bond coat, and thermal cycling resistance are discussed alongside future research directions. The aim is to provide a comprehensive overview that assists researchers in selecting optimal material-process combinations for next-generation TBC systems.

Keywords: Thermal barrier coatings, YSZ, rare earth zirconates, APS, EB-PVD, CMAS attack

1. Introduction

Thermal barrier coatings (TBCs) are advanced protective layers widely used in high-temperature environments, such as gas turbine blades, combustor liners, and aerospace engine components. These coatings play a critical role in enhancing the durability, thermal efficiency, and operational life of components subjected to extreme thermal stresses. They enable higher turbine inlet temperatures, improve overall engine performance, and reduce fuel consumption and emissions [2,1]. As the demand for more efficient and environmentally friendly power generation increases, the importance of reliable and high-performance TBC systems continues to grow [3,4] (Figure 1) [12].

Figure 45. Thermal barrier coating (colored white) on a turbine guide vane in a V2500 turbofan engine. Source: Wikipedia contributors, Thermal barrier coating*, Available: https://en.wikipedia.org/wiki/Thermal_barrier_coating, License: CC BY-SA 4.0 [12].*

A typical TBC system is composed of three key layers: the substrate, usually a nickel-based superalloy that provides mechanical strength; a metallic bond coat, typically made from MCrAlY alloys (where M = Ni, Co, or Fe), which enhances adhesion between the substrate and the ceramic top coat and also provides oxidation and corrosion resistance; and a ceramic top coat, which primarily functions as a thermal insulator to reduce heat transfer to the underlying substrate [1,5,6]. The most commonly used ceramic material for the top coat is yttria-stabilized zirconia (YSZ), appreciated for its low thermal conductivity, high thermal expansion compatibility with metallic substrates, and relatively good phase stability up to about 1200°C [1,6,9] (Figure 2) [13].

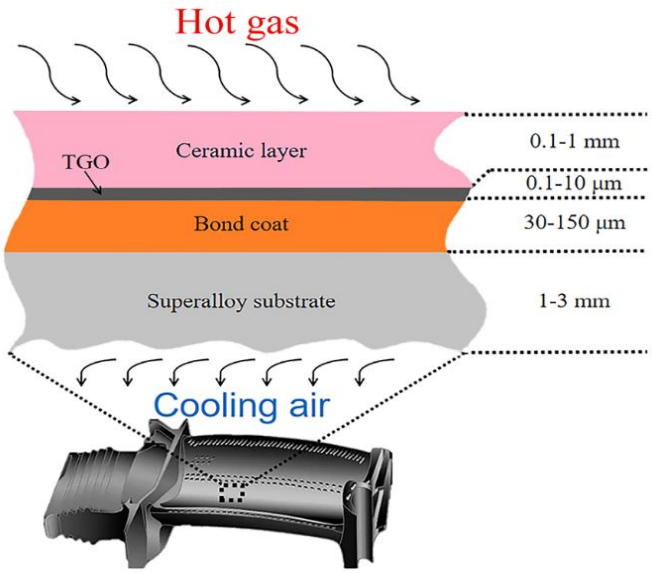

Figure 46. Schematic diagram of thermal barrier coatings (TBCs) structure(reprinted from [13])

Despite the widespread industrial use of YSZ, its effectiveness is constrained at temperatures exceeding 1200°C due to phase instability, sintering, and microstructural degradation. These factors diminish its thermal insulation capacity and mechanical integrity over time [3,7,8]. Consequently, extensive research has been conducted to develop alternative ceramic materials with enhanced high-temperature stability and resistance to environmental degradation. Among these, rare earth zirconates, such as gadolinium zirconate ($Gd_2Zr_2O_7$) and ytterbium zirconate ($Yb_2Zr_2O_7$), have attracted significant attention due to their superior phase stability, lower thermal conductivity, and enhanced resistance to CMAS (calcium–magnesium–alumino–silicate) attack—a major environmental challenge affecting TBC longevity [3,4,9](Table 1) [2–4,7].

In addition to material selection, the deposition technique plays a vital role in determining the microstructure, porosity, adherence, and overall performance of TBCs. Common deposition methods include air plasma spray (APS), electron beam physical vapor deposition (EB-PVD), and high-velocity oxy-fuel (HVOF) spraying. Each method produces coatings with distinct microstructural features that influence thermal conductivity, strain tolerance, and resistance to degradation mechanisms such as spallation and erosion [5,6,10]. Recent advances in deposition technologies, including suspension plasma spraying (SPS) and plasma spray-physical vapor deposition (PS-PVD), offer new pathways for tailoring microstructures and enhancing coating properties [11].

This review provides a comprehensive overview of the current state of TBC materials, deposition processes, and degradation mechanisms. It highlights future research directions aimed at optimizing coating designs to extend the service life of critical high-temperature components in the energy and aerospace industries.

Table 9. Comparison of key properties between Yttria-Stabilized Zirconia (YSZ) and Rare Earth Zirconates used in thermal barrier coatings. The table highlights differences in thermal conductivity, thermal expansion, phase stability, CMAS resistance, sintering behavior, and typical applications (adapted from [2–4,7]).

Property	**Yttria-Stabilized Zirconia (YSZ)**	**Rare Earth Zirconates (e.g., $Gd_2Zr_2O_7$)**
Thermal Conductivity	Low (~2.0 W/m·K)	Even lower (~1.5 W/m·K)
Coefficient of Thermal Expansion (CTE)	High and close to superalloys (~10.5 $\times10^{-6}$ K^{-1})	Slightly lower but suitable (~9.5 $\times10^{-6}$ K^{-1})
Phase Stability	Limited up to ~1200°C; prone to monoclinic transformation	Higher stability at elevated temperatures; resistant to phase change
CMAS Resistance	Moderate; susceptible to CMAS infiltration and damage	Much better; high resistance against CMAS attack
Sintering Resistance	Moderate; densifies with increasing temperature	Better; more porous structure and higher stability
Typical Application	Common top coat material in gas turbine TBCs	Alternative or complementary layer in advanced coatings

2. Materials and Method

Thermal barrier coatings rely heavily on the selection of suitable ceramic materials that provide low thermal conductivity and high temperature stability. The most widely used ceramic top coat is yttria-stabilized zirconia (YSZ), valued for its excellent combination of low thermal conductivity (~2.0 W/m·K), relatively high coefficient of thermal expansion (CTE), and adequate phase stability up to about 1200°C [1,2]. YSZ's ability to accommodate thermal stresses while providing insulation has made it the benchmark material in TBC applications for decades.

However, YSZ exhibits several limitations that restrict its performance under increasingly harsh operating conditions. At temperatures above 1200°C, YSZ undergoes phase transformations, notably the detrimental monoclinic phase, and experiences sintering which reduces porosity and degrades thermal insulation [3,4]. These drawbacks have motivated extensive research into alternative ceramic materials.

Rare earth zirconates such as gadolinium zirconate ($Gd_2Zr_2O_7$) and ytterbium zirconate ($Yb_2Zr_2O_7$) have gained attention due to their superior phase stability at higher temperatures and enhanced resistance to CMAS attack [3,5]. These materials offer lower thermal conductivity (~1.5 W/m·K) and reduced sintering rates, making them promising candidates for next-generation TBC top coats. However, their lower thermal expansion coefficients compared to YSZ may introduce thermal mismatch stresses, requiring careful design in multilayer coating systems [6].

n addition to ceramic top coats, the bond coat plays a critical role in TBC systems. Common bond coats are based on MCrAlY alloys (where M = Ni, Co, or Fe), which provide oxidation resistance and promote adhesion between the ceramic top coat and the metallic substrate [1,7]. The growth of a thermally grown oxide (TGO) layer at the bond coat interface is inevitable during service and influences coating lifetime significantly [1].

2.1. Deposition Methods of Thermal Barrier Coatings

- **Thermal barrier coatings (TBCs)** can be deposited using several advanced techniques, each influencing the microstructure, porosity, and performance of the final coating. The most common methods include air plasma spray (APS), electron beam physical vapor deposition (EB-PVD), and high-velocity oxy-fuel (HVOF) spraying [5,6].

- **Air plasma spray (APS)** is widely used due to its cost-effectiveness and versatility. APS produces coatings with a lamellar structure and relatively high porosity, which contribute to good thermal insulation but can reduce resistance to CMAS attack and erosion [5]. Electron beam physical vapor deposition (EB-PVD), on the other hand, creates columnar microstructures with controlled porosity and excellent strain tolerance, improving resistance to thermal cycling and spallation [6] (Figure 3) [14].

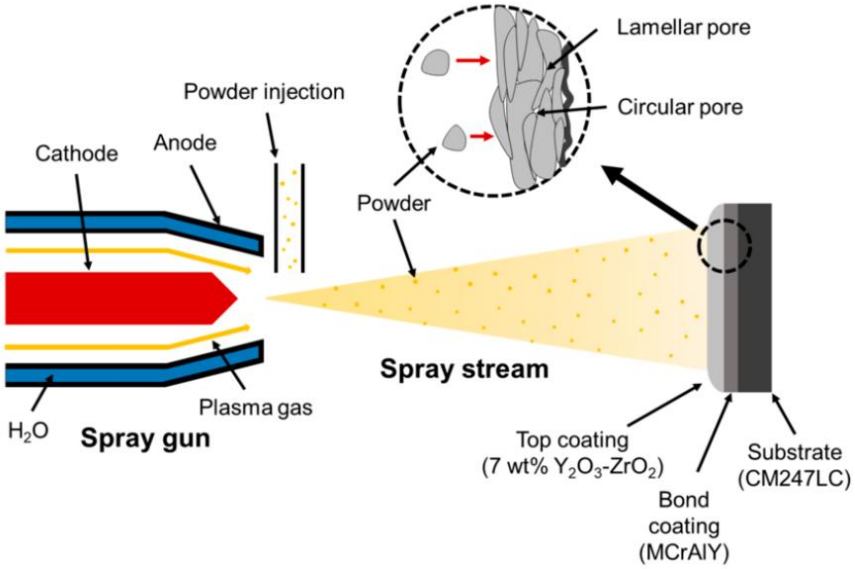

Figure 47. Schematic of the APS system and TBC coating(reprinted from [14])

- **High-velocity oxy-fuel (HVOF)** spraying is typically applied to deposit bond coats rather than ceramic top coats. HVOF provides dense coatings with strong adhesion and oxidation resistance, which are essential for the integrity of the TBC system [5] (Figure 4) [15].

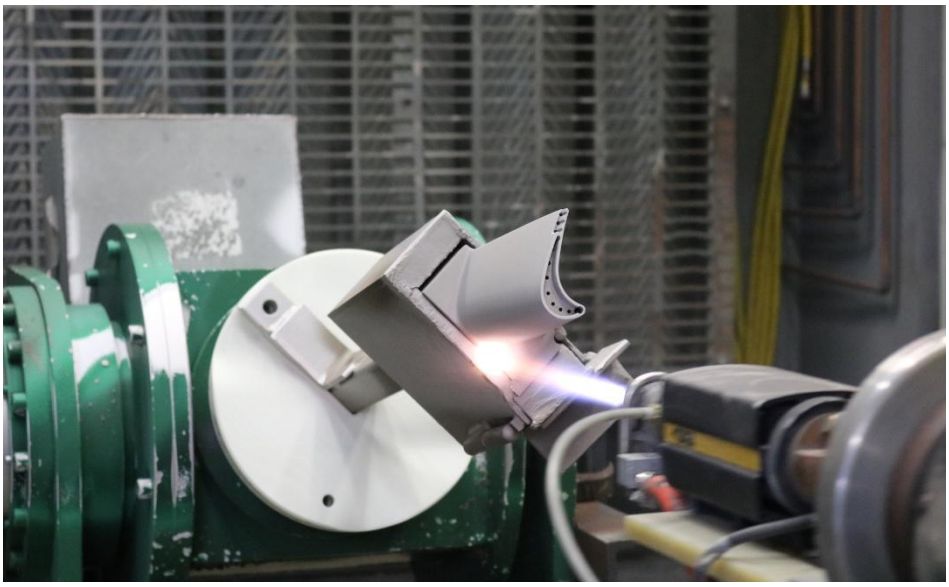

Figure 48. HVOF MCrAlY coating characteristic(reprinted from Trinity Coatings (2018) [15])

In recent years, novel deposition techniques such as suspension plasma spraying (SPS) and plasma spray-physical vapor deposition (PS-PVD) have emerged, offering improved microstructural control and the ability to produce advanced coatings with tailored properties [5].

Each deposition method presents trade-offs between coating density, porosity, thermal conductivity, and durability, making the choice of technique critical depending on the application requirements(Table 2) [4–6].

Table 10. Comparison of common deposition methods for thermal barrier coatings, highlighting their microstructural characteristics, thermal insulation performance, CMAS resistance, typical applications, advantages, and disadvantages (adapted from [4–6]).

Deposition Method	**Microstructure Characteristics**	**Thermal Insulation Performance**	**CMAS Resistance**	**Typical Application**	**Advantages**	**Disadvantages**
Air Plasma Spray (APS)	Lamellar splat structure, relatively high porosity	Good	Moderate	Ceramic top coat	Cost-effective, versatile, fast	Lower thermal cycling resistance, more prone to erosion and CMAS damage
Electron Beam Physical Vapor Deposition (EB-PVD)	Columnar, vertically oriented grains, controlled porosity	Excellent	High	Ceramic top coat	Excellent strain tolerance, superior thermal cycling resistance	Expensive equipment, slower deposition rate
High-Velocity Oxy-Fuel (HVOF)	Dense and smooth coating	Not typically used for insulation	High	Bond coat	High adhesion and oxidation resistance	Not suitable for ceramic top coats
Suspension Plasma Spray (SPS)	Nanostructured, porous coatings	Potentially superior	High	Ceramic top coat	Tailored microstructure, enhanced properties	Emerging technology, requires optimization
Plasma Spray-Physical Vapor Deposition (PS-PVD)	Columnar structure similar to EB-PVD	Excellent	High	Ceramic top coat	Combines advantages of APS and EB-PVD	New technique, higher complexity

2.2. Degradation Mechanisms of Thermal Barrier Coatings

Thermal barrier coatings (TBCs) are subjected to various degradation mechanisms during service, which ultimately limit their lifespan and performance. Understanding these mechanisms is essential for improving coating design and durability.

One of the primary degradation modes is thermal cycling-induced stress, which causes crack initiation and propagation due to the mismatch in thermal expansion coefficients between the ceramic top coat, bond coat, and substrate [1,3]. Repeated heating and cooling lead to the formation of microcracks, which can coalesce and result in spallation or delamination of the top coat [1] (Figure 5) [16].

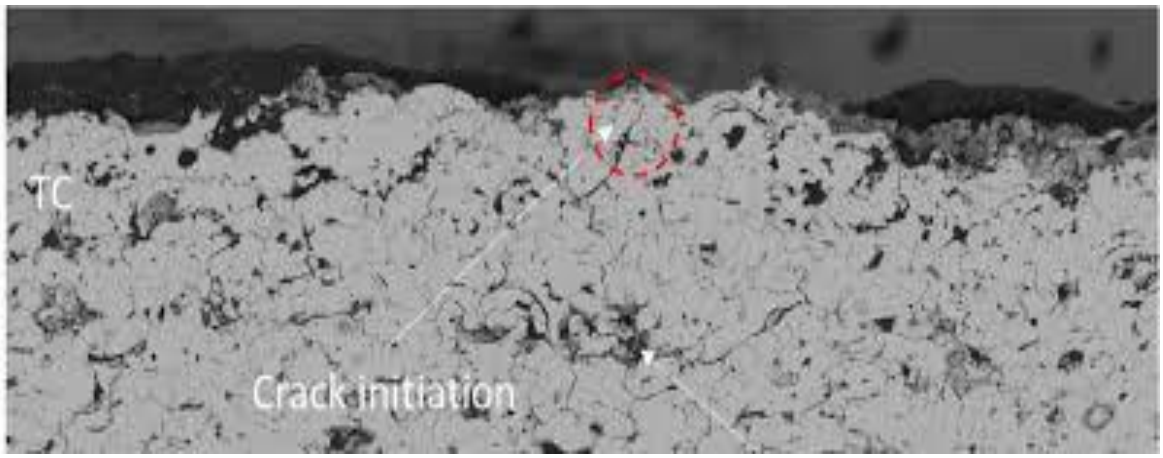

Figure 49. Crack initiation in APS TBC microstructure(reprinted from Amer et al. *[16])*

Another significant factor is the growth of the thermally grown oxide (TGO) layer at the bond coat interface. While the TGO layer provides oxidation protection, its continuous growth induces stresses that can weaken the bond and promote coating failure [1,7] (Figure 6) [17].

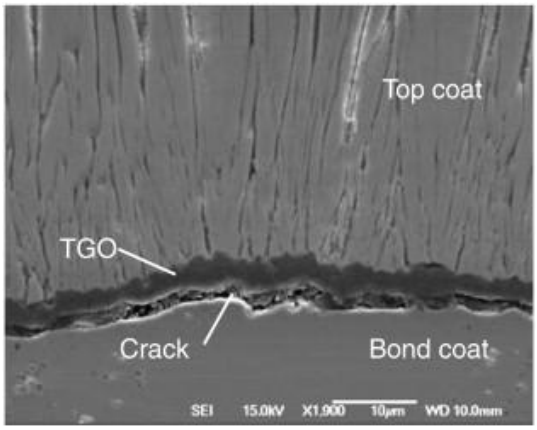

Figure 50. Crack and TGO development in TBC fracture process(reprinted from Evans [17])

CMAS (calcium–magnesium–alumino–silicate) attack is a major environmental challenge for TBCs. Deposits of molten CMAS can penetrate porous coatings, reacting with the ceramic material and causing accelerated degradation and spallation [3,4]. Research efforts focus on developing CMAS-resistant materials and protective strategies to mitigate this problem.

Sintering of the ceramic top coat at high temperatures reduces porosity, increasing thermal conductivity and decreasing the coating's ability to insulate [4]. This densification process also contributes to the embrittlement of the coating, making it more susceptible to cracking.

Overall, these degradation mechanisms interact, complicating the failure behavior of TBCs. Addressing them requires an integrated approach combining material selection, coating architecture, and optimized deposition techniques.

3. Discussion

Thermal barrier coatings (TBCs) have seen significant advancements in materials and deposition methods, improving their performance in high-temperature applications. Yttria-stabilized zirconia (YSZ) remains the industry standard due to its favorable thermal and mechanical properties. However, its limitations at temperatures above 1200°C, such as phase instability and sintering, have led researchers to explore alternative ceramics like rare earth zirconates, which offer better phase stability and higher resistance to environmental degradation [3,4].

Deposition techniques play a crucial role in determining coating microstructure and durability. Air plasma spray (APS) is cost-effective and versatile but results in coatings with higher porosity and moderate resistance to CMAS and thermal cycling. Electron beam physical vapor deposition (EB-PVD) produces columnar coatings with excellent strain tolerance and thermal cycling resistance, although at higher cost and slower deposition rates [5,6]. Emerging methods like suspension plasma spray (SPS) and plasma spray-physical vapor deposition (PS-PVD) provide promising avenues for tailoring microstructures and enhancing properties [5].

Key degradation mechanisms, including thermal cycling stresses, growth of the thermally grown oxide (TGO) layer, CMAS infiltration, and sintering, collectively limit the lifespan of TBCs [1,3,7]. Addressing these challenges requires an integrated approach combining advanced ceramic materials, multilayer coating architectures, and optimized deposition processes to improve coating reliability.

Future research should focus on developing novel materials with improved phase stability and thermal expansion matching, alongside advanced deposition technologies that enable precise microstructural control. A better understanding of the synergistic effects of degradation mechanisms under real operating conditions will support the design of longer-lasting and more reliable TBC systems [4,8].

This review provides insights into current challenges and future directions for advancing thermal barrier coating technologies.

4. Conclusions

Thermal barrier coatings (TBCs) are essential for improving the efficiency and lifespan of high-temperature components in gas turbines and aerospace applications. Yttria-stabilized zirconia (YSZ) has been the dominant ceramic top coat material for decades due to its excellent thermal insulation properties and good compatibility with metallic substrates. However, challenges such as phase instability, sintering, and limited resistance to CMAS attacks at temperatures above 1200°C limit its long-term performance and durability. This has driven significant research efforts toward alternative ceramic materials like rare earth zirconates, which offer superior phase stability, lower thermal conductivity, and enhanced environmental resistance.

Deposition methods greatly influence the microstructure, porosity, and overall performance of TBCs. Air plasma spray (APS) and electron beam physical vapor deposition (EB-PVD) remain the most widely used techniques, each with distinct advantages and limitations regarding coating density, strain tolerance,

and resistance to degradation. Emerging technologies such as suspension plasma spray (SPS) and plasma spray-physical vapor deposition (PS-PVD) show promise in tailoring coating microstructures for improved durability and thermal performance.

Understanding the complex degradation mechanisms affecting TBCs—including thermal cycling-induced stresses, growth of the thermally grown oxide (TGO) layer, CMAS infiltration, and sintering—is critical to designing coatings that can withstand harsh operating environments. The interplay between these mechanisms often accelerates coating failure, underscoring the need for integrated approaches that combine advanced ceramic compositions, multilayer coating architectures, and optimized deposition processes.

Future research should prioritize the development of novel materials with enhanced phase stability and thermal expansion compatibility, as well as innovative deposition techniques capable of precise microstructural control. Additionally, studying the synergistic effects of multiple degradation factors under real service conditions will be vital to advancing TBC technology. By addressing these challenges, researchers and engineers can develop next-generation thermal barrier coatings that provide superior durability, reliability, and efficiency, ultimately contributing to more sustainable and high-performing energy systems.

This comprehensive review provides a detailed foundation for ongoing research and development efforts aimed at overcoming current limitations and pushing the boundaries of TBC.

5. Acknowledge

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Design, Development, and Optimization of Friction Stir Spot Welding Parameters for Aluminum Alloys

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ABSTRACT

This study examined the process parameters of Friction Stir Spot Welding for Aluminum alloys. The work focused on how various process parameters and tool design influenced the thermal and mechanical responses, ultimately affecting joint strength and hardness. A fixture was designed and manufactured to support the welding process, and two different welding tools were prepared to study their effect on the weld formation. A load cell and a thermocouple were integrated into the setup to measure force and temperature during welding. Tensile shear tests showed a maximum joint strength of 1968 N, while the weld zone reached a hardness of 72.2 HV. The two-step method used successfully eliminated the key hole defect. The microstructure of the stir zone showed refined grains with a stable pattern. These results indicated that controlled process parameters and the selected tool designs produced consistent joints with improved mechanical performance.

Keywords: Aluminum Alloys, Fixture Design, Friction Stir Spot Welding, Process Parameters, Tool Design

1. Introduction

The conventional welding techniques present significant challenges when applied to aluminum alloys, particularly in automotive and aerospace sectors where weight reduction remains a critical design consideration. Friction Stir Spot Welding has emerged as an alternative approach that differs fundamentally from traditional methods rather than inducing melting, a rotating tool generates heat through friction while mechanically stirring the material to form a joint [1]. This solid-state process avoids typical fusion-related defects such as porosity and solidification cracking commonly observed in aluminum welds [2]. The procedure involves plunging a rotating tool into overlapped sheet configurations, generating localized frictional heating that plasticizes the material, followed by tool retraction leaving a consolidated joint [3]. Moreover, it is also an ecofriendly and operator-friendly technique because no protective gases, arcs, smoke and fumes are generated in the process [4,5].

The selection of 6061-T6 aluminum alloy for this investigation was based on its widespread industrial application. This alloy exhibits favorable characteristics including high strength-to-weight ratio, corrosion resistance, and machinability [6-8]. However, joining this material through conventional means presents difficulties related to high thermal conductivity and native oxide layer formation [9]. FSSW addresses these limitations more effectively than established welding procedures.

A significant consideration exists regarding process control. Joint quality in FSSW exhibits substantial variation based on tool geometry, rotational velocity, penetration depth, and dwell duration [10]. Conventional pin-tool configurations characteristically produce a central keyhole defect that serves as a stress concentration site, thereby compromising fatigue performance [11]. Various advanced approaches including refill welding and pin-less tool designs have been investigated to mitigate this limitation [12].

The present work was performed to design appropriate tooling, develop measurement capabilities for process monitoring, and establish optimal parameter combinations for producing high-strength 6061-T6 aluminum joints suitable for manufacturing applications. Most previous work used a single tapered pin tool, which has limitations in achieving optimal joint strength. In this work, a two-step tool is compared with the conventional tapered pin. A fixture was designed and manufactured, and a load cell and thermocouple were integrated to measure force and temperature during welding. The objective of this study is to investigate how process parameters and tool design affect the mechanical performance of aluminum alloy joints in FSSW. The results focus on improving joint strength, reducing defects, and enhancing weld zone hardness.

2. Materials and Method

This section explains the materials, fixture design, tools, instrumentation setup, welding procedure, and sample preparation steps that were used to produce the friction stir spot welds. Practical observations from the trials are included only where necessary to describe the method.

2.1. Materials

AA6061-T6 aluminum sheets were used. Each sheet had a thickness of 3 mm. For the experiments, the sheets were cut to 100 mm × 25 mm, and the overlap was kept at 25 mm for every sample. The base material selected was 6061-T6 aluminum alloy sheets with dimensions of 100 mm × 30 mm × 1 mm. This alloy contains 0.8–1.2% Mg, 0.4–0.8% Si, and has a tensile strength of 310 MPa with hardness of 75–78 HV [13]. Surface cleaning was performed with an abrasive pad before clamping.

Each weld used the lap configuration with the fixed overlap. The sheets were placed inside the fixture so that the intended weld zone remained centered under the tool. This arrangement allowed uniform heat distribution during both passes.

2.2 Fixture System

2.2.1 Fixture Design

The fixture was designed in Creo Parametric 6.0. The design in Fig. 1 included clamping plates, a backing plate, a load cell compartment, and base material attachment. The geometry ensured that the sheets remained aligned and firmly held during the welding process.

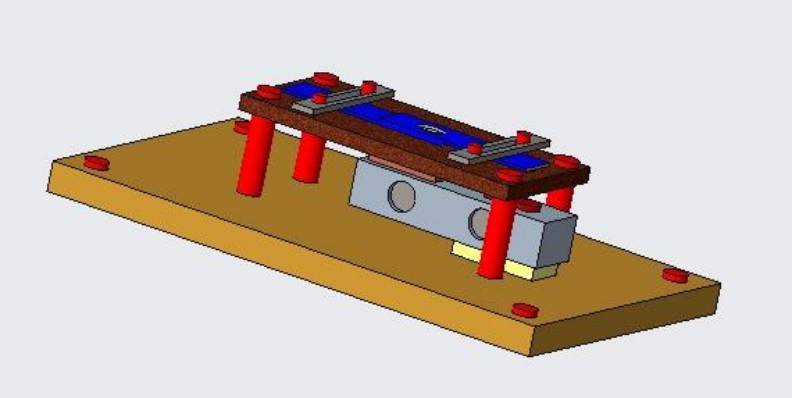

Figure 51: 3D View Of CAD Model

2.2.2 Fixture Manufacturing

The fixture components were produced in the workshop from Stainless Steel (SS) plates. The plates were cut, milled, and drilled according to the Creo drawings. Sensor ports and bolt holes were machined to the required tolerances. After fabrication, the fixture was assembled as shown in Fig. 2, and checked for flatness and consistent clamping pressure.

Figure 52: Assembled Fixture With Integrated Load Cell

2.2.3 Backing Plate and Sensor Housing

A hardened backing plate supported the sheets during welding. The fixture contains a load cell HX711 of 10 kN which is positioned directly under the workpiece. The load cell kept monitoring how strong the FSSW tool was pressing into the weld joint. A K-type thermocouple was inserted into the fixture, underneath the center of the weld nugget as shown in Fig. 3, to monitor the temperature at the join seam. An ESP microcontroller interfaced with Arduino software is used for data collection. The load cell was placed directly beneath this plate so that the axial force from the shoulder would transfer cleanly to the sensor. The thermocouple channel was positioned close to the weld center to capture temperature changes beneath the spot.

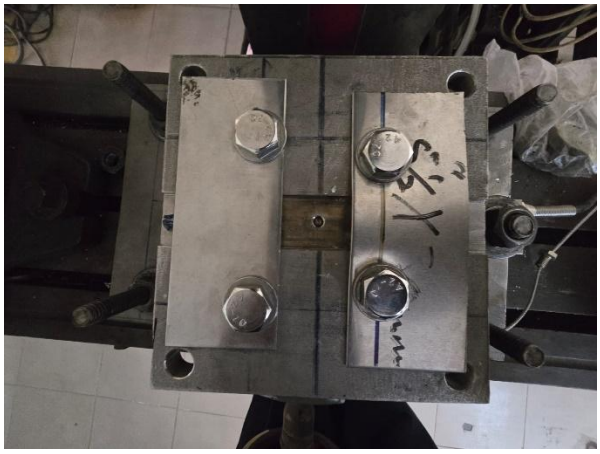

Figure 53: Top View Of Fixture Showing Clamping Plates, Groove And Hole For Thermocouple Sensor

2.3 Tools

The tool material selected was H-13 tool steel because it is well suited for the heat and durability challenges of FSSW at high temperatures. It has to be also able to resist heat and pressure when welding is in progress. The conventional lathe machine is used to shape the tools as per desired dimensions. Following machining, both tools underwent heat treatment procedures. Austenization was conducted at 1010°C followed by air quenching. Subsequent tempering at 565°C for 2 hours yielded final hardness values between 50-60 HRC, appropriate for aluminum alloy welding applications while maintaining adequate toughness [14-16].

2.3.1 Tapered Pin Tool

The first tool was an H13 steel tapered pin tool. It had a 4 mm pin base diameter, and a 3.1 mm pin height. Shoulder diameter measured 12 mm with a 10° taper angle and 2° shoulder concavity. The tool on the left side in Fig. 4 produced the stirring action and formed the keyhole at the center.

2.3.2 Pin-less Tool

The second tool had the same 12 mm shoulder diameter but with no protruding pin as shown in Fig. 4. It was used in the second pass in two-step method to refill the keyhole and smooth the weld surface. This tool also produced additional forging and heat input in the region. Table 1 summarizes the dimensions for both the tools.

Table 11: Dimensions Of Tools

Tool Parameter	**Pin-less Tool**	**Tapered Pin Tool**
Shoulder Diameter	12 mm	12 mm
Shoulder Length	21 mm	20 mm
Pin Diameter	-	Base: 3 mm Tip: 2 mm
Pin Length	-	3.1 mm
Taper Angle	-	10°
Shoulder Concavity	-	2°

Figure 54: Tapered Pin Tool (Right) And Pin-Less Tool (Left)

2.5 Welding Procedure

All welding trials were carried out on a vertical milling machine. The fixture containing the sheets was clamped on the machine table. The tool was mounted in the spindle, and its alignment with the weld center was confirmed before each pass. Fig. 5 illustrates the complete setup, including the conventional milling machine, the custom fixture integrated with a load cell and thermocouple, and the circuit connected to a laptop for force and temperature measurements displayed on the screen.

Figure 55: Experimental Setup Along With Data Collection

2.6. Experimental Trials and Parameter Optimization

The experimental program involved systematic trials to establish optimal welding parameters. Initial attempts with pin-less tool application on flat surfaces at 1000 RPM resulted in tool slippage as shown in Fig. 6., due to insufficient mechanical interlocking between the flat shoulder and workpiece surface. This limitation led to the development of a two-step methodology wherein the tapered pin tool was employed first to initiate material plasticization, followed by pin-less tool application for keyhole consolidation.

Early two-step trials at 1000 RPM with minimal dwell time and shallow penetration depth exhibited excessive vibration and off-center weld as shown in Fig. 6. Subsequent parameter adjustments reduced rotational speed to 580 RPM (calculated based on pulley diameter ratios) to enhance process stability within manual milling machine constraints.

Initial pin tool experiments at 580 RPM with 20-30 second dwell time and 0.5 mm shoulder penetration produced centered welds but demonstrated insufficient strength due to limited penetration depth (total penetration depth of 3.6 mm). Additional complications arose from inadequate fixture stabilization, resulting in load cell displacement and inconsistent sensor readings.

Further optimization with increased shoulder depth to 1.0 mm (total penetration depth 4.1 mm) improved weld appearance but failed tensile testing. Analysis indicated that process temperatures remained below the aluminum recrystallization range, limiting material plasticity and consolidation. Circuit connection instability continued to compromise data acquisition reliability.

Figure 56: Failed Pin-less Sample (Slippage) And Tapered Pin Tool (Off-Center)

2.5. Optimized Experiments

Following continuous refinement, four successful experimental Experiments were established:

Experiment 1 - Basic Pin Tool: Rotational speed 580 RPM, shoulder penetration 1.0 mm, total penetration depth 4.1 mm, dwell time 30-40 seconds. Process monitoring recorded axial force of 2792 N and maximum temperature of 204°C. This configuration achieved tensile load capacity of 885 N.

Experiment 2 - Two-Step Process: Sequential application of tapered pin tool followed by pin-less tool, both at 580 RPM. Pin tool phase employed shoulder penetration of 1.0 mm with dwell time sufficient to achieve 337°C to reach the recrystallization temperature of Aluminum. Pin-less consolidation phase

reached 120°C with measured force of 2513 N. This results in joint strength of 1341 N tensile load while successfully eliminating keyhole defect.

Experiment 3 - Enhanced Pin Tool: Increased shoulder penetration to 1.5 mm (total penetration depth 4.6 mm) with extended dwell time of 30-40 seconds at 580 RPM. Temperature monitoring confirmed achievement of recrystallization range at 344°C with axial force of ≈ 2.5-2.7 kN (intermittent force peaks due to pausing). This optimization yielded maximum tensile strength of 1968 N.

Experiment 4 - Microstructural Analysis Specimen: Identical parameters to Experiment 3, prepared specifically for hardness profiling and optical microscopy examination to correlate process parameters with microstructural evolution. The summary of all successful experiments are shown in Table 2.

Table 12: Summary Of Successful FSSW Experiments

Experiment	Method	Peak Force (kN)	Temperature (°C)	Strength (N)
1	Tapered Pin	2.79	204	885
2	Two-Step	2.51	337 (Pin) 120 (Pin-less)	1341
3	Tapered Pin	≈ 2.5 – 2.7	344	1968

Force and temperature data were continuously recorded throughout all successful trials via the integrated measurement system. The dwell time varied between 30 and 40 seconds because the welding process needed occasional pauses to stabilize the setup due to vibrations in the milling machine. This range worked well to achieve proper material flow and successful welds as shown in Fig. 7. Experiment 4 was prepared using the same parameters as Experiment 3 for microstructural and hardness analysis and is not included in the tensile test summary table.

Figure 57: Welded Sample

2.6 Sample Preparation

After welding, the joints were sectioned using an abrasive cutter. Tensile shear test specimens and metallographic samples were taken from the welded region. Samples for microstructural examination were mounted in epoxy and then ground with 400 and 600 grit papers. Polishing was done with fine abrasives until a smooth surface was obtained. Keller's reagent was used to reveal the weld regions. The etching step made the stir zone, the thermo-mechanically affected zone, and the heat-affected zone

visible under the microscope. The sample cut and mounted for microhardness and microstructure is depicted in Fig. 8.

Figure 58: Sample Mounted For Microhardness And Microstructure

2.7 Characterization Methods

Visual Inspection: Surface characteristics, flash formation patterns, and keyhole geometry were assessed using stereomicroscopy at 5x magnification.

Tensile Shear Test: Tensile shear tests were conducted on a Universal Testing Machine (UTM) at a crosshead speed of 1mm/min in accordance with ASTM E8 standards [17]. Each sample was loaded until fracture. The failure location and maximum load were recorded separately for each specimen.

Microhardness Testing: Vickers microhardness measurements were taken across the weld cross-section. Vickers hardness measurements were obtained at 0.8 mm intervals across weld cross-sections using 200g indentation load following ASTM E384 specifications [18]. Indents were placed at uniform spacing to study hardness variation from the base metal toward the stir zone.

Microstructural analysis: Cross-sectional specimens were prepared through standard metallographic procedures including mounting, grinding, and polishing. Keller's reagent was applied for 10-20 seconds to reveal grain structure. Optical microscopy at 400x magnification was employed to examine grain morphology in the stir zone, thermo-mechanically affected zone, heat-affected zone, and base material regions.

3. Results and Discussion

3.1 Visual Inspection

The stereomicroscopic examination of the weld surfaces at 580 RPM showed limited flash formation in both the pin tool and two-step FSSW samples, indicating controlled material flow and stable heat input during the welding process. This controlled flash distribution indicates that the selected plunge depths and clamping pressures successfully maintained plasticized material within the intended weld zone. The reduced flash formation at 580 RPM, compared to higher speeds reported by Zhang et al. [10],

demonstrates the advantage of operating within the mechanical constraints of manual milling equipment while achieving adequate heat generation.

The two-step process produced the most uniform surface finish, and importantly, eliminated the central keyhole by refilling the cavity in the second stage, as shown in Fig. 9. This demonstrates improved material consolidation during the secondary pin-less pass, which reduces stress concentration and enhances load transfer across the joint. Similar benefits of keyhole-elimination techniques have been reported in refill FSSW systems. These observations validate the two-step approach as a viable alternative to more complex refill FSSW techniques which were previously reported for keyhole elimination by Tier et al. [12] and Mazzaferro et al. [19]. This is particularly beneficial for applications where specialized refill tooling is unavailable.

In contrast, the single-stage pin tool weld displayed a shallow but visible keyhole at the center as shown in Fig. 9, due to pin withdrawal. These findings align with observations by Wang and Lee [20] who documented similar keyhole dimensions in 6061-T6 FSSW joints. The pin tool weld showed sharper concentric rings and slightly more flash, reflecting higher local material expulsion during plunging. Overall, visual inspection confirms that the two-step method improves surface integrity by eliminating the withdrawal defect, while the enhanced pin tool weld benefits from deeper penetration and greater stirring stability.

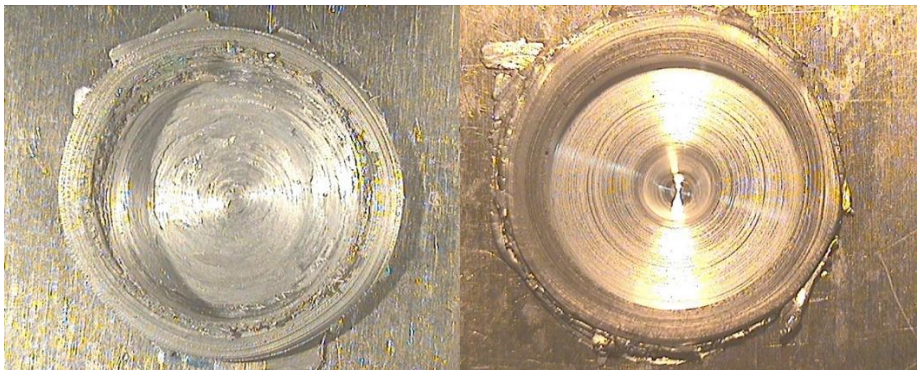

Figure 59: Surface Macrograph Of Two-Step (Right) And Pin (Left) FSSW Sample At 5x

3.2 Hardness Distribution

The hardness profile measured through the weld thickness revealed significant softening compared to the base material hardness of 107 HV. The stir zone exhibited hardness values between 60.8 HV and 72.2 HV, with the highest value recorded near the mid-depth of the stirred region. These results reflect the competition between dynamic recrystallization, which refines grains, and thermal over-aging, which dissolves Mg_2Si strengthening precipitates. At the applied conditions of 580 RPM, 2.5 kN axial force, and dwell time of 30–40 seconds, precipitate dissolution dominates, resulting in lower hardness despite grain refinement. Ahmed et al. [21] reported similar stir zone hardness ranges of 60-70 HV for AA6082-T6 (a closely related 6xxx-series alloy) depending on sheet thickness and welding parameters, confirming the typical softening behavior observed in heat-treatable aluminum alloy spot welds.

Table 3 shows microhardness values measured along a 4 mm line with 0.8 mm spacing between indentations.

Table 13: Hardness Values

Indent	Hardness (HV)	Zones
Original Hardness	107	Base Material
1st	60.8	Weld Nugget
2nd	70.6	Stir Zone
3rd	72.2	Stir Zone
4th	64.7	Thermo-Mechanically Affected Zone
5th	63.6	Heat Affected Zone

Softening increased outward into the TMAZ and HAZ, where hardness decreased to nearly 63.6 HV. These regions experienced high temperatures but minimal plastic deformation, causing precipitate coarsening without recrystallization. This behaviour aligns closely with reported hardness patterns in 6061-T6 FSSW joints, where both the SZ and HAZ typically soften relative to the parent alloy due to precipitate instability at elevated temperatures Wang and Lee [20] and Yang et al. [22]. The hardness profile in Fig. 10 begins at the base material (x = 0 mm, 107 HV).

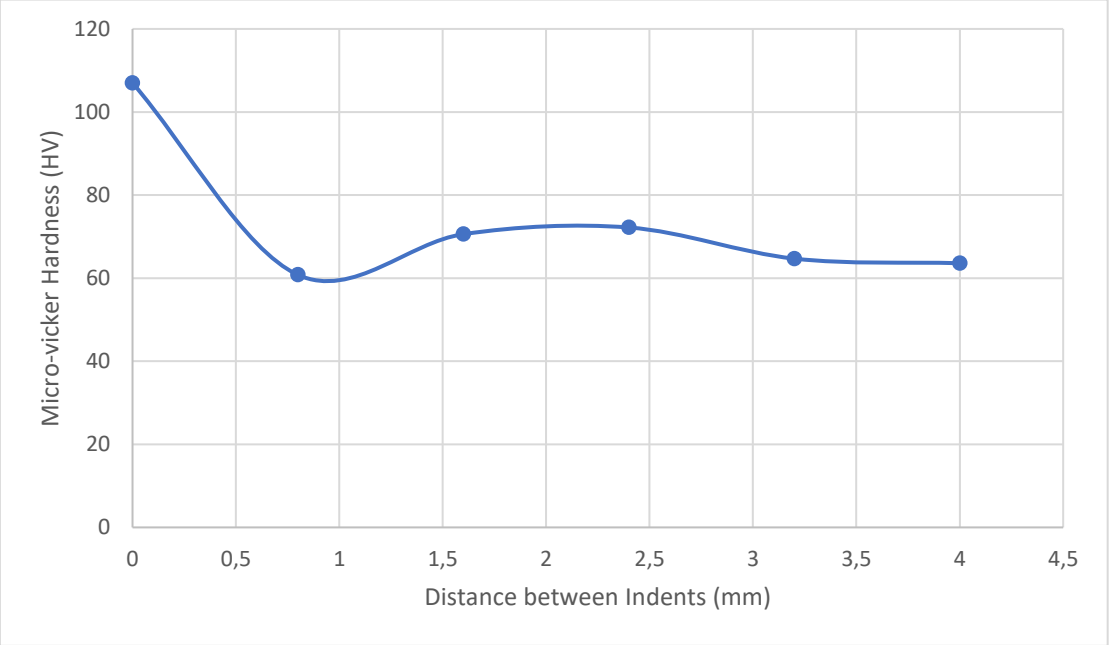

Figure 60: Hardness Profile Across The Weld Traverse Beginning From The Base Material (BM)

3.3 Tensile Shear Strength

The tensile shear performance varied significantly with tool design and parameter selection. The initial pin tool weld reached strength of 11.81 N/mm^2, a maximum load of 885 N, which is consistent with typical strengths of conventional FSSW joints containing a keyhole defect [11]. The presence of the withdrawal cavity reduces the effective load-bearing area and leads to early crack initiation, explaining the limited deformation and abrupt failure observed in the stress–strain response shown in Fig. 11.

The two-step weld improved strength to 17.89 N/mm^2 which equals the tensile load of 1341 N, owing to the successful elimination of the keyhole and enhanced continuity in the center of the joint. The secondary

refilling action allows the stirred material to bond more uniformly, reducing stress concentration and promoting ductile failure as shown in Fig. 11. These results compare favorably with Fujimoto et al. [23] who reported maximum tensile loads of approximately 1350 N for 6061-T6 FSSW joints using optimized dwell time and tool threading. Similar improvements have been reported in refill-style FSSW studies where the keyhole is closed during processing [12,13,24].

The highest tensile load, 1968 N, and strength of 26.2 N/mm^2 was achieved using the enhanced pin tool condition, which employed a deeper shoulder penetration and longer dwell time (30–40 s). These parameters increased heat input to approximately 343 °C and promoted more complete plastic flow and consolidation of the weld nugget. This temperature lies within the recrystallization range for 6061-T6 aluminum, enabling dynamic recrystallization and improved material consolidation despite the presence of a keyhole defect. Although high heat can cause softening, prolonged stirring in this case improved bonding across the interface and expanded the effective welded area, resulting in the strongest joint. Similar strength values approaching 2000 N were reported by Chiou et al. [25] using embedded pin tools with extended dwell times, and Tashkandi et al. [26] achieved fracture loads close to 2800 N with deeper pin penetration on 3 mm thick sheets.

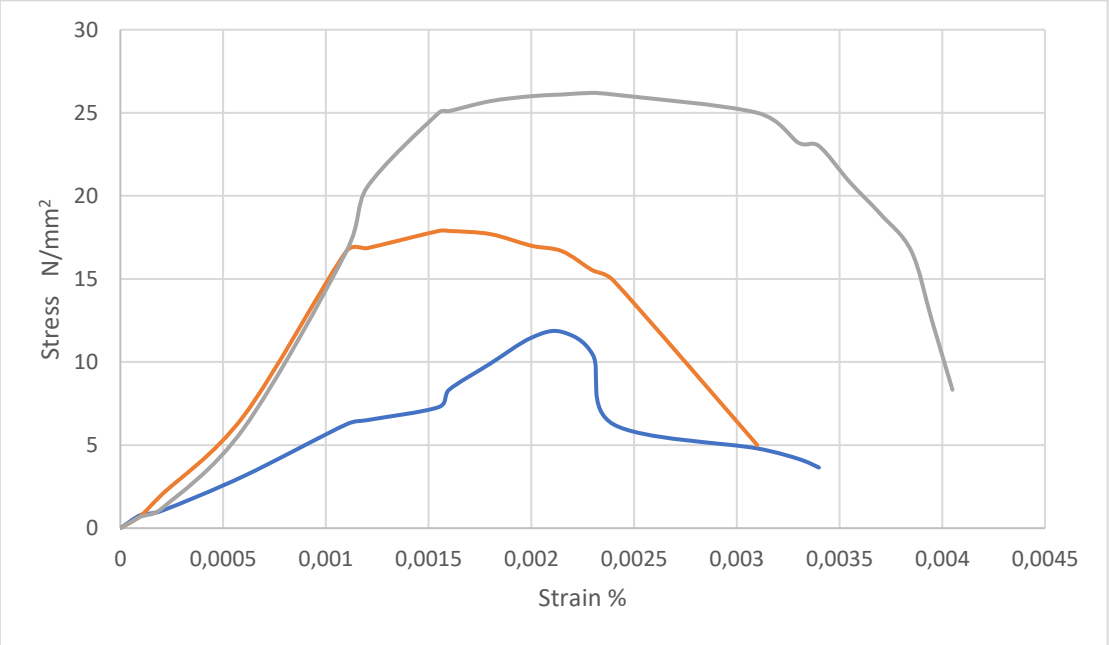

Figure 61: Comparative Stress Strain Diagram

3.4 Optical Microscopy

Microstructural observations at 400x magnification showed clear distinctions between the base material, HAZ, and stir zone. The base material retained its uniform equiaxed grains and fine Mg_2Si precipitates characteristic of the T6 condition. In the HAZ, grain size remained similar, but the precipitates experienced coarsening and partial dissolution due to exposure to temperatures approaching 340 °C. This transformation explains the pronounced softening recorded in this region.

The stir zone displayed refined, equiaxed grains produced by dynamic recrystallization, confirming effective plastic flow during tool rotation. However, despite grain refinement, the hardness did not recover to base-metal levels due to significant precipitate dissolution caused by the long dwell time and sustained heat input. The difference between both the zones can be observed in Fig. 12. Full

recrystallization and the formation of homogeneous equiaxed grains in the stir zone are generally achieved only at higher rotational speeds and longer dwell times than those applied in the present study. This suggests that the relatively coarse grains observed here result from the moderate heat input and the limited mechanical stirring due to limitations of manual milling machine [27,28].

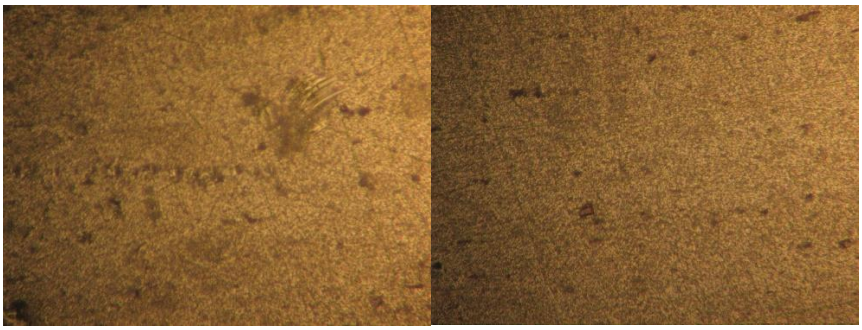

Figure 62: Optical Microstructures At 400× Magnification: Base Metal (Left) With The Original Grain Structure And The Stir Zone (Right) With Refined Grains

3.5 Summary of Results

The overall interpretation of visual, mechanical, and microstructural results shows that weld quality in 6061-T6 FSSW is controlled by heat input and material flow. The low flash and smooth surface in both pin tool and two-step welds indicate stable thermal conditions at 580 RPM. Softening in the SZ and HAZ is caused by precipitate dissolution. The grain refinement improves ductility but cannot compensate for the loss of precipitation hardening. The tensile strength comparison highlights how keyhole elimination (two-step) and optimized stirring (enhanced pin tool) significantly improve load-carrying ability by increasing bonded area and reducing stress concentrators. These findings agree with established FSSW behavior and confirm that optimal joint strength is achieved by balancing heat input, controlled stirring, and sufficient dwell time.

4. Conclusions

Several significant findings emerged from this investigation of friction stir spot welding in 6061-T6 aluminum alloy:

1. Substantial improvements in joint strength were achieved through parameter optimization. The tapered pin tool at 580 RPM, 1.5 mm shoulder penetration, 30–40 s dwell time, and 340°C produced joints with 1968 N strength. This represented a 122% increase compared to basic parameter sets.

2. The two-step methodology proved effective for keyhole defect elimination. Joints maintained strength at 1341 N while exhibiting improved surface characteristics.

3. The custom measurement system of the designed fixture successfully enabled real-time monitoring of force and temperature. Data acquisition confirmed that process temperatures reached the aluminum recrystallization range, which was determined to be necessary for proper joint formation.

4. Microstructural examination revealed substantial grain refinement in the stir zone. However, overall softening of the weld region was observed relative to base material properties due to dissolution of strengthening precipitates under thermal exposure.

5. Comparison with conventional fusion-based welding demonstrated that this friction-based methodology exhibited superior energy efficiency while avoiding typical defects such as porosity and solidification cracking. Results support the potential application of FSSW in lightweight structural manufacturing.

Future investigations could explore more sophisticated tool geometries, automated process control systems, or computational modeling approaches to further enhance weld consistency and mechanical performance.

5. Acknowledge

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Synthesis and Characterization of Silica Nanoparticles Through Chemical and Green Method for Gas Sensor Application

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ABSTRACT

This study focuses on the synthesis, characterization, and gas sensing application of silica nanoparticles for efficient ammonia gas detection at room temperature. The synthesized silica nanoparticles were incorporated with cerium oxide via a precipitation method to form silica modified ceria nanostructures, capitalizing on the high surface area and functional versatility of silica combined with the excellent redox properties of ceria. These nanostructures were subsequently used to fabricate a chemiresistive-type gas sensor. SEM analysis revealed a homogenous, porous structure suitable for gas adsorption, while EDS confirmed the presence of silica, cerium, and oxygen in appropriate ratios. The sensor demonstrated a clear, consistent response at room temperature, confirming the effective interaction between ammonia and the silica modified CeO_2 surface. The successful incorporation of an agricultural by-product for functional sensor fabrication highlights the potential of integrating green nanotechnology into practical environmental applications.

Keywords: Silica nanoparticles, silica modified cerium oxide, $Ce0_2$ nanostructures, ammonia gas sensor, gas sensing properties, sensor fabrication.

1.Introduction

Silica based nanoparticles are considered very effective as they possess unique properties, among them large surface area, tunable particle size, thermal stability and biocompatibility are most prominent (Nayl et al., 2022). All these makes these nano particles very versatile towards many applications like sensor technology, drug delivery, remediation of environmental pollutants and catalysis. The unique surface chemistry has enabled silica nanoparticles to enhance their sensitivities and specificity towards diverse analytics thereby ensuring some of the more promising applications to be sensors. Conventional methods used for synthesizing these silica bases nanoparticles mainly involve chemical process, which results in controlled particle size and morphology. However, these processes have major environmental implications due to the use of different frequently used chemicals and procedures that requires high energy usage.

To address these challenges green synthesis approaches have gained a lot of momentum. In this context, sugarcane bagasse, which is an agricultural waste product, has been found particularly promising, given its high silica content and its abundance. The integration of green synthesis with traditional chemical methods thus offers a great way to synthesize environmentally friendly and cost-effective silica nanoparticles while not losing their desirable properties (Shafiei et al., 2021). In this project, a dual route of preparing silica nanoparticles would be developed: one is via the chemical synthesis route through sodium silicate and the other one is by the green synthesis route using sugarcane bagasse. The characterization of the resulting nanoparticles and assessment of their suitability for sensor applications are goals toward advancements in sustainable nanotechnology and critical need in the realm of sensors.

In addition to this, silica modified CeO_2 nanostructure are considered as a hybrid approach to refine sensor performance. This is because cerium oxide nanostructures are known for their excellent redox behavior and catalytic activity making them an excellent choice for sensing materials. However, when we combine them with silica nanoparticles it further increases structural stability and improves the porosity that allows for better diffusion of gas molecules (Wang et al., 2018). In this way the sensors exhibit faster electron response that leads to lower detection limits when sensing gases like NH_3. Additionally, SiO_2 fine tunes the electronic properties of cerium oxide, which improves the performance of sensors by operating at even lower operating temperatures. This will increase the sensor's energy efficiency and extends the senor's life span. By leveraging the combined benefit of cerium oxide's catalytic and silica oxide's structural properties, the sensor represents a promising gas sensor with superior stability and performance.

2. Materials and Method

2.1. Materials

The chemicals used for preparation of silica nanoparticles through chemical and green method are sodium silicate, hydrochloric acid, distilled water, silver nitrate, sugarcane bagasse, ethanol, nitric acid, and sodium hydroxide.

2.2. Method

2.2.1 Chemical Synthesis of Silica Nanoparticles

A cloudy, viscous gel was produced by adding diluted sodium silicate drop-wise (at a rate of approximately two drops per second) to 28 milliliters of 2.5% hydrochloric acid while stirring at a speed of 250 revolutions per minute at a temperature of 60°. 10 mm was the amount of sodium silicate that was recorded. It then underwent several cycles of distilled water washing until it was totally devoid of Cl- ions. To determine whether Cl- ions were successfully removed, a solution of diluted silver nitrate was added to the filtrate. When the precipitates white in color were formed, they served as evidence of its presence of Cl ions. Until there was no longer any white precipitate formed because of the addition of silver nitrate, this test was repeated. The product was then air calcinated at 1000°C for one hour after drying at 100°C for twenty-four hours. After washing of gel as it undergoes drying, where the remaining water is removed and amorphous silica transitions towards a more crystallized form. This step finally produces silica nanoparticles with enhanced mechanical and thermal properties.

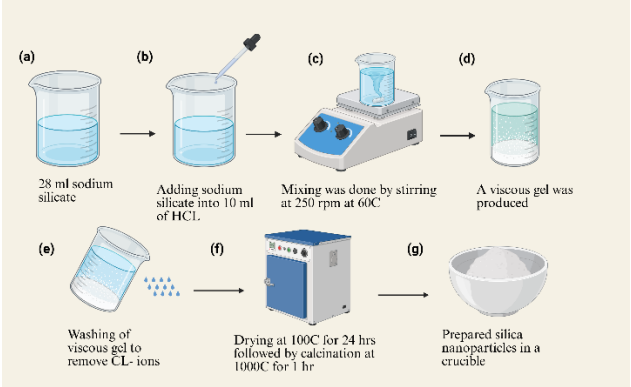

Figure 63 (a) 28 ml of sodium silicate in beaker, (b) addition of sodium silicate into 10 ml of HCL, (c) mixing, (d) viscous gel production, (f) removal of CL- ions, (f) drying, (g) prepared silica nanoparticles

2.2.2 Green Synthesis of Silica Nanoparticles

Overnight in the lack of sunlight, the sugarcane bagasse dried. It then spent 24 hours submerged in distilled water, washed in distilled water to remove contaminants, and finally dried in an oven set at 90°C. To extract metallic pollutants from the sugarcane bagasse, a 1N HCl solution was added to the sample. This combination was kept in a water bath set at 75°C. After filtering and many times washing to remove any last metallic ions, the sugarcane bagasse sample was dried at 90°C. To extract silica and produce sodium silicate, the bagasse was placed in 1 Molar NaoH solution and was heated in water bath at 90°C for 1 hour. Sodium silicate solution was then filtered which removes the bagasse, and the solution was stirred for about 1 hour. Drop by drop nitric acid was added during the precipitation process until the PH dropped to 8.20 ml; ethanol then was added to the solution. The mixture was constantly swirled for 45 minutes then centrifuged at 4000 rpm to generate precipitate. The ready sample was next repeatedly cleaned with distilled water. To get silica nanoparticles, the precipitates were then gathered and fired in a furnace at 600°C for half an hour.

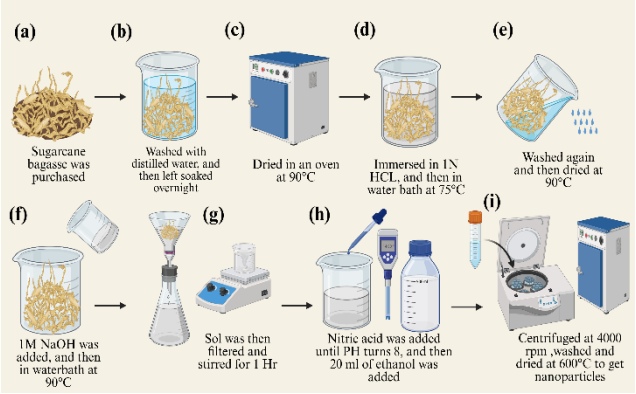

Figure 64 (a) Sugarcane bagasse, (b) washing, (c) drying at 90C, (d) immersed in HCL, (e) washing again, (f) addition of NaOH, (g) filtering of solution, (h) addition of nitric acid, (i) centrifuged to obtain nanoparticles

2.2.3 Formation of Silica Modified CeO_2 Nanostructures

Firstly, about 6 gm of silica nanoparticles are added into 100 ml of distilled water in a beaker, it is then ultrasonicated for 30 minutes to ensure proper uniform dispersion. In a separate beaker dissolve 2.17 gm of cerium nitrate ($Ce(NO_3)_3.6H_2O$) into 50 ml of distilled water. Now the cerium nitrate solution was slowly added to SiO_2 dispersion under stirring. After stirring for 15 minutes, ammonium hydroxide (NH_4OH) is added dropwise until the pH reaches to 10-11. The solution was then heated at 80°C for 2 hours on continuous stirring, as this will allow the CeO_2 to be coated on silica nanoparticles. After stirring, the solution was centrifuged at 10,000 rpm for 10 minutes to collect the CeO_2-SiO_2 composite. Washing was done using distilled water, after that it was dried at 80°C for 12 hours in a drying oven. This will result in forming silica modified ceria base nanostructure or also known as CeO_2-SiO_2 composite.

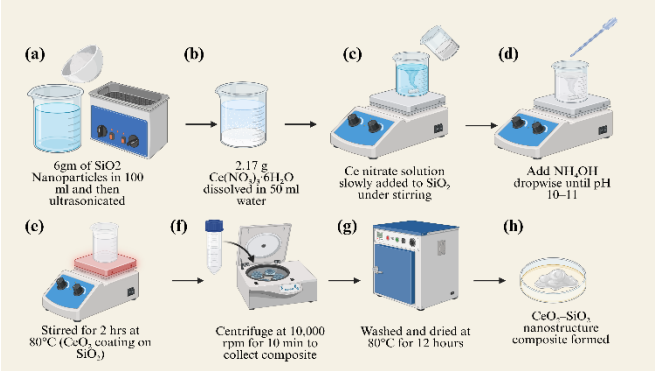

Figure 65 (a) 6 gm of SiO_2 nanoparticles in 100ml then ultrasonicated, (b) cerium nitrate dissolved in water, (c) stirring of solution, (d) addition of NH_4OH, (e) coating on nanoparticles, (f) centrifuge to collect composite, (g) washing and drying, (h) formation of CeO_2-SiO_2 nanostructures

2.2.4 Fabrication of Gas Sensor Using Silica Modified CeO_2 Nanostructures

First substrate that is glass plate is sonicated using ethanol and acetone separately for 10 minutes each, followed by drying at 90℃. Gold is used for electrodes as a thin conductive layer to enhance charge transfer, we have used the firing method for gold deposition in which first a thin conductive seed layer (silver paste) is applied on the glass plate. Then gold is applied over it, and it is allowed to dry in drying oven at 90℃ to solidify the gold contact. Here ceria modified silica nanoparticles serves as the sensing material as it offers high surface area. To form a paste that is applied on the substrate first dissolve PVA in ethanol under stirring to create a uniform polymer solution. Then, the silica-CeO_2 composite powder is gradually added to the PVA-ethanol solution on continuous stirring that ensures even distribution of composite particles with liquid medium. In the mixture, more PVA is added to reach the required viscosity. In this process PVA acts as the binder, which means it helps hold the composite particles together and ethanol acts as solvent, which dissolves the PVA and particles to form a homogenous, spreadable paste. The paste is then applied over the surface of the substrate where platinum wires were attached on gold electrodes. This paste was covered over the substrate to guarantee good contact. After application of the paste, ethanol evaporates leaving behind a strong PVA bound silica-ceria composite. Curing is then done by drying it at 400°C for 2 hours. This promotes nanoparticles adhesion and enhances film stability. The sensor is then mounted inside an airtight chamber, ensuring the electrodes in the form of wires are accessible outside the chamber with sealed ports. The sensor is then connected to Keithley's source meter. Initially a bias voltage is recorded that acts as reference, and then ammonia is introduced into the chamber in form of ammonia solution, which is placed inside to measure the change in voltage and observe the sensor response.

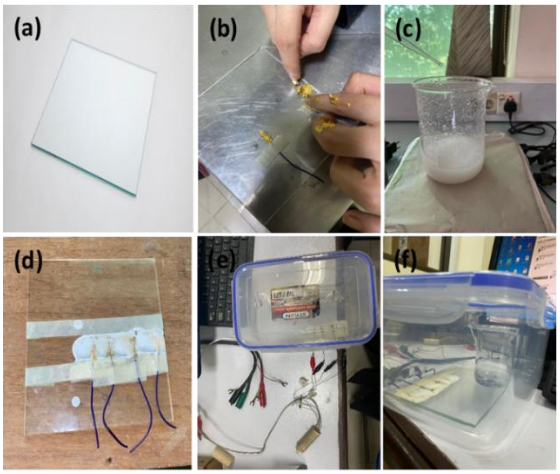

Figure 66 (a) Glass substrate, (b) applying silver paste and then gold paste, (c) dissolving PVA into ethanol, (d) mounting sensor in airtight chamber, (e) introduction of ammonia, (f) sensor response was recorded.

2.2.5 Measuring Sensor Response

By assessing the electrical response to ammonia gas (NH_3) in a room setting, the sensing behavior of the manufactured sensor was determined. The prepared sensor device was installed inside an airtight, sealed chamber. It is made up of silica-modified ceria nanostructures coated on a glass substrate with gold electrodes. Platinum wires were connected electrically using gold electrodes, enabling external interface with a Keithley source meter for accurate resistance readings.

Initially, the sensor was exposed to ambient air inside the chamber, and its baseline resistance (Ra) was noted at room temperature. This resistance value determines the electrical response of sensor when it is surrounded by clean air, where the oxygen molecules adsorb onto the sensor surface and forms an electron depletion layer.

Then, in the form of ammonia solution, a regulated volume of ammonia gas was added to the chamber. The volatile NH_3 gas then interacts with the sensor's surface, changing its electrical resistance because of ammonia molecules reacting with the oxygen species that were previously detected on the sensor's surface. Up until fifteen minutes, the sensor's real-time resistance in the presence of ammonia (Rgas) was continuously measured every five minutes.

The gas sensing response was calculated based on the widely accepted chemiresistive formula. The working voltage was set as 5 volts. The gas response formula is as:

$$\text{Gas response} = R_{air} - R_{gas} / R_{gas} * 100$$

where the electrical resistance of NH_3 and air are denoted by Rgas and Rair, respectively. The redox process between molecules of ammonia and chemisorbed oxygen was predicted to cause a notable decrease in resistance by exposure to NH_3. The level of sensitivity and stability of the sensor at room temperature were evaluated by recording and analyzing the sensor response values.

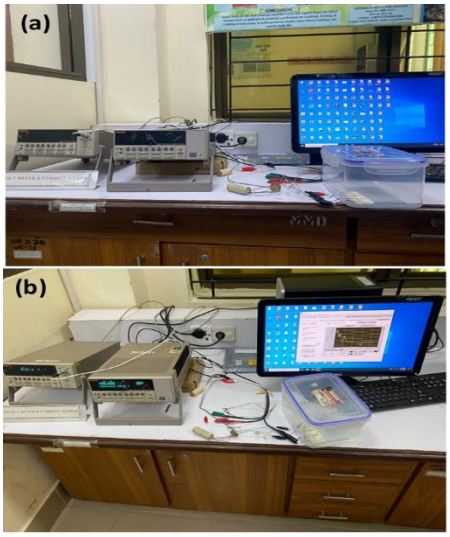

Figure 67 (a) Complete setup for measuring gas response, (b) recording sensor response

3. Results and Discussion

3.1. SEM Analysis

The SEM images of our sample reveal a morphology that is dominated by elongated, rod like grains, which forms continuous and porous channels in between (Tian et al., 2015). This rod morphology indicates the formation of silica-ceria nanostructures. It is noted that it shows the growth of ceria over the prefabricated silica nanoparticles, where ceria doesn't form isolated nanoparticles instead it grows into larger units.

Comparing with literature shows that our SEM micrographs observe a densely intergrown film made of elongated silica-ceria grains. The research (Kitsou et al., 2019) shows fabricated core shell structures formed when silica is combined with ceria in form of silica-ceria nanostructures, where the SEM images confirmed smooth particles, showcasing the effectiveness of silica as a template for uniform ceria deposition. However, our sample also observes fractured morphology due to thermal history(Pandey et al., 2017). The reference studies(Newbury* & Ritchie, 2013) also reveal the similar rod like CeO_2 structures fabricated, which identifies that ceria can produce nanorod structures when synthesized through controlled precursor chemistry.

Additionally, elongated rod like structures or flake like CeO_2 grains provide large surface area and active sites as compared to bulk or spherical particles(Akbari-Saatlu et al., 2020). This means that larger surface area promotes exposed active sites for gas molecules to adsorb and improves the sensitivity of the sensor.

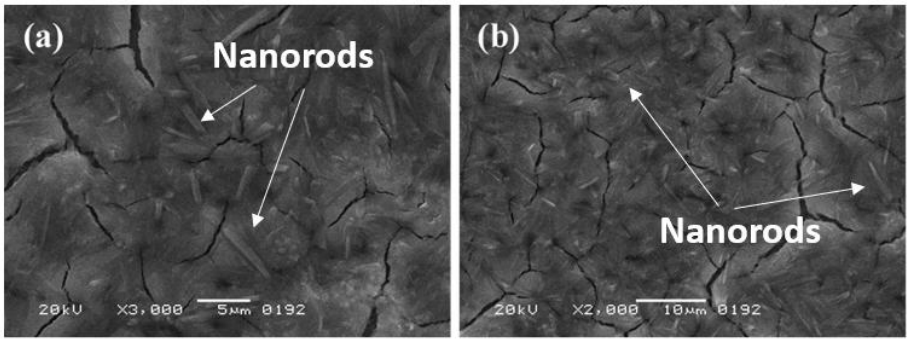

Figure 6 SEM results of silica modified ceria nanostructure, (a) shows magnification at 3000x, (b) shows magnification at 2000x

3.2. EDS Analysis

The EDS analysis shows the presence of three primary elements found in the sample that are oxygen (O), silicon (Si), and Cerium (Ce), which corresponds to their respective oxides, SiO_2 and CeO_2. The results revealed that the synthesized nanostructures contain 50.23 wt% of oxygen, 42.67 wt% of silicon and 7.10 wt% of cerium. The high content of silica present shows that the nanocomposite is predominantly rich in silica where ceria is coated onto the silica matrix (Vaizoğullar et al., 2016). This structural arrangement is beneficial for gas sensing properties of the nanocomposite as it allows high surface area due to high silica content, while the surface dispersed cerium oxide particles act as active sensing sites. Here the presence of oxygen further provided the confirmation of oxidation due to silicon oxide and ceria oxide phases within the sample.

Comparing the results, we observed that the core shell structure of SiO_2 and CeO_2 nanoparticles often observe this phenomenon, having silica rich composition, where Ce acts as coating on silica shell(Vos et al., 2014). It also revealed that such type of elemental composition is useful for enhanced selectivity.

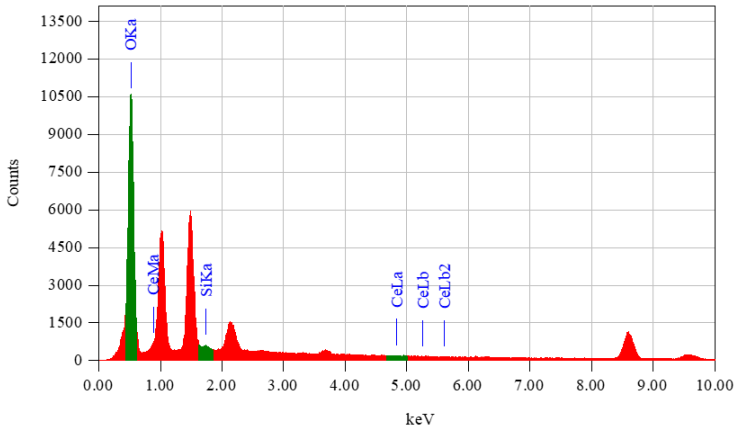

Figure 7 EDS pattern of silica modified ceria nanostructure

3.3. Measuring Gas Response of Sensor

The Chemi resistive sensing principle, which is typical of these kinds of gas sensors, is what drives the gas sensing function of the manufactured sensor based on silica-modified ceria nanostructures. Here, the electrical resistivity of the sensor's material when exposed to ammonia gas over varying time periods is used to measure the sensor response.

The oxygen molecules in clean air are adsorbed onto the CeO2 nanostructures' surface, which pulls free electrons out of the material's conduction band. As a result, oxygen species such as O_2^-, O^-, and O^{2-} are formed. The extraction of the electrons by these oxygen species creates an electron depletion layer (EDL), that increases the materials resistance (Jang et al., 2013). This provides the initial resistance Rair under atmospheric conditions.

3.3.1 Sensor gas response at 0 minutes

The electrical resistivity of the sensor significantly drops once the NH3 gas is introduced into the chamber, but it returns to its initial state when the gas is expelled. The response of gas sensor when NH_3 was introduced is shown in figure 35. Figure 35 shows that molecules in the ammonia gas react with the adsorbed oxygen ions that accumulate on the surface when the ammonia gas is introduced, which functions as a reducing gas. The following is the surface reaction that takes place:

$$NH_{3(ads)} + 3O2^-_{(ads)} \rightarrow 2N_2 + 6H_2O + 3e^-$$

The gas response curve recorded at 0 minutes demonstrates a sharp rise in % gas response immediately upon exposure to ammonia gas, peaking at 630-650% within the first second. This behavior reflects an extremely rapid adsorption of NH_3 molecules onto the sensor surface, that is a characteristic of high sensitivity gas sensors (Wang et al., 2017).

This trend is also observed in the research (Tang et al., 2006), reporting a response of over 1000%, along with sub second rise time. It is then noted that after the initial peak, the % response declines gradually over the next several seconds. This indicates the recovery or saturation phase. The small secondary bump around 5-6 seconds likely reflects multi step adsorption dynamics. By 10 s the response has leveled off around 390-400%.

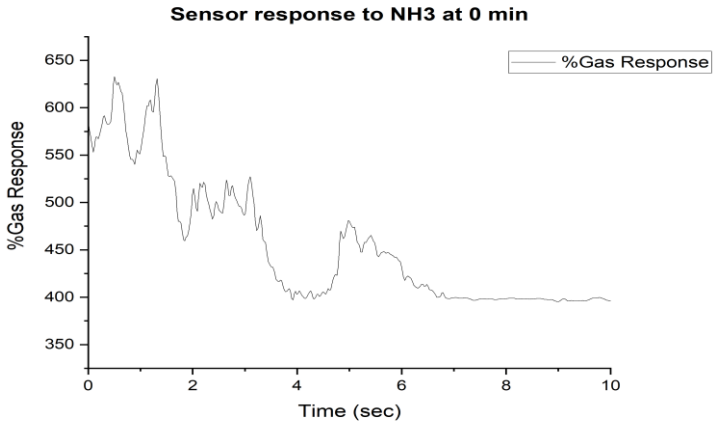

Figure 8 Sensor response to ammonia at 0 minutes

3.3.2 Sensor gas response at 5 minutes

After noting the gas response at 0 mins, the next response was measured at 5 mins. At 5 mins of constant NH_3 exposure the sensor demonstrates a distinct and well-defined dynamic response, which highlights its sensitivity and surface interaction kinetics. The figure 36, which shows the gas response at 5 mins which also display a rapid initial rise, reaching a peak of 450% within the first 1-2 seconds. This sharp increase relates to the swift adsorption of NH_3 molecules onto the sensor surface which yields a high transient response, that is typical of such gas sensors (Choi et al., 2010). The jump is driven by ammonia reacting with the pre-adsorbed oxygen species on CeO_2.

From figure 36, it is also observed that around 15 s the signal drops abruptly to 375%. After the decline the signal recovers to 395% then falls to 370% by 25s. This behavior suggests the sensor is desorbing the ammonia gas.

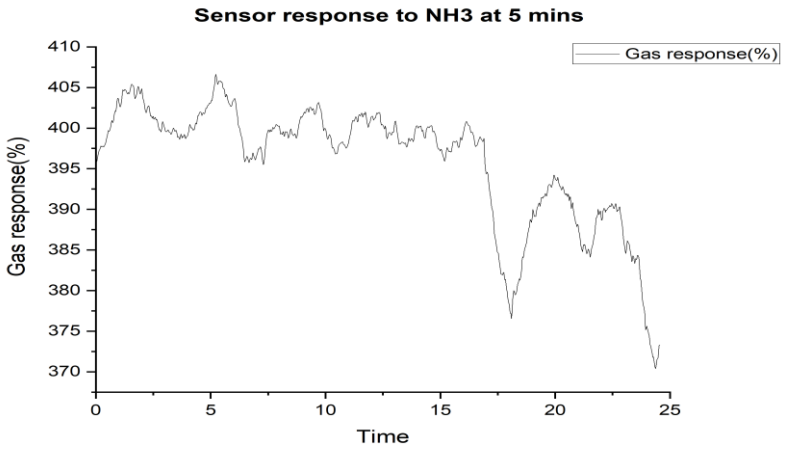

Figure 9 gas response of sensor at 5 mins

3.3.3 Sensor gas response at 10 minutes

At 10 mins of continuous ammonia exposure the gas response was again measured, the sensor response shows notable evolution in behavior compared to earlier stages, reflecting the effect of prolonged gas sensor interaction on the silica modified ceria surface. As shown in the response curve in figure 37, the signal exhibits a sharp rise peaking rapidly to 710 % within the first few seconds. This surge surpasses the initial and 5-minute responses indicating a progressive enhancement in sensitivity that is due to deeper surface activation and increased ammonia diffusion into porous regions. This identifies that extended exposure time activates more surface sites for the sensor.

Following the peak, the curve enters a fluctuating plateau, where the response oscillates between 660 to 700% from around 3 to 15 seconds. This behavior suggests that system is in a dynamic equilibrium, characterized by the simultaneous processes of ammonia adsorption and reaction with surface oxygen ions. The oscillations likely arise from a combination of gas diffusion and the porous nanostructure (Tong et al., 2017). As the curve progressed beyond 15 seconds, a gradual decline in signal is observed falling to approximately 610% by 25 seconds. This decrease while maintaining a high relative response compared to earlier time points suggest that the onset of surface saturation is due to prolonged ammonia exposure.

This 10-minute profile highlights a time dependent evolution of the sensor gas response, showcasing a transition from initial high sensitivity to a dynamic state regime. Such behavior has been reported in literature for other high surface area metal oxide sensors, where extended exposure leads to delayed saturation, enhanced charged starts transfer kinetics (Sun et al., 2012). And activation of previously inaccessible adsorption sites.

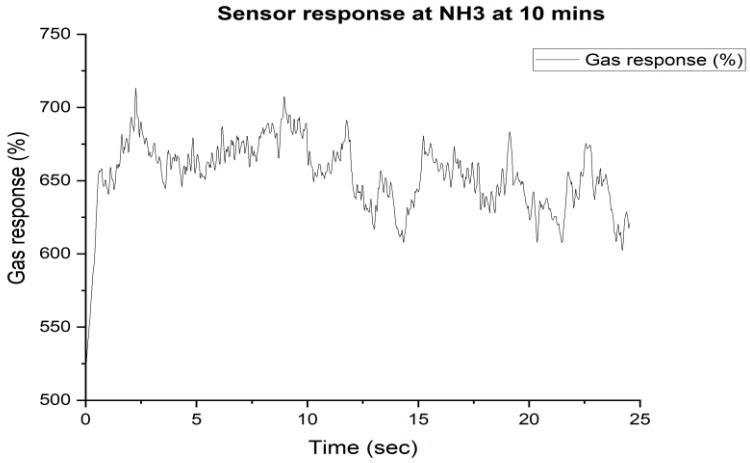

Figure 10 Sensor response to ammonia at 10 minutes

3.3.4 Sensor gas response at 15 minutes

At the 15-minute mark of uninterrupted ammonia exposure, the sensor exhibits a significant deviation from its earlier behavior. Initially, the sensor demonstrated a positive response for 0, 5 and 10 minutes, characterized by a decrease in resistance upon ammonia exposure due to the reaction;

$$NH_3(ads) + 3O_2{-}(ads) \rightarrow 2N_2 + 6H_2O + 3e{-}$$

By increasing the number of free electrons, this action lowers the resistance of the sensor. However, after prolonged exposure, the sensor response not only diminishes but also transitions into negative values, indicating an anomalous behavior. This identifies that the sensor surfaces become saturated with ammonia molecules, leading to a reduction in available active sites or further reaction.

The response at 15 minutes in figure 38 shows a decline into negative values suggesting a potential reversal degradation in sensor behavior that is due to prolonged exposure. The percent gas response begins near 0% and then drops steadily to around -2% to -3% within the 1st 10 seconds. The relatively flat profile is observed from 3-15 seconds, which could indicate that most of the absorption sites are fully saturated which is due to irreversible binding of ammonia.

Notably, after 15 seconds, the curve exhibits a sharp and continuous decline in gas response, reaching approximately -11% by 25 seconds, this negative response trend may arise from inversion in the conduction view of their material such as excessive electron accumulation that shifts the sensor's baseline or alter the dominant surface reaction pathway. This behavior at 15 minutes is consistent with findings reported in(Mei et al., 2024) that shows, prolonged exposure to reducing gases such as ammonia often results in signal saturation. For instance (Takte et al., 2023), reported that extended exposure times led to the formation of ammonia like surface residues that altered the electronic structure of ceria-based sensors reducing the availability of active oxygen species for subsequent reactions.

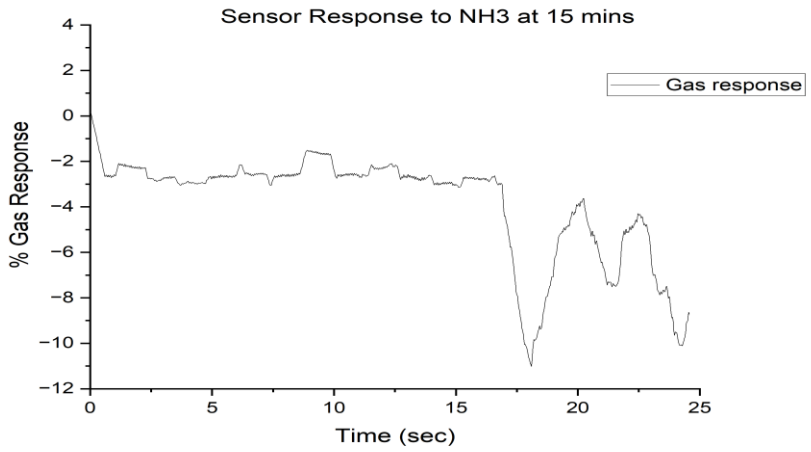

Figure 11 Sensor response to ammonia at 15 minutes

4. Conclusion

This research successfully illustrates the synthesis, characterization, and utilization of silica nanoparticles made using both chemical and green synthesis techniques. The nanoparticles are integrated into silica modified ceria nanostructures for gas sensing applications, specifically room temperature ammonia detection. The research addressed critical concerns of sustainable nanomaterial synthesis and showcased the potential of environmentally friendly route using agricultural waste, such as sugarcane bagasse, for producing valuable nanomaterials without compromising performance. The fabricated gas sensor incorporated silica modified ceria nanostructures as the active sensing layer. The SEM analysis revealed dense rod like microstructure, which facilitates the gas adsorption pathways which are required for achieving accurate and highly sensitive responses. The EDS analysis also further confirms the successful incorporation of silica and ceria elements.

This work thus, successfully demonstrated the feasibility and advantages of combining green nanotechnology to produce high performance gas sensors. The incorporation of silica modified ceria nanostructures as active sensing layers achieved efficient, sensitive and stable detection of ammonia gas, making them promising candidate for future environmental monitoring systems. The project aligns with global sustainable development goals by promoting ways to wealth technology, reducing environmental hazards, and advancing green material science.

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Investigation of Porous Glass Formation Using Waste Glass and Calcium-Based Additives via Sintering

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ABSTRACT

This study explores the potential for producing porous glass materials using Güral glass cullet as the primary raw material and CaO and $CaCO_3$ as functional additives. Glass particles of varying sizes (250 µm, 500 µm, and 1 mm) were mixed with calcium-based additives at different concentrations. Although the original experimental design considered 30%, 40%, and 50% additive ratios, no porous structure formation was observed at these levels. Therefore, the study was revised to test lower additive contents of 5%, 15%, and 20%. The mixtures were sintered at 950 °C without using any binders.

The influence of both particle size and additive content on porosity development was systematically examined. Results demonstrated that increasing both the particle size of the glass and the percentage of additives enhanced the porosity of the final product. The homogenized mixtures were shaped and loaded into custom molds made of “Crom-350” grade refractory material, which withstands temperatures up to 1050 °C.

The findings highlight that the combination of additive concentration and particle size plays a crucial role in tailoring the pore structure of sintered glass. This approach presents a promising route for valorizing glass waste in the fabrication of porous materials suitable for filtration, insulation, or lightweight structural applications.

Keywords: Porous glass, Waste glass recycling, CaO, $CaCO_3$, Sintering.

1. Introduction

Glass is traditionally defined as an inorganic product of fusion which has cooled to a rigid condition without crystallizing. It is composed primarily of supercooled alkali and alkaline earth metal oxides that solidify while maintaining their amorphous and disordered atomic structure characteristic of the molten state. Due to its chemical stability and physical properties, glass has been a fundamental material for human civilization for millennia [1]. However, with the rapid industrialization and increased consumption in recent decades, the accumulation of glass waste has become a significant environmental challenge. Since glass is non-biodegradable, finding sustainable routes for the valorization of industrial and post-consumer glass waste (cullet) is of paramount importance for the circular economy [2].

Today, the utilization of glass is shifting beyond its traditional transparent applications—such as beverage bottles, windows, or containers—towards more functional forms. Among these, "porous glass," also

known as cellular glass or foam glass, is gaining increasing widespread attention [3]. Unlike bulk glass, porous glass is a lightweight material characterized by a unique cellular structure containing a large volume of pores. This structural configuration endows the material with superior properties, including low density, high thermal and acoustic insulation, non-flammability, and chemical inertness. Consequently, it serves as an excellent insulation material in the construction, chemical, and energy industries, offering a high-value alternative to polymeric insulators. The fundamental mechanism for porous glass production is based on the powder technology method, specifically the sintering of glass powders mixed with a gas-forming (foaming) agent [4]. The process relies on the delicate match between the softening temperature of the glass particles and the decomposition temperature of the foaming agent. As the glass viscosity decreases and softens during heat treatment, the foaming agent decomposes and releases gases. These gases are trapped within the viscous glass melt, expanding to create a porous, cellular structure. If the viscosity is too low, the gas escapes, leading to structural collapse; if too high, the expansion is restricted. Therefore, controlling the sintering parameters is critical for tailoring the pore morphology [5].

In this study, Calcium Oxide (CaO) and Calcium Carbonate ($CaCO_3$) were selected as functional additives. While CaO acts primarily as a stabilizer to modify the chemical durability and viscosity of the glass network, $CaCO_3$ serves a dual purpose. It acts as a potent pore-forming agent by releasing carbon dioxide (CO_2) gas from the structure during heat treatment through the calcination reaction ($CaCO_3$ -> CaO + CO_2). The released CO_2 generates the porosity, while the residual CaO is incorporated into the glass matrix, further stabilizing the final product [6]. The primary aim of this study is two-fold: firstly, to recycle industrial waste glass cullet into the economy by converting it into a value-added porous material, thereby reducing environmental pollution and landfill usage. Secondly, the study aims to microstructurally investigate the influence of critical processing parameters—specifically different glass grain sizes and varying additive ratios—on the porosity, pore size distribution, and general morphology of the final sintered product. By optimizing these parameters, it is possible to tailor the properties of porous glass for specific insulation or filtration applications.

2. Materials and Method

The experimental stages of this study were carried out under four main headings: raw material procurement and preparation, mixture formation, shaping, and sintering. The general flow of the experimental program is schematized in Figure 1.

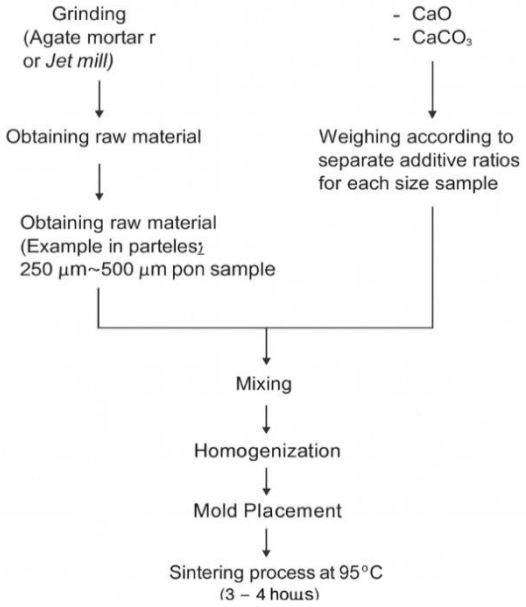

Figure 1. Experiment flow plan

2.1. Supply and Preparation of Raw Materials

Industrial waste glass cullet obtained from the Kütahya Güral Glass Factory was used as the main matrix material in the study. Analytical grade calcium oxide (CaO) and calcium carbonate $CaCO_3$ were used as the pore-forming agent and stabilizer.

The supplied waste glass cullet was first cleaned of coarse impurities and dried. It was then ground using an agate mortar and vibrating/jet mill to reduce it to the desired particle size. The ground glass powder was sieved using a standard sieve series and separated into three different particle size groups for use in the experiments.

Fine Grain Group: <250 μm.

Medium Grain Group: 500 μm.

Coarse Grain Group: 1 mm.

2.2. Experimental Design and Sample Preparation

In experimental studies, a systematic matrix was created to examine the effects of glass particle size and additive ratio on porosity. Initially, additive ratios of 30%, 40%, and 50% were tested based on literature data. However, the experimental set was revised because structural integrity was not achieved in pre-sintering tests performed at these ratios.

In the final experimental design, additive ratios were determined as 5%, 15%, and 20% by weight. 8888 Each sample was weighed using a precision balance to achieve a total weight of 200 grams. The prepared mixture recipes are detailed below:

5% Additive Series: 190 g cullet + 10 g CaO + $CaCO_3$.

15% Additive Series: 170 g cullet + 30 g CaO + $CaCO_3$.

20% Additive Series: 160 g Glass Cullet + 40 g CaO + $CaCO_3$.

The weighed powders were mixed by mechanical shaking in a plastic beaker until a homogeneous distribution was achieved.12 No organic or inorganic binder was used in the mixtures, and the aim was to bind the glass with its own viscous flow during sintering.

2.3. Shaping and Sintering Process

The homogenized powder mixtures were placed using the free-casting method in specially selected "Crom-350" quality stainless steel/refractory molds resistant to 1050°C to prevent deformation and glass reaction at the sintering temperature.

The molded samples were heat-treated in a laboratory-type electric furnace under a controlled atmosphere. The sintering temperature was set at a constant 950°C, and the samples were baked at this temperature for 3 to 4 hours. This time was optimized to allow the decomposition of $CaCO_3$ to release CO_2 gas, allowing the softened glass matrix to trap this gas and create a porous structure. After sintering, the samples were allowed to cool slowly to room temperature in the furnace.

2.4. Characterization

The surface morphology and pore structures of the produced porous glass samples were examined using a 50X optical microscope. The distribution, size, and interconnection of pores (open/closed porosity) were visually analyzed to determine the effects of grain size and additive ratio on the microstructure.

3. Results and Discussion

In this section, microstructure images and analysis results of samples produced with different grain sizes (250 µm, 500 µm, 1 mm) and different additive ratios (5%, 15%, 20%) are presented.

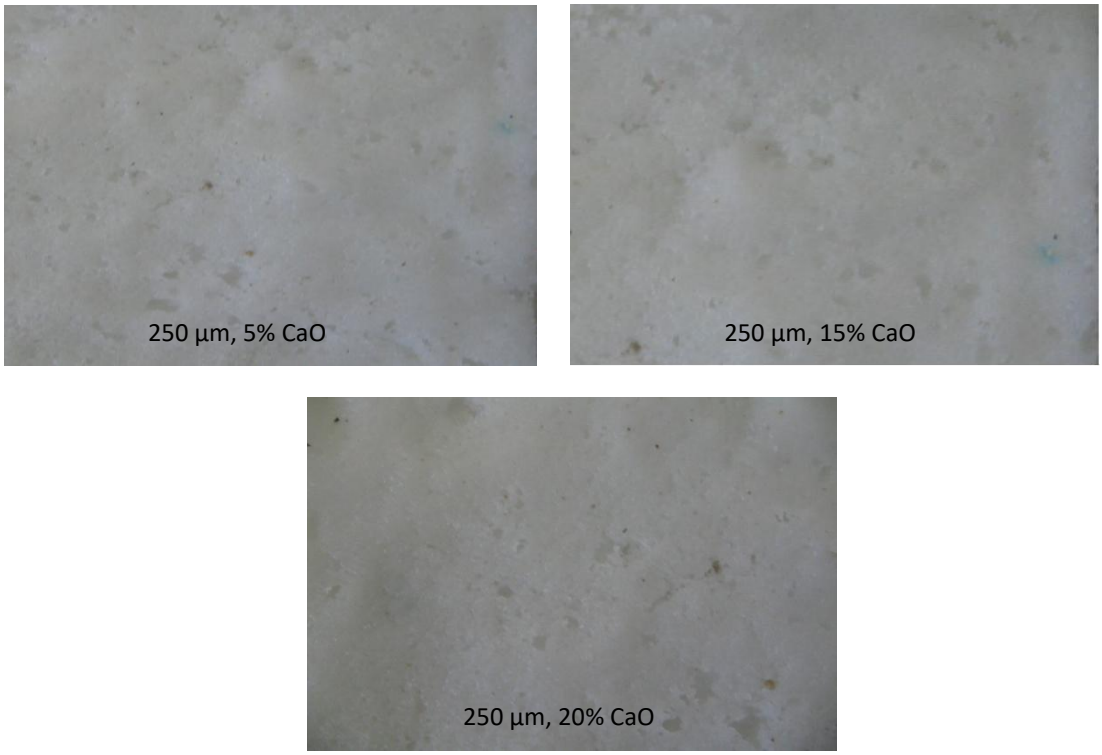

*Figure 2. Image of samples (*250 µm sized glass)

The microstructures obtained with 250 µm glass particles show a relatively homogeneous and compact surface morphology in Fig.2. At 5% CaO, the texture appears smooth with minimal porosity, indicating efficient particle packing and good sintering behavior. Increasing the CaO content to 15% and 20% leads to slightly more visible pores and localized agglomerations. This suggests that higher CaO ratios promote partial melting or uneven diffusion, which in turn creates microvoids and heterogeneities. Overall, the finest particle size exhibits the most uniform microstructure among all groups.

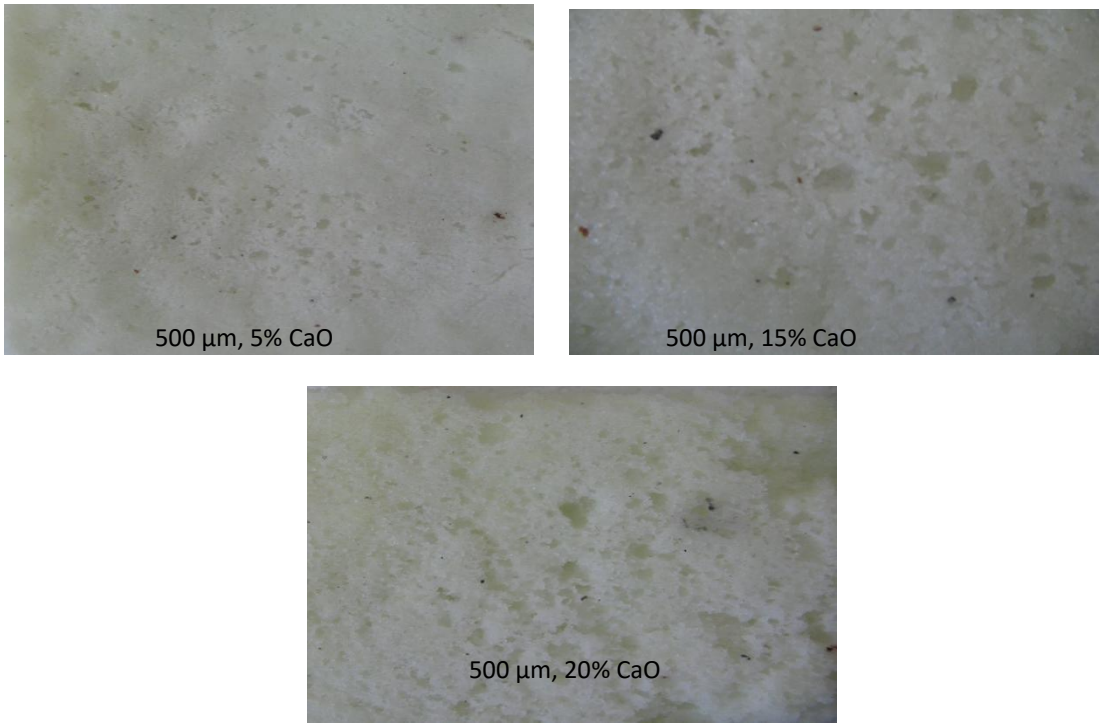

Figure 3. Image of samples (500 µm sized glass)

In Fig 23, for samples produced with 500 µm particles, a noticeable increase in surface roughness and porosity is observed compared to the 250 µm group. At **5% CaO**, the surface shows larger, more irregular voids due to the reduced packing efficiency of coarser particles. With **15% CaO**, the microstructure becomes more granular, and pore distribution becomes more apparent. In the **20% CaO** sample, the extent of porosity and surface irregularity is further enhanced, indicating that the combined effect of larger grain size and higher CaO content reduces densification and promotes microcrack formation. These images demonstrate that as particle size increases, structural uniformity decreases.

The samples containing 1 mm glass particles exhibit the most porous and heterogeneous microstructures in Fig. 4. At 5% CaO, the surface displays large voids and weakly bonded regions, characteristic of inadequate sintering among coarse particles. The 15% CaO addition results in even more pronounced surface irregularities, with visible gaps and non-uniform melting regions. At 20% CaO, the microstructure becomes highly discontinuous, suggesting that excessive CaO further disrupts the bonding between large particles and leads to significant surface deformation. These findings confirm that coarser particle sizes contribute to poor densification and increased defect formation during processing.

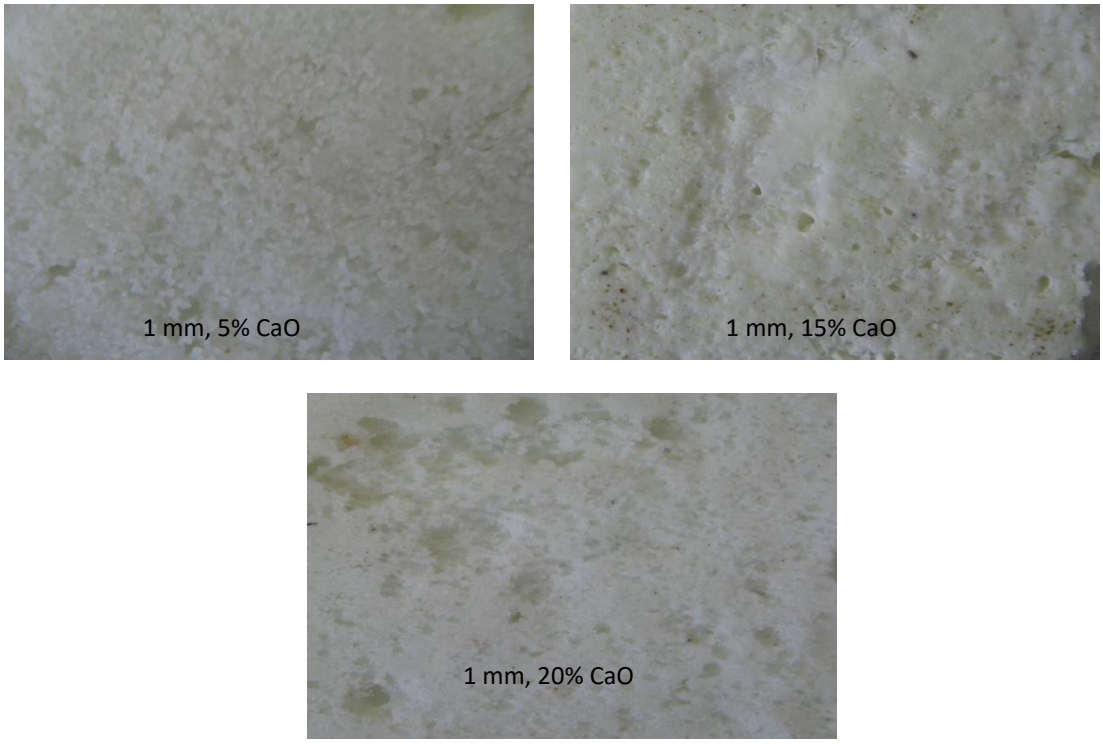

Figure 4. Image of samples (1 mm sized glass)

4. Conclusions

The microstructure analysis of samples produced with different glass particle sizes (250 µm, 500 µm, and 1 mm) and varying CaO additive ratios (5%, 15%, 20%) demonstrates that particle size and additive content play critical roles in determining the surface morphology and densification behavior of the composites. The samples prepared with 250 µm particles exhibited the most homogeneous and densely packed microstructures, indicating efficient sintering and minimal defect formation. As the particle size increased to 500 µm and 1 mm, the surfaces became progressively more porous and heterogeneous due to reduced packing efficiency and incomplete bonding between coarse particles.

Additionally, increasing the CaO addition consistently led to greater surface roughness, pore formation, and local agglomeration across all particle sizes. This trend suggests that higher CaO content modifies the melting characteristics and diffusion processes, resulting in uneven densification. Overall, the findings highlight that smaller particle sizes and lower CaO ratios are more favorable for achieving uniform and well-densified surfaces, while coarse particles combined with high CaO amounts can significantly degrade microstructural integrity.

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Utilization of Granite Cutting Waste in Ceramic Glaze Compositions: An Experimental Approach to Waste Valorization

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ABSTRACT

This study explores the potential use of granite cutting waste (GCW) as a functional raw material in ceramic glaze formulations. Granite waste, which poses significant environmental and storage challenges due to its high volume and fine particle size, was evaluated for its compatibility and performance within traditional ceramic glaze systems. Granite cutting waste was first dried and milled to a fine powder before being incorporated into glaze compositions at varying ratios. The mixtures were applied onto biscuit-fired ceramic tiles and subjected to a second firing. Visual, physical, and surface characteristics of the resulting glazed surfaces were analyzed, including color, gloss, surface smoothness, and adhesion behavior. The results indicate that granite waste can successfully replace part of the traditional raw materials in ceramic glaze recipes without compromising visual quality or performance. Moreover, the use of GCW contributes to sustainability in the ceramic industry by reducing dependency on virgin raw materials and minimizing waste accumulation. This study demonstrates a promising circular economy approach for the reuse of industrial stone processing residues.

Keywords: Granite cutting waste, Ceramic glaze, Waste valorization, Sustainable ceramics.

1. Introduction

The natural stone industry generates a significant amount of fine-grained granite sludge and granite cutting waste during the sizing and surface processing stages of granite blocks. Although these wastes generally contain high amounts of SiO_2 and Al_2O_3, are mineralogically stable, and environmentally inert, they are often landfilled or released into the environment. The increasing production of granite cutting waste not only increases the need for landfill space but also leads to economic losses in terms of sustainable production. Therefore, the recycling of granite waste represents a significant alternative raw material potential for the ceramic and glass-ceramic industries (Strzałkowski, 2021, Lokeshwari, Jagadish, 2016, Zichella, 2019, Heuss-Aßbichler, Bayuseno 2021, Hairi, Syazana, 2014).

Raw materials used in ceramic material production are generally classified as plastic and non-plastic. Among non-cored raw materials such as quartz, feldspar, talc, and dolomite, silica group minerals, particularly granite-derived materials, play a significant role. Indeed, the high SiO_2 content, low organic matter content, and fine-grained structure of granite waste make it a suitable alternative to quartz and feldspar in ceramic formulations. The raw material classifications provided in the file also confirm that granite waste exhibits similar properties to many coreless raw materials in the ceramics industry (Montana 2017, Ryan 2013, Zouaoui et al 2017).

The use of this waste, either alone or in combination with other waste types, is becoming increasingly common in studies aimed at utilizing granite cutting waste. In this context, boron waste, in particular, is

notable for its ability to stimulate the formation of a glassy phase at low temperatures thanks to its boron oxide (B_2O_3) phase. The experimental results in the file demonstrate that by mixing and sintering granite and boron waste in specific proportions, glassy phase formation is possible at high temperatures, and these mixtures have the potential to be utilized in ceramic glaze or ceramic body production.

This study aims to evaluate granite cutting waste with boron waste at different mixing ratios, to investigate the effect of sintering temperature on material properties, and to examine the performance of the resulting samples in terms of strength and glassy phase formation. This aims to both provide environmental benefits in waste management and to provide the ceramics industry with low-cost alternative raw material sources.

2. Materials and Method

2.1. Materials

Granite cutting waste and boron waste were used as the primary raw materials in this study. The mineralogical composition of the boron waste, in accordance with the analysis tables provided in the file, contains high amounts of silica (SiO_2), alumina (Al_2O_3), and low amounts of boron oxide (B_2O_3). Granite waste, on the other hand, is rich in quartz and feldspar minerals, which are among the ceramic raw materials, and has a non-plastic (non-plastic) raw material structure. Both waste materials were mixed in different proportions according to the specified recipes and used in the experimental studies. Two groups of samples were produced in the study with two different sintering temperatures (1100 °C and 1300 °C).

2.2. Sample Preparation

2.2.1. Creating Recipes

Samples were prepared in two groups. Sample groups and mixing ratios are given in Tables 1 and 2. The ingredients were weighed with a precision scale in the specified proportions and mixed until a homogeneous mixture was obtained.

Table 1. Group 1 (samples sintered at 1100 °C)

Group 1 / 1100C°/ 2 hours	Mixing ratios
Sample 1	90% Boron waste + 10% Granite waste
Sample 2	80% Boron waste + 20% Granite waste
Sample 3	70% Boron waste + 30% Granite waste
Sample 4	50% Boron waste + 50% Granite waste

Table 2. Group 2 (samples sintered at 1300 °C)

Group 2 / 1300C°/ 2 hours	Mixing ratios
Sample 1	90% Boron waste + 10% Granite waste
Sample 2	80% Boron waste + 20% Granite waste
Sample 3	70% Boron waste + 30% Granite waste
Sample 4	50% Boron waste + 50% Granite waste

2.3. Shaping Process

The prepared mixtures were shaped in strength bar molds using a hydraulic press under 50 bar pressure. After the shaping process, the samples were dried at room temperature.

2.4. Sintering Process

The dried samples were sintered at two different temperatures (1100-1300 °C) in an electrically controlled sintering furnace. The sintering time for both groups was 2 hours. After sintering, the samples' form changes and the formation of a glassy phase on the surface were observed.

2.5. Strength Test

Sintered samples were prepared according to standard strength bar dimensions, and their fracture strengths were measured on a strength testing machine.

3. Results and Discussion

In this study, the structural and mechanical behaviors of samples obtained by sintering granite cutting waste and boron waste at different ratios at 1100 °C and 1300 °C were evaluated. Experimental findings are discussed using figures and tables.

3.1. Effect of Sintering Temperature on Sample Morphology

Images of samples sintered at 1100 °C and 1300 °C are presented in Figures 1.

T °C	Sample 1	Sample 2	Sample 3	Sample 4
1100				
1300				

No significant glassy phase formation was observed on the surface of these samples. Despite the high silica content of the granite waste in all recipes, the sintering temperature was not sufficient to form a glassy phase. It was determined that the samples retained their forms, and cracking and deformation were at a low level. This indicates that the low amount of B_2O_3 phase in the boron waste was insufficient to form a fluid phase at 1100 °C. A significant glassy phase formation occurred in all recipes at this high temperature. This finding is consistent with the observation in the file. Although the samples prepared at 1300 °C lost their form, they formed a glassy phase on the surface due to the influence of the boron waste. At 1300°C, boron oxide formed a low-melting phase and interacted with the silica in the granite waste to form a glassy surface phase. Deformation was observed in some samples due to the high temperature. These results demonstrate that 1300°C is a suitable glassy phase transition temperature for the boron-silica interaction.

3.2. Mechanical Properties

The fracture strength of the samples is given in Table 3. It is observed that the strength values increase as the boron waste ratio decreases, as the granite waste ratio increases.

Table 3. Fracture strength results

Samples	Fracture Strength (MPa)
90% Boron waste + 10% Granite waste	7.35
80% Boron waste + 20% Granite waste	7.60
70% Boron waste + 30% Granite waste	7.85
50% Boron waste + 50% Granite waste	8.83

The highest strength was achieved with a 50% boron + 50% granite mixture. Strength decreased as the boron waste content increased. This is due to the mechanical strength-enhancing effect of the high SiO_2 and feldspathic phases contained in the granite waste. Although boron waste has the potential to form a glassy phase in the structure, it weakens structural integrity after sintering when used in high quantities.

4. Conclusions

This study investigated the potential use of granite cutting waste and boron waste, mixed at different ratios, as raw materials in ceramic production. Experimental results showed that no glassy phase formed at 1100°C, while a distinct glassy phase developed at 1300°C due to boron oxide. This suggests that these two wastes can be used together, particularly in high-temperature glaze applications.

Strength measurements showed that strength increased as the granite content increased, with the highest value being achieved in a 50% boron–50% granite mixture. However, sample disintegration in water absorption tests indicated the need for improved structural integrity.

In general, granite and boron waste represent a potential alternative raw material for ceramic glazes and glass-ceramic coatings when the appropriate sintering temperature and recipe optimization are achieved; however, additional development is required for their use in body ceramics.

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Gömülü nanoçubukların diferansiyel transformasyon yöntemi ile burulma titreşimi

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ÖZET

Bu çalışma, elastik bir ortama gömülü dairesel nanoçubukların atomik boyut etkili serbest burulma titreşimine yönelik sayısal bir çözümü araştırmaktadır. Buna göre, ilgili nanoçubuk modelinin hareket denklemi ve sınır koşulları, diferansiyel dönüşüm yöntemi kullanılarak yaygın bilinen fonksiyonlar yardımıyla dönüştürülmüştür. Gömülü nanoçubukların farklı modlarının yerel olmayan boyutsuz burulma frekansları analitik sonuçlarla karşılaştırılmıştır. Ayrıca, sayısal çalışmalar tartışılmış ve tartışmadan elde edilen genel sonuçlar da paylaşılmıştır.

Anahtar Kelimeler: Burulma titreşimi, Diferansiyel transformasyon yöntemi, Gömülü nanoçubuk, Yerel olmayan elastisite teorisi

Torsional dynamics of nonlocal embedded rods using differential transformation method

ABSTRACT

This study investigates a numerical solution for atomic size-dependent torsional vibration of circular nanorods embedded in elastic medium. According to this, the equation of motion and boundary conditions of the relevant nanorod model are transformed with the help of conventional functions by using the differential transformation method. The nonlocal torsional frequencies of different modes of embedded nanorods are compared with the analytical results. Additionally, numerical studies are discussed and the general conclusions obtained from the discussion are shared.

Keywords: Differential transformation method, Embedded nanorod, Nonlocal elasticity, Torsional vibration

1. Introduction

Nanostructures are known as important components for nano- and micro-scaled electromechanical systems (NEMS/MEMS) technology. Materials such as carbon nanotubes, silica carbide nanotubes, boron nitride nanotubes, nanowires, and nanosheets are examples of various classes of nanostructures. These structures can participate in systems such as biosensors, gas sensors, nanocircuits, and microprocessors.

The stability of nano- and micro- structures within their respective systems is extremely importance to ensure their proper functionality. Therefore, it is essential to develop designs that can withstand the external loads to which such structures may be exposed within the system. Mechanical behaviour must also be known for the design. Mechanical behaviour of nanostructures can be investigated by using semi-experimental methods such as molecular dynamics simulation. Because the simulations require high cost, time-consuming processes, and specialized knowledge, researchers have performed investigation of mechanical behaviour through the theoretical approaches. The nonlocal elasticity theory of Eringen's is a popular approach worldwide for the determination of mechanical behaviour of atomic structures [1,2].

According to classical elasticity theory, value of the strain energy of a nanostructure is infinite. Therefore, classical theory cannot provide a valid solution. Nonlocal theory eliminates this deficiency by utilizing the atomic size effect of the nanostructure. In the nonlocal theory, one-dimensional nanomaterials are modelled as continuum mechanical models such as beams [3-11] and rods [12-19].

On the other hand, analytical solutions are often insufficient for nonlocal mechanical analyses of nanostructures because atomic parameters and environmental factors (such as elastic medium, thermal environment) complicate the governing equation. Therefore, approximated (numerical) solutions are preferred to solve the governing equations. The finite element method, finite difference method, differential quadrature method, differential transformation method are some examples of approximated methods. Since the differential transformation method (DTM) includes the subject of this study, a brief literature review is provided below on selected studies focusing on this method for nonlocal mechanical analyses of nanostructures:

Jena and Chakraverty [20] presented the vibration of Euler-Bernoulli nanobeams. Ebrahimi et al. [21] formulated the vibration of Timoshenko nanobeams. Applications of the differential transformation method have also been carried out on the vibration of functionally graded nanobeams [22,23]. The buckling analyses of Euler-Bernoulli [24,25] and Timoshenko [26] nanobeams have been investigated. Pradhan and Reddy [27] examined the buckling analysis of nanobeams resting on Winkler foundation. In addition to these, thermal effects on the vibration of Euler-Bernoulli nanobeams have been studied [28]. Moreover, the vibration of nanobeams resting on Winkler foundation was investigated by Demir [29]. Furthermore, the flapwise bending of double-tapered nanobeams was given based on the Euler-Bernoulli beam theory by Kurt and Kaya [30].

Determining the torsional behaviour of NEMS/MEMS organizations containing the circular cross-sectional nanomaterials is essential to understand the mechanical characteristics of nanostructures. With this motivation, the nonlocal free torsional vibration of nanorods embedded in a fully elastic medium is examined with the differential transformation method. According to this, the nonlocal free torsional vibration is introduced in Section 2. Then, the differential transformation solution for the nonlocal free vibration is developed in Section 3. For the applications of formulation, nonlocal nondimensional frequencies and the accuracy of method are presented and numerical findings are discussed in detail in Section 4. Finally, conclusions summarized from the numerical discussion are given in Section 5.

2. Nonlocal Equation of Motion

Figure 1 shows the free body diagram of a torsional nanorod embedded in elastic medium. Where x is longitudinal position and t is time. $\theta = \theta(x, t)$ is the torsional motion. Also, the cross-section axes of nanorod are given as y and z. According to this, the rotational equilibrium can be written as follows:

$$-M\left(x,t\right)+\left[M\left(x,t\right)+\mathrm{d}M\left(x,t\right)\right]+m\mathrm{d}x-k_t\theta\mathrm{d}x=\rho I_p\frac{\partial^2\theta}{\partial t^2}\mathrm{d}x \tag{1}$$

where $M = M(x, t)$ is the internal torsional moment, $m = m(x, t)$ is the external torsional excitation, k_t is the elastic medium stiffness, ρ is the unit weight, and I_p is the polar moment of inertia. After both sides of the equation are divided by $\mathrm{d}x$, with the using of Taylor series for the torsional moment:

$$\frac{\partial M}{\partial x}+m-k_t\theta=\rho I_p\frac{\partial^2\theta}{\partial t^2} \tag{2}$$

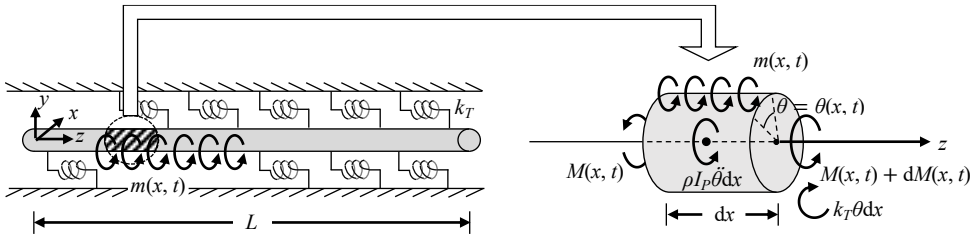

Figure 1. Schematic representation and free body diagram of torsional nanorod

To derive the equation of motion, we need to know the constitutive relation for torsional moment [7]:

$$\left(1-(e_0a)^2\frac{\partial^2}{\partial x^2}\right)M = M_{cl} = GI_p\frac{\partial\theta}{\partial x} \tag{3}$$

where M_{cl} means the classical (local) torsional moment and is calculated as in the following equation. If both sides of this equation are derived according to position and Equation (2) is used, the nonlocal equation of motion is obtained as follows:

$$GI_p\frac{\partial^2\theta}{\partial x^2}-\rho I_p\frac{\partial^2\theta}{\partial t^2}+(e_0a)^2\rho I_p\frac{\partial^4\theta}{\partial x^2\partial t^2}+m-(e_0a)^2\frac{\partial^2 m}{\partial x^2}-k_t\theta+(e_0a)^2k_t\frac{\partial^2\theta}{\partial x^2}=0 \tag{4}$$

On the other hand, the torsional moment that is a mechanical boundary condition should also be obtained. After using Equation (2) into Equation (3) yields the nonlocal torsional moment as follows:

$$M = GI_p\frac{\partial\theta}{\partial x}-(e_0a)^2\rho I_p\frac{\partial^3\theta}{\partial x\partial t^2}-(e_0a)^2\frac{\partial m}{\partial x}+(e_0a)^2k_t\frac{\partial\theta}{\partial x}=0 \tag{5}$$

The following expression is required for the analytical solution of equation of motion:

$$\theta(x,t)=\phi(x)e^{i\omega t} \tag{6}$$

where ϕ is the static mode shape and ω is the natural frequency. The mode shape is obtained analytically through a series of mathematical operations by applying Equation (6) into Equations (4) and (5). Details of analytical solution is not expressed in this study. First, $m = 0$ is used for free vibration in Equations (4) and (5). It should also be noted that two boundary conditions are considered for the mechanical structure:

$$\text{Clamped-clamped: } \phi(0)=0,\ \phi(L)=0,$$
$$\text{Clamped-free: } \phi(0)=0,\ M(L)=\left[GI_p+\omega^2(e_0a)^2\rho I_p-(e_0a)^2k_t\right]\phi'(L)=0 \tag{7}$$

By applying these boundary conditions into the analytical solution of Equation (4), the frequency equations are reached as follows [7]:

$$\omega=\sqrt{\frac{\left[GI_p+(e_0a)^2k_t\right]R^2+k_t}{\rho I_p\left[1+(e_0a)^2R^2\right]}} \tag{8}$$

Here the following definitions for the boundary conditions should be given:

$$\text{Clamped-clamped: } R=\frac{n\pi}{L},\ \text{Clamped-free: } R=\frac{(2n-1)\pi}{2L} \tag{9}$$

3. Differential Transformation Method

The differential transformation method (DTM) is an approximate solution method based on the Taylor series. The solution is explained by using power series. It is a quite useful method to solve boundary value problems in linear and nonlinear differential equations.

According to this solution method, the solution of differential equation is introduced by the following series:

$$x(t)=\sum_{n=0}^{\infty}\frac{(t-t_i)^n}{n!}\left(\frac{\mathrm{d}^n x(t)}{\mathrm{d}t^n}\right)\Bigg|_{t=t_i} \tag{10}$$

Here, t_i is known as any point in the field where t variable is taken part. The differential transformation of solution function is defined as:

$$F(n)=\sum_{n=0}^{\infty}\frac{H^n}{n!}\left(\frac{\mathrm{d}^n f(t)}{\mathrm{d}t^n}\right)\Bigg|_{t=0} \tag{11}$$

where F denotes the transformed function and f explains the original function. H is a constant value. Also, the inverse differential transformation is written as:

$$f(t)=\sum_{n=0}^{\infty}\left(\frac{t}{H}\right)^n F(n) \tag{12}$$

In DTM method, the equation whose solution is searched should be nondimensionalized. This study focuses on the free vibration frequencies of nonlocal torsional vibration and to obtain the frequencies depends on the solution of differential equation given by Equation (4). Therefore, nondimensionalization can be written after Equation (6) is used into Equation (5):

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}\xi^2}+\alpha^2 K_t\frac{\mathrm{d}^2\phi}{\mathrm{d}\xi^2}-\alpha^2\bar{\omega}^2\frac{\mathrm{d}^2\phi}{\mathrm{d}\xi^2}-K_t\phi+\bar{\omega}^2\phi=0 \tag{13}$$

The following definitions are given here:

$$\xi=\frac{x}{L},\ \bar{\omega}=\omega L\sqrt{\frac{\rho}{G}},\ \alpha=\frac{e_0 a}{L},\ K_t=\frac{k_t L^2}{GI_p}. \tag{14}$$

In addition to this, nondimensionalized boundary conditions can be expressed as:

$$\text{Clamped-free: } \phi(0)=0,\ \phi(1)=0,\ \text{Clamped-free: } \phi(0)=0,\ B\phi'(1)=0 \text{ or } \phi'(1)=0 \tag{15}$$

Where,

$$B=\frac{1}{L}\left[GI_p+\omega^2(e_0 a)^2\rho I_p-(e_0 a)^2 k_t\right] \tag{16}$$

In the solution of differential equations with the DTM, transformation equivalents of the original functions are available [27, 29]. According to this, the transformed functions for different original functions are written below for the arrangement of Equation (13):

$$\text{Original: } f(t)=\alpha x(t)+\beta y(t),\ \text{Transformed: } F(n)=\alpha X(n)+\beta Y(n) \tag{17}$$

$$\text{Original: } f(t)=\frac{\mathrm{d}^m x(t)}{\mathrm{d}t^m},\ \text{Transformed: } F(n)=\frac{(n+m)!X(n+m)}{n!} \tag{18}$$

Based on the DTM solution, the transformed equation of motion is firstly attained. By applying Equations (17) and (18) into Equation (13), the following expression can be obtained:

$$X(n+2)=\frac{-\bar{\omega}^2+K_t}{1+\alpha^2\omega^2\rho I_p-\alpha^2 k_t}\times\frac{X(n)}{(n+2)(n+1)} \tag{19}$$

On the other hand, the boundary conditions are transformed as follows for the clamped-free [27, 29]:

$$X(0)=0\,,\ \sum_{n=0}^{n} nX(n)=0 \tag{20}$$

A critical issue in the DTM solution is the number of terms used. A higher number of terms can increase the accuracy of the results. The number of terms used here affects the second boundary condition. However, to apply this boundary condition, the transformed mode shape for $n=1$ should also be formulated due to Equation (19):

$$X(1)=a \tag{21}$$

As a result of the values of mode shape in the transformation function for $n=0$ and $n=1$, the second boundary condition in Equation (20) is used according to the number of terms selected and the roots of the equation obtained yield the nondimensional frequency values. On the other hand, for the clamped-clamped boundary condition, the transformed boundary conditions are defined as follows [27, 29]:

$$X(0)=0\,,\ \sum_{n=0}^{n} X(n)=0 \tag{22}$$

where an appropriate expression for Equation (21) and the first boundary condition should be used into the second boundary condition.

4. Numerical Results and Discussions

In this section, the numerical findings obtained by using the differential transformation method are presented in tables and graphics for nonlocal torsional vibration of nanorods embedded in elastic medium. Also, numerical findings are discussed in detail. The mathematical parameters used in the numerical calculations are given in Equation (14). Where $\bar{\omega}$ is the nondimensional frequency, α is the nondimensional atomic parameter, and K_t is the nondimensional stiffness of elastic medium.

The following parameters are considered for the computations. The length of torsional nanorod: $L=20$ nm, the diameter of circular cross-section: $D=1$ nm, modulus of elasticity: $E=1$ TPa, and mass of unit volume: $\rho=2300\ \mathrm{kg/m^3}$.

Firstly, comparison studies for nondimensional frequencies of nanorods where the effect of the elastic medium is neglected are presented in Tables 1 and 2, respectively, for the first and second modes. According to this, the analytical (exact) results obtained based on Equations (8) and (9) and the nonlocal finite element analysis results given by Numanoğlu and Civalek [7] are compared with the differential transformation results. For the nanostructure mechanics, it should be noted that frequencies decrease as the nondimensional atomic parameter increases, and therefore the atomic parameter is an important factor at the nano scale. Moreover, the nondimensional atomic parameter more reduces the frequencies of clamped-clamped nanorods. On the other hand, approximation studies generally reveal a significant success of DTM method. Although high deviations from the analytical results are obtained at low term numbers, the results are exactly the same at high term numbers. In the meanwhile, the numerical algorithm does not give a result for some term numbers. This indicates that the number of terms used in the computation should be high.

The nondimensional frequencies of nanorods embedded in elastic medium are listed in Tables 3 and 4 for the first two modes. The elastic medium generally has an enhancing effect on the torsional frequencies of the nanorods. Moreover, DTM method has provided very successful results. The table results show that DTM is successful than FEM in converging to analytical results.

Table 1. Nondimensional frequencies of fundamental mode for nonlocal torsional vibration of nanorods

Boundary Condition	e_0a/L	Reference Study		Differential Transformation Results (This Study)				
		Analytical	FEM [7]	$n = 51$	$n = 21$	$n = 11$	$n = 5$	$n = 3$
C-F	0	1.5708	1.5711	1.5708	1.5708	1.5708	1.5925	1.4142
	0.05	1.5660	1.5662	1.5660	1.5660	1.5660	1.5874	1.4107
	0.1	1.5518	1.5520	1.5518	1.5518	1.5518	1.5726	1.4003
C-C	0	3.1416	3.1437	3.1416	3.1416	3.1411	-	2.4495
	0.05	3.1035	3.1055	3.1035	3.1035	3.1031	-	2.4313
	0.1	2.9972	2.9990	2.9972	2.9972	2.9968	-	2.3792

Table 2. Nondimensional frequencies of second mode for nonlocal torsional vibration of nanorods

Boundary Condition	e_0a/L	Reference Study		Differential Transformation Results (This Study)				
		Analytical	FEM [7]	$n = 51$	$n = 21$	$n = 11$	$n = 5$	$n = 3$
C-F	0	4.7124	4.7194	4.7124	4.7124	-	3.0764	-
	0.05	4.5868	4.5932	4.5868	4.5868	-	3.0406	-
	0.1	4.2628	4.2680	4.2628	4.2628	-	2.9404	-
C-C	0	6.2832	6.2997	6.2832	6.2831	-	-	-
	0.05	5.9943	6.0087	5.9943	5.9943	-	-	-
	0.1	5.3202	5.3302	5.3202	5.3201	-	-	-

Figure 2 illustrates the deviations (error percentages) of DTM method for first three modes of nanorods in response to the increasing of term numbers. Numerical results are not obtained for the regions where the lines cut. Generally, results are not obtained at low term numbers for the higher modes. The results of all modes express that DTM yields very successful results at higher term numbers. On the other hand, DTM results converged slightly faster as the atomic parameter increases in the nonlocal mechanical analysis. Additionally, the findings in Figure 3 indicate that DTM also provides faster convergence performance in the analysis with the elastic medium.

Table 3. Nondimensional frequencies of fundamental mode of nonlocal torsional vibration of embedded nanorods ($K_t = 10$)

Boundary Condition	e_0a/L	Reference Study		Differential Transformation Results (This Study)				
		Analytical	FEM [7]	$n = 51$	$n = 21$	$n = 11$	$n = 5$	$n = 3$
C-F	0	3.5309	3.5310	3.5309	3.5309	3.5309	3.5406	3.4641
	0.05	3.5288	3.5289	3.5288	3.5288	3.5288	3.5384	3.4627
	0.1	3.5225	3.5226	3.5225	3.5225	3.5225	3.5317	3.4584
C-C	0	4.4575	4.4590	4.4575	4.4575	4.4572	-	4.0000
	0.05	4.4308	4.4322	4.4308	4.4308	4.4305	-	3.9889
	0.1	4.3570	4.3582	4.3570	4.3570	4.3567	-	3.9573

Table 4. Nondimensional frequencies of second mode of nonlocal torsional vibration of embedded nanorods ($K_t = 10$)

Boundary Condition	e_0a/L	Reference Study		Differential Transformation Results (This Study)				
		Analytical	FEM [7]	$n = 51$	$n = 21$	$n = 11$	$n = 5$	$n = 3$
C-F	0	5.6751	5.6751	5.6751	5.6751	-	4.4118	-
	0.05	5.5712	5.5765	5.5712	5.5712	-	4.3870	-
	0.1	5.3077	5.3118	5.3077	5.3077	-	4.3181	-
C-C	0	7.0341	7.0489	7.0341	7.0340	-	-	-
	0.05	6.7773	6.7900	6.7773	6.7773	-	-	-
	0.1	6.1890	6.1977	6.1890	6.1890	-	-	-

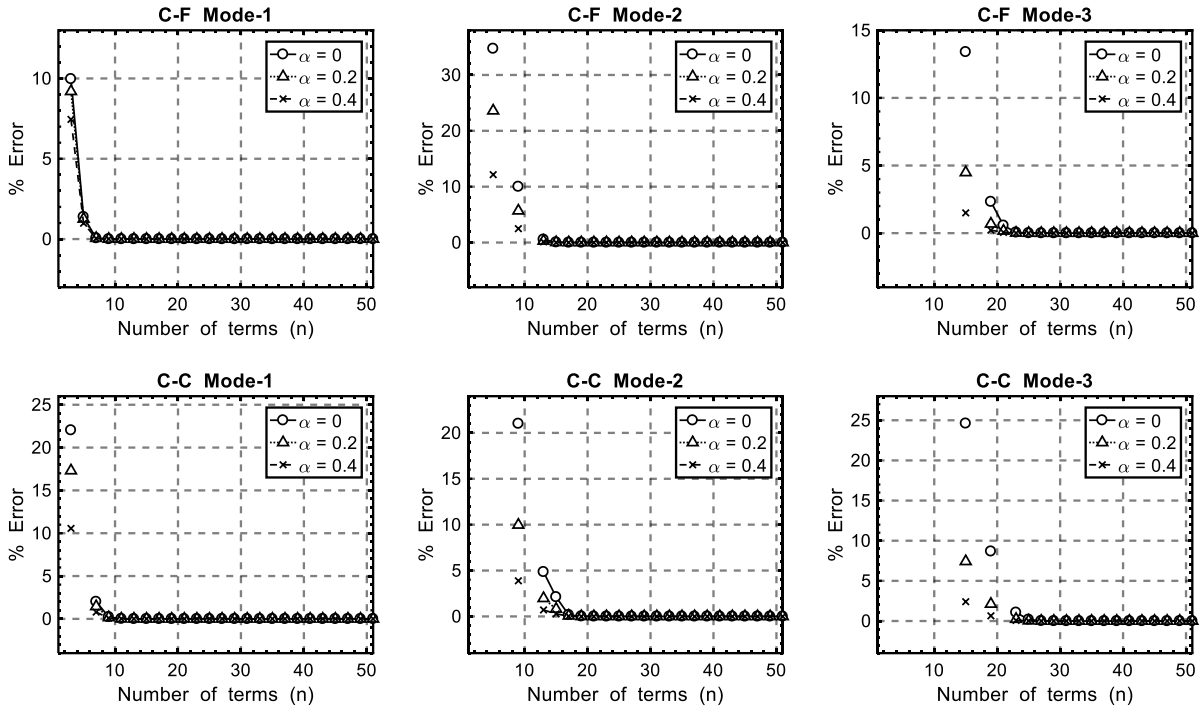

Figure 2. Deviation percentages for first three modes nondimensional frequencies of torsional nanorods

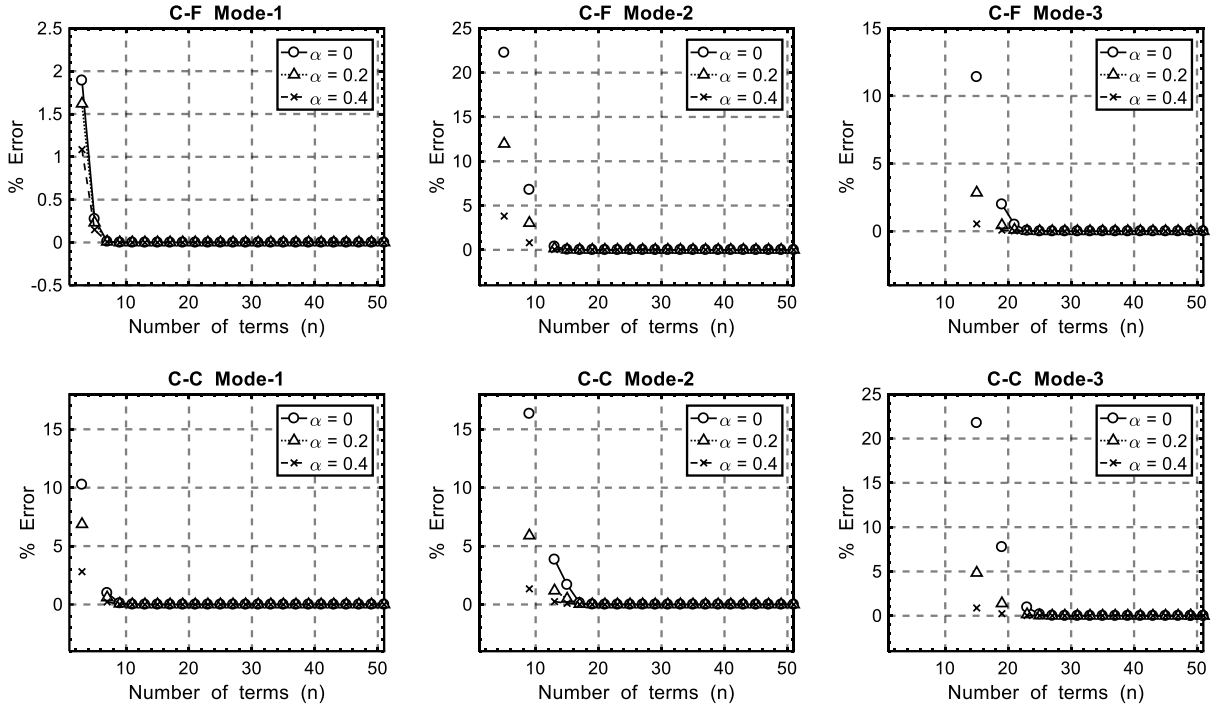

Figure 3. Deviation percentages for first three modes nondimensional frequencies of embedded torsional nanorods (K_t = 10)

The variations of nondimensional frequencies of first three modes of nanorods embedded in elastic medium with increment of elastic medium stiffness are plotted in Figures 4 and 5. To ensure high accuracy in the calculations, $n = 51$ terms are used with the DTM. Elastic medium stiffness is seen as a parameter

that increases frequencies. The atomic parameter has less effect on the frequencies of nanorods with high elastic medium stiffness.

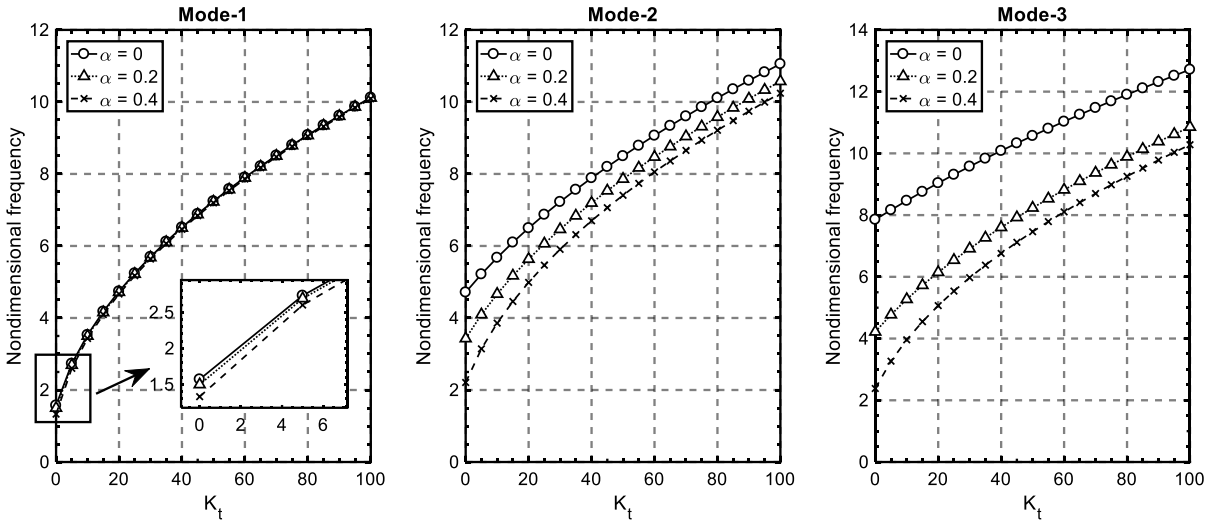

Figure 4. Variations of nondimensional frequencies of embedded clamped-free nanorods according to the increment of nondimensional nonlocal parameter

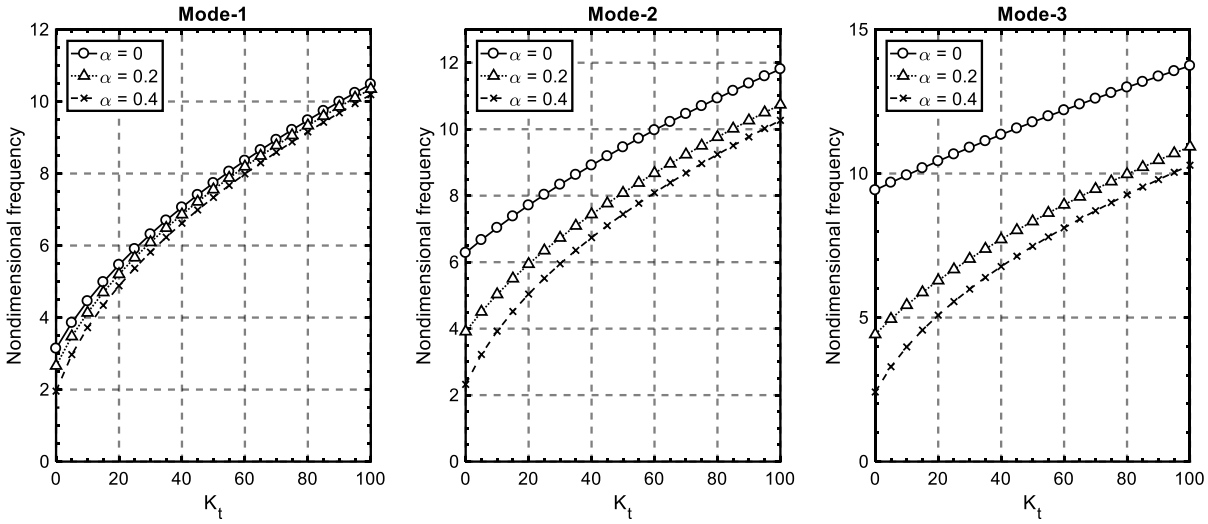

Figure 5. Variations of nondimensional frequencies of embedded clamped-clamped nanorods according to the increment of nondimensional nonlocal parameter

5. Conclusions

In this study, the nonlocal free torsional vibration of nanorods embedded in elastic medium is investigated by employing the differential transformation method. Firstly, the equation of motion is derived based on the equilibrium approach. Then, the differential transformation solution is obtained by using the transformed functions. Within the scope of the numerical results, the torsional frequencies calculated with DTM are compared with analytical and finite element results. Also, the numerical results are discussed in detail and the following conclusions are reached:

- The atomic parameter reduces the torsional frequencies. Therefore, the atomic parameter is indispensable for the mechanical analysis of nanostructures.

- The atomic parameter is more effective in the clamped-clamped nanorod that are more rigid than clamped-free nanorod.
- The elastic medium increases the frequencies. In this case, the lowering effect of atomic parameter on the frequencies decreases.
- While the DTM results are not inappropriate for low term numbers, these agree with the analytical results for high term numbers.
- In DTM analysis, the deviation decreases as the nonlocal parameter increases. This conclusion demonstrates that DTM can be useful for nonlocal mechanical analysis problems.

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Daralan eksenel nanoçubukların Rayleigh-Ritz yöntemi kullanılarak yerel olmayan serbest titreşimi

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ÖZET

Bu çalışmada, genel uç koşullarına sahip basit eksenel nanoçubukların boyuta bağlı boyuna titreşimi için Rayleigh-Ritz formülasyonu sunulmuştur. Nanoçubuğun değişken (konik veya daralan) dikdörtgen kesite sahip olduğu varsayılmıştır. Serbest titreşimin enerji ifadeleri, atomik boyut bağımlılığı için yerel olmayan elastisite teorisi kullanılarak türetilmiştir. Enerji ifadeleri uygun deneme fonksiyonları ile çözülerek, uçları tutulu ve serbest daralan nanoçubuklar için boyutsuz frekans değerleri elde edilmiştir. Sayısal sonuçlar detaylı olarak tartışılmıştır. Son olarak, tartışmalardan faydalanılarak elde edilen bazı sonuçlar da belirtilmiştir.

Anahtar Kelimeler: Daralan nanoçubuk, Eksenel titreşim, Frekans, Rayleigh-Ritz yöntemi, Yerel olmayanlılık

Nonlocal free vibration of tapered axial nanorods by using Rayleigh-Ritz solution

ABSTRACT

In this study, Rayleigh-Ritz formulation is presented for the size-dependent longitudinal vibration of simple nanorods with general end conditions. The nanorod is considered to have a variable (tapered) rectangular cross-section. The energy expressions of free vibration are derived by using the nonlocal elasticity theory for atomic size-dependency. By solving the energy expressions with appropriate trial functions, the nondimensional frequency values are obtained for nanorods with clamped and free ends. Numerical results are discussed in detail. Finally, some conclusions via discussions are also mentioned.

Keywords: Axial vibration, Frequency, Nonlocality, Rayleigh-Ritz method, Tapered nanorod

1. Introduction

Materials that have dimensions between 1 and 100 nm form the components of today innovative devices and systems. Research for this technology generally defines nanoscience and the relevant technology is known as nanotechnology. When the effectiveness of nanotechnology is considered, significant progress has been observed since the mid-1900s. Dimensions of devices with high volume have decreased, their storage capacity has increased, and processing speeds have increased. It should also be noted that strengths to electromechanical effects have also increased.

In the nano-electro-mechanical systems (NEMS) that is general focus of nanotechnology, understanding the mechanical behavior of nanomaterials that is the system components against external factors is crucial for accurate design. Although the use of continuum mechanical models is appropriate for mechanical behavior, the necessary elasticity theory has posed a problem. Experimental and semi-experimental studies on nanostructures have revealed that mechanical behavior cannot be understood by using classical elasticity. To overcome this problem, new elasticity approaches that contain the size

effect of nanostructure have been developed. The mechanics of nanostructures has been intensively investigated over the past 20 years through these new approaches.

Nonlocal elasticity theory is the well-known member of the class of elasticity approaches based on nano scale effects. This theory states that stresses at one point of the atomic structure are reconstructed by considering stresses and strains at neighbour points [1-3]. Nonlocal elasticity theory has enabled the investigation of behaviours of various mechanical models, such as nanobeams, nanorods, nanoplates, and nanoshells.

NEMS components may be constant cross-section or tapered cross-section. Examples of tapered nanorods include levers which are members of atomic force microscopy (AFM) systems [4], nanowire resonators [5], silica carbide cantilever nanobeams [6], and boron nitride nanobeams [7]. Analytical methods are insufficient for mathematical analysis of the mechanical behavior of such components because the variable cross-section makes difficult the mathematical solutions. Instead, numerical approaches can be preferred. A brief literature review is presented by considering Rayleigh-Ritz method that is the numerical method used in this study.

The atomic size-dependent axial free vibration analyses of tapered nanorods have been investigated with different numerical solutions [8-11]. Also, it can be stated that the mechanical behavior of tapered nanobeams has been studied [12-17]. In addition to these, the axial vibration of nanorods was investigated by using Rayleigh-Ritz and truncated Fourier series expansion methods by Bao et al. [18]. Studies focusing on the vibration [19,20], buckling [21,22], and statics [23] of nanobeams via Rayleigh-Ritz method can also be indicated. Abdullah et al. [24] investigated the effects of temperature and elastic environment on the torsional vibration of nanorods using Rayleigh-Ritz method.

To understand the behavior of tapered nanorods that are components of NEMS structures under mechanical forces is important for design and stability of system. This study aims to investigate the nonlocal axial free vibration behavior of tapered nanorods with Rayleigh-Ritz method. The equation of motion of nonlocal axial free vibration is introduced in Section 2. Rayleigh-Ritz method for nonlocal free vibration is presented in Section 3. In Section 4, computations of the nondimensional frequency parameters of nonlocal tapered nanorods are presented and discussions are also given. Several conclusions based on the discussion are given in Section 5.

2. Nonlocal Equation of Motion

Nonlocal theory is a higher-order continuum approach frequently used in the mechanical modelling of atomic scaled solids. According to the theory, stresses at one point in an atomic solid are related to stresses and strains at neighbour points. The mathematical expressions of nonlocal theory are written as follows [1]:

$$\sigma_{ij} = \int_V \alpha\left(|\mathbf{x}-\mathbf{x}'|,\varphi\right) s_{ij}\mathrm{d}V\,,\ \varepsilon_{ij} = \frac{1}{2}\left(u_{i,j}+u_{j,i}\right) \tag{1}$$

where σ_{ij} is known as the nonlocal stress tensor, ε_{ij} denotes the strain tensor. α is the nonlocal modulus, $|\mathbf{x}-\mathbf{x}'|$ is the distance from the reference point in Euclidean form. In addition to these, s_{ij} is the local (classical) stress tensor. V is the volume of atomic solid. u is the deformation component. Apart from these, φ means the atomic parameter:

$$\varphi = \frac{e_0 a}{L} \tag{2}$$

where a and L are the internal (nano/micro-morphic) and external characteristic lengths of the atomic solid, respectively. Furthermore, e_0 defines the atomic material constant. The nonlocal modulus must yield the following equation [1]:

$$L_0\sigma_{ij} = s_{ij} \tag{3}$$

where L_0 is called as linear differential operator:

$$L_0 = 1 - L^2\varphi^2\nabla^2 = 1 - L^2\varphi^2\frac{\partial^2}{\partial x^2} \tag{4}$$

where ∇ denotes the second-order derivative operator. By substituting Eq. (2) into Eq. (4), the constitutive equation of nonlocal elasticity is obtained with the final form of Eq. (3) as follows:

$$\sigma_{ij} - (e_0 a)^2\frac{\partial^2\sigma_{ij}}{\partial x^2} = s_{ij} \tag{5}$$

In this study, the free vibration behavior of nanorods with variable cross-section is investigated with the nonlocal theory by using Rayleigh-Ritz method. Firstly, geometry of rod with variable cross-section is given in Figure 1. Where L is length of rod, x and y are section axes, and z is longitudinal axis. According to this, the rod cross-section is rectangular but becomes narrow linearly in x and y- directions. Thickness and height of tapered geometry can be defined as follows [14]:

$$b(x) = b_L\left(1 - \beta_b\frac{x}{L}\right),\ h(x) = h_L\left(1 - \beta_h\frac{x}{L}\right) \tag{6}$$

in which, tapering ratios are given as follows:

$$\beta_b = 1 - \frac{b_R}{b_L},\ \beta_h = 1 - \frac{h_R}{h_L} \tag{7}$$

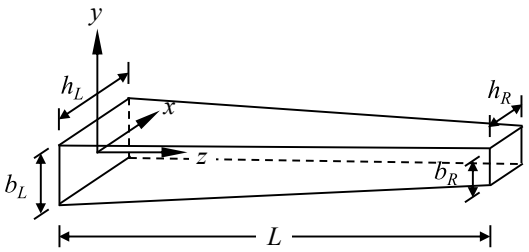


Figure 1. Tapered axial nanorod model

The equilibrium of internal forces of rod and the nonlocal stress should be used to obtain the equation of motion. The dynamic equilibrium for free vibration of the nanorod [25] is expressed as follows:

$$\rho A(x)\frac{\partial^2 u}{\partial t^2} = \frac{\partial N}{\partial x} \tag{8}$$

where ρ is the unit volume weight, $A(x)$ is the cross-section area function, and u is the axial displacement. N means axial normal force. On the other hand, we can integrate the stress equation given by Equation (5) as follows:

$$\left(1 - (e_0 a)^2\frac{\partial^2}{\partial x^2}\right)\int_{A(x)}\sigma_{xx}\mathrm{d}A(x) = \int_{A(x)}s_{xx}\mathrm{d}A(x) \tag{9}$$

The following definitions are valid here:

$$\int_{A(x)}\sigma_{xx}\mathrm{d}A(x) = N,\ \int_{A(x)}s_{xx}\mathrm{d}A(x) = EA(x)\frac{\partial u}{\partial x} \tag{10}$$

where E is modulus of elasticity. If Equation (8) is used after Equation (10) is substituted into Equation (9), Equation (11) is obtained. Also, axial normal force is obtained via a similar operation here as in Equation (12):

$$EA(x)\frac{\partial u}{\partial x}+(e_0a)^2\rho\frac{\partial^2}{\partial x^2}\left(A(x)\frac{\partial^2 u}{\partial t^2}\right)-\rho A(x)\frac{\partial^2 u}{\partial t^2}=0 \tag{11}$$

$$N=EA(x)\frac{\partial u}{\partial x}+(e_0a)^2\rho\frac{\partial}{\partial x}\left(A(x)\frac{\partial^2 u}{\partial t^2}\right) \tag{12}$$

3. Rayleigh-Ritz Solution

According to Rayleigh-Ritz method, the motion of system is defined with approximation functions that satisfy the geometric boundary conditions. The total displacement is written as follows [14]:

$$u(x)=\sum_{i=1}^{n}c_i\phi_i(x) \tag{13}$$

where ϕ_i are the approximation functions for the i-th displacement. n is the approximation function number and c_i is coefficient of approximation function. After the appropriate displacement functions are selected, c_i coefficients are determined by applying the formulation. To formulate the method, the energy formulations for the nanorod should be determined. For this, the displacement components are required:

$$u=u(x,t)=0\ ,\ v=v(x,t)=0\ ,\ w=w(x,t)=0 \tag{14}$$

where u, v, and w represent the axial, lateral, and transverse displacement components, respectively. Based on these, the energy equations of nanostructure are derived as follows:

$$U=\int_V\sigma_{xx}\varepsilon_{xx}\mathrm{d}V=\int_{A(x)}\int_0^L\sigma_{xx}\frac{\partial u}{\partial x}\mathrm{d}x\mathrm{d}A(x)=\int_0^L\left(EA(x)\frac{\partial u}{\partial x}+(e_0a)^2\rho\frac{\partial}{\partial x}\left(A(x)\frac{\partial^2 u}{\partial t^2}\right)\right)\frac{\partial u}{\partial x}\mathrm{d}x \tag{15}$$

$$T=\int_V\rho\left(\frac{\partial u}{\partial t}\right)^2\mathrm{d}V=\int_{A(x)}\int_0^L\rho\left(\frac{\partial u}{\partial t}\right)^2\mathrm{d}x\mathrm{d}A(x)=\int_0^L\rho A(x)\left(\frac{\partial u}{\partial t}\right)^2\mathrm{d}x \tag{16}$$

where U denotes internal energy and T expresses kinetic energy. The template of separation of variables that transforms partial derivatives to ordinary derivatives is written as follows:

$$U(x)=u(x)\sin(\omega t-\alpha) \tag{17}$$

By substituting Equation (17) into Equations (15) and (16), the following expressions can be obtained:

$$U_{\max}=E\int_0^L A(x)\left(\frac{\mathrm{d}U(x)}{\mathrm{d}x}\right)^2\mathrm{d}x-\omega^2(e_0a)^2\rho\int_0^L\frac{\mathrm{d}}{\mathrm{d}x}\left[A(x)U(x)\right]\frac{\mathrm{d}U(x)}{\mathrm{d}x}\mathrm{d}x \tag{18}$$

$$T_{\max}=\omega^2\rho\int_0^L A(x)\left[U(x)\right]^2\mathrm{d}x \tag{19}$$

According to the principle of minimum potential energy, the following equation is known:

$$U_{\max}-T_{\max}=0 \tag{20}$$

Substituting Equations (18) and (19) into Equation (20) presents Rayleigh's quotient [14, 19]:

$$R\left[U(x)\right]=\omega^2=\frac{U_{\max}{}^*}{T_{\max}{}^*} \tag{21}$$

where new energy expressions can be derived as follows:

$$U_{\max}{}^*=E\int_0^L A(x)\left(\frac{\mathrm{d}U(x)}{\mathrm{d}x}\right)^2\mathrm{d}x \tag{22}$$

$$T_{\max}^{*} = \left(e_0 a\right)^2 \rho \int_0^L \frac{\mathrm{d}}{\mathrm{d}x}\left[A(x)U(x)\right]\frac{\mathrm{d}U(x)}{\mathrm{d}x}\mathrm{d}x + \rho\int_0^L A(x)\left[U(x)\right]^2\mathrm{d}x \tag{23}$$

The stationarity condition for frequency calculation is mentioned as follows:

$$\frac{\partial R}{\partial c_i} = \frac{\partial \omega^2}{\partial c_i} = 0 \tag{24}$$

The following expression is obtained by using Equations (22) and (23) into Equation (24):

$$\frac{\partial U_{\max}^{*}}{\partial c_i} - \omega^2 \frac{\partial T_{\max}^{*}}{\partial c_i} = 0 \tag{25}$$

where the following definitions are made:

$$\frac{\partial U_{\max}^{*}}{\partial c_i} = \mathbf{c}K\ ,\ \frac{\partial T_{\max}^{*}}{\partial c_i} = \mathbf{c}M \tag{26}$$

where $\mathbf{c}$ is the mode shape, K is the stiffness matrix, and M is the mass matrix. Here, the frequency solution is performed as follows:

$$\det\left(K - \omega_i^2 M\right) = 0 \tag{27}$$

The selection of approximation functions for the frequency solutions is important in the Rayleigh-Ritz method. Since this study analyses the natural frequencies of clamped-free (C-F) and clamped-clamped (C-C) boundary conditions, the approximation functions can be considered as follows:

$$\text{C-C: } U_i(x) = x\left(L-x\right)^i,\ \text{C-F: } U_i(x) = \left(x/L\right)^i \tag{28}$$

4. Numerical Results and Discussions

The results of Rayleigh-Ritz formulation developed for the nonlocal free vibration of tapered axial nanorods are presented in this section. According to this, nondimensional frequencies are calculated and compared with analytical results. The parameters considered in the calculations are written as follows:

$$\alpha = \frac{e_0 a}{L}\ ,\ \overline{\omega} = \omega L\sqrt{\frac{\rho}{E}} \tag{29}$$

where α is the nondimensional nonlocal parameter and $\overline{\omega}$ is the nondimensional frequency. The left cross-section of nanorod is assumed to be constant. The following parameters are used in the computations. The length of nanorod: $L = 20$ nm, the height and width of the left cross-section: $h_L = 1$ nm and $b_L = 2$ nm, modulus of elasticity: $E = 1$ TPa, and mass of unit volume: $\rho = 2300\ \mathrm{kg/m^3}$.

A comparison of nondimensional frequencies of first three modes of constant cross-section nanorods is presented in Tables 1-3 for three different nonlocal parameters by considering a reference study [25]. The reference study presents these frequencies through the exact solution. Firstly, it is understood that the nondimensional frequencies decrease as the nondimensional atomic parameter increases. Also, the atomic parameter more reduces the frequencies in the higher modes. Moreover, it is observed that the atomic parameter more reduces the frequencies in C-C nanorods that is more rigid than C-F nanorods. Furthermore, it can be stated that Rayleigh-Ritz formulation presented in the study agrees perfectly with the analytical results. Deviations that appear in the third mode for low term numbers are eliminated as the term numbers is increased. These results clearly reveal the useful for the Rayleigh-Ritz formulation in the atomic size-dependent free vibration of tapered nanorods.

Table 1. Comparisons of fundamental mode nondimensional frequencies of nanorods with constant section

Boundary Condition	e_0a/L	Analytical [25]	Rayleigh-Ritz Results (This Study)			
			$N = 10$	$N = 8$	$N = 6$	$N = 4$
C-F	0	1.57080	1.5708	1.5708	1.5708	1.5708
	0.1	1.55177	1.5518	1.5518	1.5518	1.5518
	0.2	1.49858	1.4986	1.4986	1.4986	1.4986
C-C	0	3.14159	3.1416	3.1416	3.1416	3.1416
	0.1	2.99717	2.9972	2.9972	2.9972	2.9972
	0.2	2.66009	2.6601	2.6601	2.6601	2.6601

Nonlocal nondimensional frequencies of first three modes of tapered nanorods are listed in Table 4. The calculations are performed for 10 terms by using Rayleigh-Ritz method. The tapering ratios in both directions are assumed to be equal. The tapering ratio does not change the frequencies in the classical vibration of C-C nanorods but increases continuously for other cases. More detailed discussions are provided for the graphical results. Also, the graphical results are obtained by Rayleigh-Ritz method.

Table 2. Comparisons of second mode nondimensional frequencies of nanorods with constant section

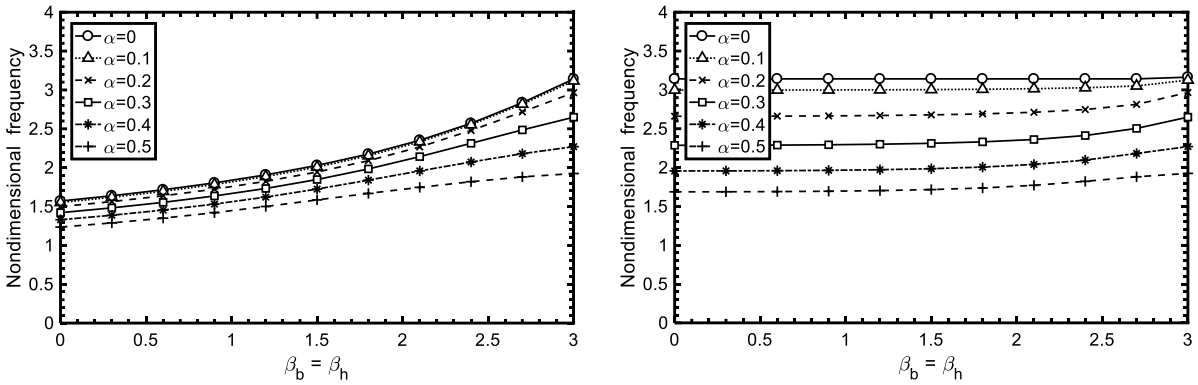
Boundary Condition	e_0a/L	Analytical [25]	*Rayleigh-Ritz Results (This Study)*			
			$N = 10$	$N = 8$	$N = 6$	$N = 4$
C-F	0	4.71239	4.7124	4.7124	4.7124	4.7246
	0.1	4.26279	4.2628	4.2628	4.2628	4.2718
	0.2	3.42933	3.4293	3.4293	3.4293	3.4340
C-C	0	6.28319	6.2832	6.2832	6.2832	6.2850
	0.1	5.32018	5.3202	5.3202	5.3202	5.3213
	0.2	3.91239	3.9124	3.9124	3.9124	3.9128

Table 3. Comparisons of third mode nondimensional frequencies of nanorods with constant section

Boundary Condition	e_0a/L	Analytical [25]	Rayleigh-Ritz Results (This Study)			
			$N = 10$	$N = 8$	$N = 6$	$N = 4$
C-F	0	7.85398	7.8540	7.8541	7.8653	8.3309
	0.1	6.17668	6.1767	6.1767	6.1822	6.4008
	0.2	4.21782	4.2178	4.2178	4.2196	4.2871
C-C	0	9.42478	9.4248	9.4249	9.4432	10.1060
	0.1	6.85867	6.8587	6.8587	6.8657	7.1082
	0.2	4.41692	4.4169	4.4169	4.4188	4.4815

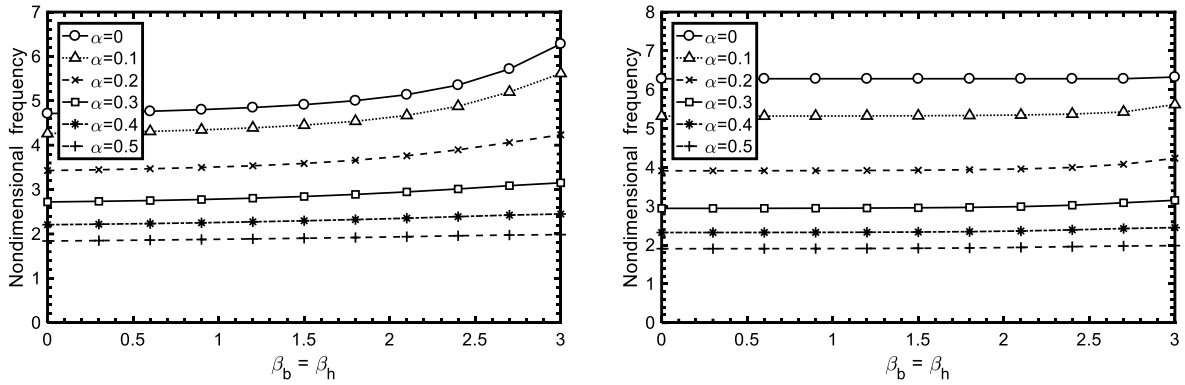
Table 4. First three modes nondimensional frequencies of tapered nanorods ($\beta_b = \beta_h = \beta$)

e_0a/L	Mode	C-F				C-C			
		$\beta = 0$	$\beta = 0.25$	$\beta = 0.5$	$\beta = 0.75$	$\beta = 0$	$\beta = 0.25$	$\beta = 0.5$	$\beta = 0.75$
0	1	1.5708	1.7582	2.0288	2.4556	3.1416	3.1416	3.1416	3.1416
	2	4.7124	4.7820	4.9132	5.2329	6.2832	6.2832	6.2832	6.2832
	3	7.8540	7.8962	7.9787	8.2045	9.4248	9.4248	9.4248	9.4248
0.1	1	1.5518	1.7373	2.0070	2.4364	2.9972	2.9983	3.0035	3.0205
	2	4.2628	4.3271	4.4522	4.7617	5.3202	5.3218	5.3295	5.3592
	3	6.1767	6.2114	6.2835	6.4844	6.8587	6.8602	6.8677	6.8977
0.2	1	1.4986	1.6788	1.9443	2.3680	2.6601	2.6632	2.6780	2.7267
	2	3.4293	3.4826	3.5885	3.8242	3.9124	3.9149	3.9273	3.9752
	3	4.2178	4.2422	4.2929	4.4061	4.4169	4.4185	4.4266	4.4590



(a) C-F *(b) C-C*

Figure 2. Variations of fundamental mode nondimensional frequencies of tapered nanorods according to the increment of tapering ratio

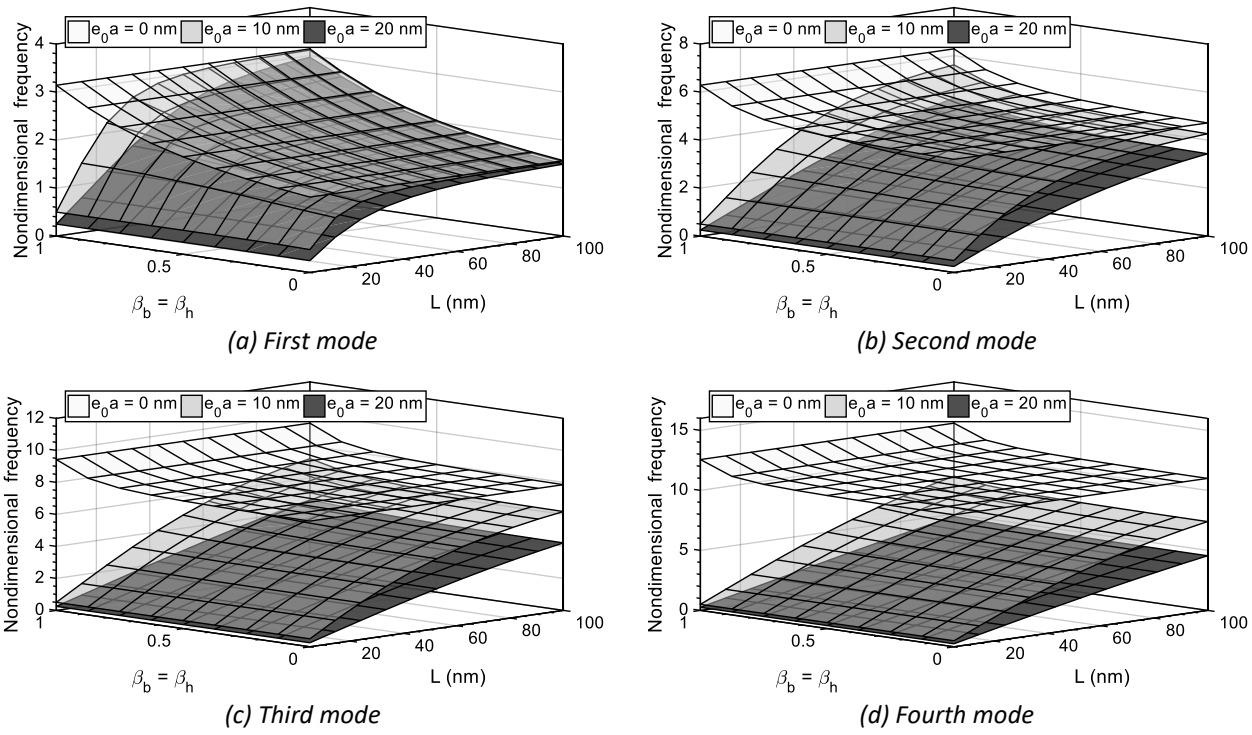


(a) C-F *(b) C-C*

Figure 3. Variations of second mode nondimensional frequencies of tapered nanorods according to the increment of tapering ratio

Figures 2 and 3 plot the changes in the first and second modes nonlocal nondimensional frequencies of C-F and C-C nanorods, respectively, in respect to tapering ratio. The results show that the tapering ratio generally increases the frequencies of the fundamental mode at a higher rate. Additionally, the nondimensional atomic parameter more decreases the frequencies in C-F nanorods with higher tapering ratios. This result is remarkable for NEMS applications involving tapered nanostructures such as atomic force microscopy. On the other hand, the tapering ratio is less effective in C-C compared to C-F.

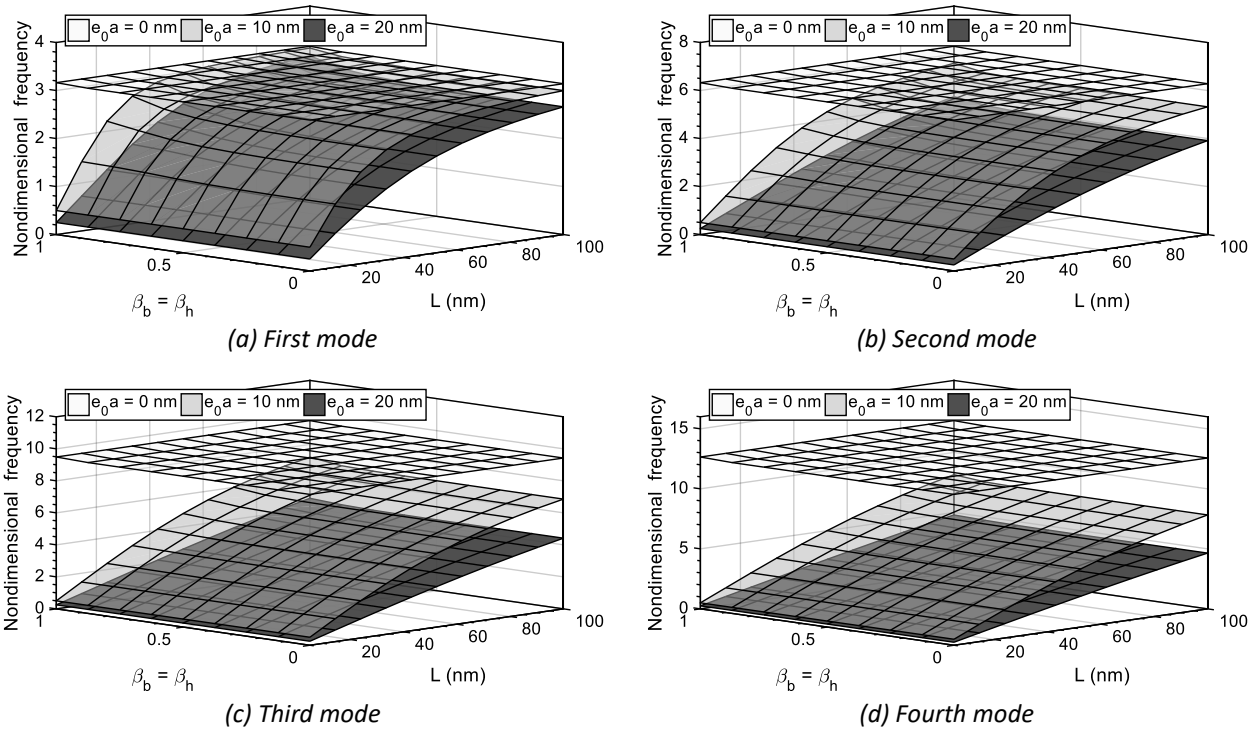
The surfaces showing the variation of the nondimensional frequencies of first four modes of C-F and C-C nanorods are depicted under increments of tapering ratio and rod length in Figures 4 and 5, respectively. It should be noted that the $\theta_b = \theta_h = 0$ case indicates the nanorod with constant section. The nondimensional frequencies of nanorods with low length are more affected by the atomic parameter. In addition to this, the rod length has a greater effect on the variation of the nondimensional frequencies of tapered nanorods. Also, the atomic parameter more reduces the frequencies of tapered nanorods and this result is more pronounced at higher modes.



(a) First mode (b) Second mode

(c) Third mode (d) Fourth mode

Figure 4. Variations of nondimensional frequencies of clamped-free tapered nanorods according to the increments of tapering ratio and rod length



(a) First mode (b) Second mode

(c) Third mode (d) Fourth mode

Figure 5. Variations of nondimensional frequencies of clamped-clamped tapered nanorods according to the increments of tapering ratio and rod length

5. Conclusions

This study investigates the atomic size-dependent free vibration of tapered nanorods. Since the mechanical behavior of rods cannot be studied at the nanoscale by using classical elasticity, nonlocal elasticity theory is considered. Also, since the analytical solution of the differential equation of relevant vibration problem is difficult, Rayleigh-Ritz method that is a numerical method is utilized.

With the help of this numerical approach, the nonlocal free vibration frequency parameters of tapered nanorods are shown in tables and graphs. These findings are discussed in detail. Considering this discussion, the conclusions of this study are presented as follows:

- Axial vibration frequencies decrease under the atomic parameter. This effect is more pronounced in higher modes.
- The atomic parameter has a higher effect on the frequencies of C-C axial rods.
- Rayleigh-Ritz results show high agreement with the analytical results. In particular, the use of 10 terms is sufficient to achieve the same results with analytical ones.
- Tapering ratio is a factor that generally increases frequencies.
- It is observed that the nonlocal parameter decreases the frequencies more in the tapered rods.
- The frequencies of tapered nanorods with short length more decrease under the influence of nonlocal parameter.

Finally, it should be noted that the atomic parameter and the tapering ratio are important factors in the investigating the mechanical behavior of tapered rod-shaped nano-electro-mechanical components. Rayleigh-Ritz method is highly efficient for such studies and can be used in many mechanical behavior studies of nanostructures.

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Elastik zemine oturan kayma deformasyonlu nanokirişlerin yerel olmayan elastisite teorisi ile statik analizi

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ÖZET

Winkler elastik zeminine oturan nanokirişlerin statik yer değiştirmeleri (deplasmanları), yerel olmayan sonlu eleman formülasyonu ile incelenmiştir. Nanokirişin kinematiği birinci mertebeden kayma deformasyon teorisi (Timoshenko kiriş teorisi) ile, nano ölçek etkisi yerel olmayan elastikiyet teorisi ile düşünülmüştür. Nanokiriş modeli için enerji ifadeleri türetilmiş ve yer değiştirmelerin diferansiyel denklemleri, minimum potansiyel enerji prensibi ile elde edilmiştir. Yer değiştirme denklemine ağırlıklı kalıntı tabanlı sonlu eleman formülasyonu uygulanarak statik analiz denklemleri doğrusal cebirsel denklemler sistemine dönüştürülmüştür. Sayısal uygulamalar için, farklı parametreler altında yayılı yüke maruz iki ucu basit mesnetli (S-S) ve iki ucu ankastre mesnetli (C-C) sınır şartlı nanokirişlerin yer değiştirmeleri hesaplanmıştır. Sayısal sonuçlar detaylı olarak tartışıldıktan sonra, tartışmaya dayanılarak çıkarımlar belirtilmiştir.

Anahtar Kelimeler: Kayma deformasyonu, Nanokiriş, Sonlu elemanlar metodu, Statik analiz, Winkler zemini, Yerel olmayan elastisite

Static analysis of shear deformable nanobeams resting on elastic foundation based on nonlocal finite elements

ABSTRACT

In this study, the static displacements of nanobeams lying on Winkler elastic foundation are calculated by using a nonlocal finite element formulation. While the kinematic field of nanobeam is considered with first-order shear deformation theory (Timoshenko beam theory) and the nano scale effect is included via the nonlocal elasticity theory. Energy expressions for the nanobeam model are derived and the differential equation for displacement is obtained through the principle of minimum potential energy. By applying a weighted residual-based finite element formulation to the displacement equation, the static analysis is converted to a system of linear algebraic equations. As a numerical application, the displacements of nanobeams with simply supported (S-S) and clamped supported (C-C) ends subjected to distributed load are calculated under different parameters. After the numerical results are discussed in detail, several inferences are mentioned.

Keywords: Finite element method, Nanobeam, Nonlocal elasticity, Shear deformation, Static analysis, Winkler foundation

1. Introduction

Today's electromechanical systems that achieve smaller dimensions, higher strengths, and faster processing speeds compared to their predecessors are a result of nanotechnology research. It is aimed that to develop innovative products by investigating the scientific and engineering properties of materials that have 1-100 nm dimensions in nanotechnology. Biosensors, gas sensors, nanoprocessors, nanocircuits, and nanotransistors are produced by using this technology. These systems are exposed to electromechanical effects during the process. Therefore, these systems can be defined as sub-technology known as nano-electro-mechanical systems (NEMS).

To ensure the mechanical stability of the components of NEMS under electromechanical effects is crucial for accurate design and functionality. Therefore, analysis of NEMS components with an appropriate mechanical model is a fundamental requirement. The processes for experiments and atomistic simulations for mechanical analysis involve various difficulties. To overcome difficulties, researchers have considered theoretical analyses of nano scaled systems through the solid mechanics models. However, experiments have exhibited that classical mechanics continuum models cannot be employed at the nano scale. The main reason for this is understood to be that external effects acting on the atomic structure are related to the atomic characteristic lengths. Thus, theoretical research has focused on new continuum theories developed with atomic dimensions. One of these new approaches is the nonlocal elasticity theory proposed by Eringen [1].

Nonlocal elasticity theory argues for the necessity of adding the atomic material constant and the internal characteristic length to the constitutive equation of the structure. At the heart of this is the fact that since the additional stresses caused by deformations occurring at the atomic scale take on infinite values, internal deformation energy of the structure also takes on infinite values. It can be stated that many mechanical models and analyses of nano scaled solids have been carried out by using nonlocal elasticity theory since the beginning of the 2000s. Considering the scope of this study, literature summaries of selected studies on static bending analysis for beam models of nano scaled one-dimensional structural elements (nanobeams) are mentioned below.

Wang et al. [2] presented nonlocal static analyses of Euler-Bernoulli and Timoshenko nanobeams for cantilever, simply supported and clamped support boundary conditions. Wang et al. [3] solved the displacement, rotation, and stress analysis of Timoshenko nanobeam via the virtual work principle. Reddy [4] investigated the static behaviour of simply supported nanobeams based on Euler-Bernoulli, Timoshenko, Levinson and own theory. A finite strain gradient model has also been given for the nonlocal thermal bending behaviour of nanobeams [5]. Rezaiee-Pajand and Rajabzadeh-Safaei [6] explained the static analysis of curved nanobeams made of functionally graded material (FGM). In addition to these, a nonlocal two-phase model has been applied to the statics of Euler-Bernoulli nanobeams [7]. The initial value method was presented for the out-of-plane static investigation of curved nanobeams by Tufekci and Aya [8]. Numanoğlu and Civalek [9] calculated the classical displacements of Euler-Bernoulli nanobeams with different boundary conditions. On the other hand, Moheimani and Dalir [10] investigated the effect of neutral axis in the static analysis of cantilever FGM nanobeams. Eltaher et al. [11] presented the statics of perforated nanobeams with Euler-Bernoulli and Timoshenko theories. The displacements of Timoshenko nanobeams subjected to point and distributed loads were compared according to different cross-section geometries by Numanoğlu [12]. Tuyen and Du [13] mentioned the thermal static analysis of FGM nanobeams through analytical solution. The statics of axially FGM nanobeams were also solved with stress and strain-driven nonlocal integral models [14]. Recently, Wu et al. [15] denoted the nonlinear static analysis of nanobeams under longitudinal linear temperature change.

In the static bending analysis of nonlocal nanobeams, the results showed a paradox with nonlocal behavior, especially due to the boundary conditions of cantilever beam. It can be stated that various approaches have been developed to resolve the paradox and new results have been obtained about the statics of nanobeams [16-20]. From these theories, the static analysis values of Euler-Bernoulli nanobeams were calculated by utilizing an improved differential model by Demir and Civalek [21]. Finite element solutions for various static analyses of nanobeams can also be mentioned. Bending of homogeneous and FGM Euler-Bernoulli [22,23] and Timoshenko [24,25] nanobeams are fundamental examples in this regard. Demir et al. [26] presented the static analysis of Euler-Bernoulli nanobeams resting on Winkler foundation. Moreover, Pradhan and Mandal [27] gave the static analysis of Timoshenko nanobeams subjected to temperature effects. Furthermore, large displacements of nanobeams with the Lagrangian finite element model were formulated by Taghipour and Baradaran [28].

To know the static bending behaviour of components within NEMS organizations is essential for the design of such structures. Also, in environments where NEMS organizations are located, there is also a substrate region that suggests a foundation model. Additionally, shear deformations can also become significant in some geometric and mechanical conditions of nanobeams. Based on all this, this study

investigates the atomic size-dependent bending of shear deformable nanobeams resting on an elastic foundation based on the finite element solutions. According to this, differential equations for the statics of the nanobeam are derived in Section 2. The solution of these differential equations is examined by using a higher-order finite element formulation in Section 3. The maximum displacement values of nanobeams with simply supported (S-S) and clamped supported (C-C) are presented under different parameters in the Section 4 via the developed formulation. Also, the calculated values are also discussed in detail. Finally, the conclusions drawn from the discussion are given in Section 5.

2. Nonlocal Statics of Nanobeam

In this section, the differential equation for the static displacement of first order shear deformable nano beams resting on elastic foundation is derived based on the nonlocal elasticity theory. The beam model that rests on Winkler foundation and is subjected to a distributed load is illustrated in Figure 1. Here, k_W is stiffness of foundation and q is homogeneous distributed static load.

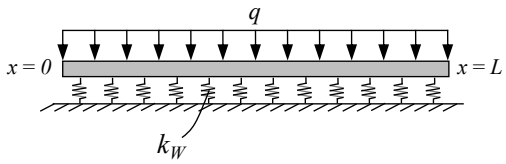

Figure 1. Static loaded nanobeam resting on Winkler foundation

According to the nonlocal elasticity theory that is quite useful for continuum mechanical models of nano scaled structures, the constitutive equation of an atomic solid is expressed as follows [1]:

$$\sigma_{ij} - \left(e_0 a\right)^2 \frac{\partial^2 \sigma_{ij}}{\partial x^2} = \sigma_c \tag{1}$$

where σ_{ij} and σ_c are the nonlocal and local (classical) stress expressions, respectively. e_0 is the atomic material constant and a denotes the internal characteristic length of nanostructure.

Kinematic theories expressing the mechanical behavior of beams may also include shear deformation. More realistic behavior is exhibited by such theories. The first order shear deformation theory for beams (Timoshenko beam theory) examines shear effects in the most fundamental sense. According to Timoshenko beam theory, the deformation components of beam should be written as follows

$$u_x\left(x,z,t\right) = u\left(x,t\right) - z\varphi\left(x,t\right) = u - z\frac{\mathrm{d}w_b}{\mathrm{d}x},\ u_y\left(x,z,t\right) = v\left(x,t\right) = v = 0,$$
$$u_z\left(x,z,t\right) = w\left(x,t\right) = w = w_b + w_s \tag{2}$$

where while x, y, and z define the axial, lateral, and axial coordinates, respectively, u_x, u_y, and u_z indicate the corresponding displacements. u is the pure axial displacement. w_b and w_s mean the bending and shear displacements, respectively. w_s is zero in beam theory that neglects shear deformations (Euler-Bernoulli beam theory). Also, φ is known as the shear rotation and assumed constant in Timoshenko theory.

The strains are obtained by using the deformation components as follows:

$$\varepsilon_{xx} = \frac{1}{2}\left(\frac{\mathrm{d}u_x}{\mathrm{d}x} + \frac{\mathrm{d}u_x}{\mathrm{d}x}\right) = -z\frac{\mathrm{d}\varphi}{\mathrm{d}x},\ \varepsilon_{xy} = \varepsilon_{yz} = \varepsilon_{yy} = \varepsilon_{zz} = 0,$$
$$\varepsilon_{xz} = \frac{1}{2}\left(\frac{\mathrm{d}u_x}{\mathrm{d}z} + \frac{\mathrm{d}u_z}{\mathrm{d}x}\right) = \frac{1}{2}\left(\frac{\mathrm{d}w}{\mathrm{d}x} - \varphi\right) \tag{3}$$

where ε_{xx} and ε_{xz} that represent the nonzero strains are axial and shear strain, respectively. Therefore, the stresses are reached as:

$$s_{xx} = E\varepsilon_{xx} = -Ez\frac{\mathrm{d}\varphi}{\mathrm{d}x},\ s_{xz} = 2G\varepsilon_{xz},\ s_{xy} = s_{yz} = s_{yy} = s_{zz} = 0 \tag{4}$$

in which, E and G are called as elasticity and shear modulus, respectively. The principle of minimum total potential energy is employed for the static analysis of continuous mechanical structures:

$$\delta U - \delta W = 0 \tag{5}$$

where U and W define the internal strain energy of nanobeam and the work potential energy of external forces, respectively. δ is the variation symbol. Energy expressions should be written as follows:

$$\begin{aligned} U &= \frac{1}{2}\int_V \left(\sigma_{xx}\varepsilon_{xx} + \sigma_{yy}\varepsilon_{yy} + \sigma_{zz}\varepsilon_{zz} + 2\sigma_{xy}\varepsilon_{xy} + 2\sigma_{xz}\varepsilon_{xy} + 2\sigma_{yz}\varepsilon_{yz}\right)\mathrm{d}V + \frac{1}{2}\int_0^L k_W w^2 \mathrm{d}x \\ &= \int_0^L \left[-M\frac{\mathrm{d}\varphi}{\mathrm{d}x} + V\left(\frac{\mathrm{d}w}{\mathrm{d}x} - \varphi\right)\right]\mathrm{d}x + \frac{1}{2}\int_0^L k_W w^2 \mathrm{d}x \end{aligned} \tag{6}$$

$$W = \int_0^L qw\mathrm{d}x \tag{7}$$

where M is the bending moment and V is the shear force. These internal effects are given for classical elasticity as follows:

$$M_c = \int_A s_{xx} z\mathrm{d}A = -\int_A Ez^2\frac{\mathrm{d}\varphi}{\mathrm{d}x}\mathrm{d}A = -EI\frac{\mathrm{d}^2 w_b}{\mathrm{d}x^2},\ V_c = \int_A k s_{xz}\mathrm{d}A = kGA\frac{\mathrm{d}w_s}{\mathrm{d}x} \tag{8}$$

where k means the shear correction factor of the cross-section of nanobeam. To modify the minimum total potential energy, variational expressions in Equations (6) should be obtained:

$$\int_0^L M\delta\frac{\mathrm{d}\varphi}{\mathrm{d}x}\mathrm{d}x = M\delta\varphi\Big|_0^L - \int_0^L \frac{\mathrm{d}M}{\mathrm{d}x}\delta\varphi\mathrm{d}x,\ \int_0^L V\delta\frac{\mathrm{d}w}{\mathrm{d}x}\mathrm{d}x = V\delta w\Big|_0^L - \int_0^L \frac{\mathrm{d}V}{\mathrm{d}x}\delta w\mathrm{d}x \tag{9}$$

By substituting Equation (9) into Equation (6), the following expression is derived:

$$\int_0^L \left(\frac{\mathrm{d}M}{\mathrm{d}x} - V\right)\delta\varphi\mathrm{d}x + \int_0^L \left(-\frac{\mathrm{d}V}{\mathrm{d}x} + k_W w - q\right)\delta w\mathrm{d}x + \left(-M\right)\delta\varphi\Big|_0^L + V\delta w\Big|_0^L = 0 \tag{10}$$

Here, the following definitions are given for the variation of different deformation components to provide above equation:

$$\delta\varphi \neq 0:\quad \frac{\mathrm{d}M}{\mathrm{d}x} - V = 0 \tag{11}$$

$$\delta w \neq 0:\quad \frac{\mathrm{d}V}{\mathrm{d}x} = k_w w - q \tag{12}$$

To obtain the equation of the static displacement of nanobeam, the nonlocal constitutive relations of the internal effects should be known. The following relations can be attained via Equations (1) and (8):

$$M - \left(e_0 a\right)^2\frac{\partial^2 M}{\partial x^2} = -EI\frac{\mathrm{d}\varphi}{\mathrm{d}x} = -EI\frac{\mathrm{d}^2 w_b}{\mathrm{d}x^2} \tag{13}$$

$$V - \left(e_0 a\right)^2\frac{\partial^2 V}{\partial x^2} = kGA\left(\frac{\mathrm{d}w}{\mathrm{d}x} - \varphi\right) = kGA\frac{\mathrm{d}w_s}{\mathrm{d}x} \tag{14}$$

Using these equations into Equations (11) and (12) yields the nonlocal bending moment and shear force, respectively:

$$M = \left(-EI - \frac{\left(e_0 a\right)^2 k_W EI}{kGA}\right)\frac{\mathrm{d}^2 w_b}{\mathrm{d}x^2} + \left(e_0 a\right)^2 k_W w_b - \left(e_0 a\right)^2 q \tag{15}$$

$$V = \left(-EI - \frac{\left(e_0 a\right)^2 k_W EI}{kGA} \right) \frac{\mathrm{d}^3 w_b}{\mathrm{d}x^3} + \left(e_0 a\right)^2 k_W \frac{\mathrm{d}w_b}{\mathrm{d}x} - \left(e_0 a\right)^2 \frac{\mathrm{d}q}{\mathrm{d}x} \tag{16}$$

The relation between shear and bending displacements is reached by utilizing Equations (15) and (16) into Equation (11):

$$w_s = -\frac{EI}{kGA} \frac{\mathrm{d}^2 w_b}{\mathrm{d}x^2} \tag{17}$$

After Equation (17) is used into the nonlocal bending moment and shear force, if the internal effects are substituted into Equations (11) and (12), the following equations are written:

$$\left(-EI - \frac{\left(e_0 a\right)^2 k_W EI}{kGA} \right) \frac{\mathrm{d}^4 w_b}{\mathrm{d}x^4} + \left(\frac{k_W EI}{kGA} + \left(e_0 a\right)^2 k_W \right) \frac{\mathrm{d}^2 w_b}{\mathrm{d}x^2} - k_W w_b = \left(e_0 a\right)^2 \frac{\mathrm{d}^2 q}{\mathrm{d}x^2} - q \tag{18}$$

$$\left[kGA + \left(e_0 a\right)^2 k_W \right] \frac{\mathrm{d}^4 w_s}{\mathrm{d}x^4} + \left(-k_w - \frac{\left(e_0 a\right)^2 k_W kGA}{EI} \right) \frac{\mathrm{d}^2 w_s}{\mathrm{d}x^2} + \frac{k_W kGA}{EI} w_s = \left(e_0 a\right)^2 \frac{\mathrm{d}^4 q}{\mathrm{d}x^4} - \frac{\mathrm{d}^2 q}{\mathrm{d}x^2} \tag{19}$$

Equations (18) and (19) define the differential equations of bending and shear displacements, respectively. In the Euler-Bernoulli theory, only Equation (18) is valid.

3. Nonlocal Finite Element Method

Equations (18) and (19) cannot be solved analytically because these equations include non-differentiated displacements. Instead, a numerical method should be used. In this study, a finite element method is preferred to solve the differential equations of displacement. The finite element formulation in structural mechanics is based on the procedure of average weighted residue. According to this procedure, the residue is the governing equation of mechanical analysis. Therefore, the weighted displacement equations are written as follows:

$$I_b = \int_0^{l_e} h \left(EI \frac{\mathrm{d}^4 w_b}{\mathrm{d}x^4} + \frac{\left(e_0 a\right)^2 k_W EI}{kGA} \frac{\mathrm{d}^4 w_b}{\mathrm{d}x^4} - \frac{k_W EI}{kGA} \frac{\mathrm{d}^2 w_b}{\mathrm{d}x^2} - \left(e_0 a\right)^2 k_W \frac{\mathrm{d}^2 w_b}{\mathrm{d}x^2} + k_W w_b + \left(e_0 a\right)^2 \frac{\mathrm{d}^2 q}{\mathrm{d}x^2} - q \right) \mathrm{d}x = 0 \tag{20}$$

$$I_s = \int_0^{l_e} h \left(kGA \frac{\mathrm{d}^4 w_s}{\mathrm{d}x^4} + \left(e_0 a\right)^2 k_W \frac{\mathrm{d}^4 w_s}{\mathrm{d}x^4} - k_w \frac{\mathrm{d}^2 w_s}{\mathrm{d}x^2} - \frac{\left(e_0 a\right)^2 k_W kGA}{EI} \frac{\mathrm{d}^2 w_s}{\mathrm{d}x^2} + \frac{k_W kGA}{EI} w_s - \left(e_0 a\right)^2 \frac{\mathrm{d}^4 q}{\mathrm{d}x^4} + \frac{\mathrm{d}^2 q}{\mathrm{d}x^2} \right) \mathrm{d}x = 0 \tag{21}$$

where l_e is the length of finite element. h is the weighting function. Although nonlocal nanobeams can be solved with the two-node - four-degree-of-freedom finite element model [22, 29-33] that is the simplest bending element in many cases, the problem in this study cannot be analyzed with this model. Because differential equation shear displacement involves four-order derivatives of the load. Therefore, the order of kinematics of the finite element model should be increased. According to this, appropriate finite element model is the three-node - six-degree-of-freedom one-dimensional linear element depicted in Figure 2. In this model, d_i, d_j, and d_k are nodal displacements and r_i, r_j, and r_k are nodal rotations. These six components are inputs of a general deflection vector.

On the other hand, shape function vector of finite element transforms the general deflection vector into deflections of physical structure. The components of shape function vector can be introduced as follows:

$$\phi_1=(\xi-1)^2(2\xi-1)^2(6\xi+1),\ \phi_2=l_e\xi(\xi-1)^2(2\xi-1)^2,\ \phi_3=16\xi^2(\xi-1)^2,$$
$$\phi_4=8l_e\xi^2(\xi-1)^2(2\xi-1),\ \phi_5=\xi^2(7-6\xi)(2\xi-1)^2,\ \phi_6=l_e\xi^2(\xi-1)(2\xi-1)^2 \tag{22}$$

where $\xi=x/l_e$ defines the nondimensional axial coordinate.

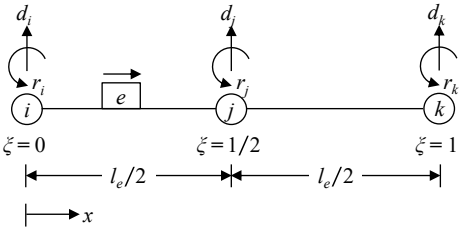

Figure 2. Three-node - six-degree-of-freedom finite element model

The basic relations of this finite element model are explained as follows [31-33]:

$$\phi=\{\phi_i\}_{6\times1},\ h=\phi^{\mathrm{T}},\ \mathbf{B}=\mathrm{D}^{\mathrm{k}}\phi=\frac{\mathrm{d}\phi}{\mathrm{d}x},\ \frac{\mathrm{d}h}{\mathrm{d}x}=\left(\phi^{\mathrm{T}}\right)'=\mathbf{B}^{\mathrm{T}},$$
$$w_b=\phi\mathbf{w_b},\ w_s=\phi\mathbf{w_s},\ \frac{\mathrm{d}w_b}{\mathrm{d}x}=\mathbf{B}\mathbf{w_b},\ \frac{\mathrm{d}w_s}{\mathrm{d}x}=\mathbf{B}\mathbf{w_s} \tag{23}$$

where ϕ is the vector of shape functions. $\mathbf{w_b}$ and $\mathbf{w_s}$ are the bending and shear deformation vectors, respectively. D^{k} is known as the differential operator.

By using Equation (23) into Equations (20) and (21), the differential equations of displacements are reduced to the following expressions:

$$[K_b]_{N\times N}\{\mathbf{w_b}\}_{N\times1}=\{\mathbf{q_b}\}_{N\times1},\ [K_s]_{N\times N}\{\mathbf{w_s}\}_{N\times1}=\{\mathbf{q_s}\}_{N\times1} \tag{24}$$

where N is reduced degree-of-freedom of finite element mesh. K_b and K_s are the total bending and total shear stiffness matrices of the finite element, respectively. Also, $\mathbf{q_b}$ and $\mathbf{q_s}$ are the bending and shear load vectors, respectively. Also, the total deflection is obtained as follows:

$$\mathbf{w}=\mathbf{w_s}+\mathbf{w_b} \tag{25}$$

where stiffness matrices and load vectors are symbolized as follows:

$$K_b=K_1+K_2+K_3+K_4+K_5,\ K_s=K_6+K_7+K_8+K_9+K_{10} \tag{26}$$

$$\mathbf{q_b}=\mathbf{q}_1-\mathbf{q}_2,\ \mathbf{q_b}=\mathbf{q}_3-\mathbf{q}_4 \tag{27}$$

According to this, the components that are determined above are presented as follows:

$$K_1=\int_0^{l_e}EI\left(\mathbf{B'}^{\mathrm{T}}\mathbf{B'}\right)\mathrm{d}x,\ K_2=\int_0^{l_e}\frac{(e_0a)^2k_WEI}{kGA}\left(\mathbf{B'}^{\mathrm{T}}\mathbf{B'}\right)\mathrm{d}x,\ K_3=\int_0^{l_e}\frac{k_WEI}{kGA}\left(\mathbf{B}^{\mathrm{T}}\mathbf{B}\right)\mathrm{d}x,$$
$$K_4=\int_0^{l_e}(e_0a)^2k_W\left(\mathbf{B}^{\mathrm{T}}\mathbf{B}\right)\mathrm{d}x,\ K_5=\int_0^{l_e}k_W\left(\phi^{\mathrm{T}}\phi\right)\mathrm{d}x,\ K_6=\int_0^{l_e}kGA\left(\mathbf{B'}^{\mathrm{T}}\mathbf{B'}\right)\mathrm{d}x,$$
$$K_7=\int_0^{l_e}(e_0a)^2k_W\left(\mathbf{B'}^{\mathrm{T}}\mathbf{B'}\right)\mathrm{d}x,\ K_8=\int_0^{l_e}k_W\left(\mathbf{B}^{\mathrm{T}}\mathbf{B}\right)\mathrm{d}x,\ K_9=\int_0^{l_e}\frac{(e_0a)^2k_WkGA}{EI}\left(\phi^{\mathrm{T}}\phi\right)\mathrm{d}x,$$
$$K_{10}=\int_0^{l_e}\frac{k_WkGA}{EI}\left(\phi^{\mathrm{T}}\phi\right)\mathrm{d}x \tag{28}$$

$$\mathbf{q}_1 = \int_0^{l_e} qh\mathrm{d}x\,,\ \mathbf{q_2} = \int_0^{l_e} (e_0a)^2\, q\frac{\mathrm{d}^2h}{\mathrm{d}x^2}\mathrm{d}x\,,\ \mathbf{q}_3 = \int_0^{l_e} (e_0a)^2\, q\frac{\mathrm{d}^4h}{\mathrm{d}x^4}\mathrm{d}x\,,\ \mathbf{q}_4 = \int_0^{l_e} q\frac{\mathrm{d}^2h}{\mathrm{d}x^2}\mathrm{d}x \tag{29}$$

4. Numerical Results and Discussions

This section presents nondimensional values for the maximum displacements (central displacements) of S-S and C-C nanobeams by using a higher-order finite element formulation developed for the nonlocal bending of shear deformable nanobeams resting on elastic foundation. The nondimensional parameters considered in the calculations are given as follows:

$$\alpha = \frac{e_0a}{L}\,,\ K_W = \frac{k_WL^4}{EI}\,,\ W = 100w\frac{EI}{qL^4} \tag{30}$$

where a, K_W, and W denote the nondimensional forms of the nonlocal parameter, Winkler foundation stiffness, and displacement respectively. Unless otherwise specified, the following parameters are considered: The length of nanobeam: $L = 20$ nm, the height and width of rectangular cross-section: $h = 1\ nm$ and $b = 2\ nm$, modulus of elasticity: $E = 1$ TPa, Poisson's ratio: $\upsilon = 0.3$, shear correction factor: $k = 5/6$, and homogeneous distributed load: $q = 1$ nN/nm.

Table 1 compares the classical and nonlocal maximum displacements of Timoshenko nanobeams with simply supported at both ends. Unlike mentioned above due to the reference studies, the following values are used: $L = 10$ nm, $h = 0.5$ nm, $E = 30\times10^6$ Pa. While Ref. [4] investigated these displacements with analytical solution, Ref. [24] computed these by using the nonlocal finite element method. Ref. [24] performed the analysis via two-node finite elements. Since elastic foundation are not considered, two-node finite element formulation is sufficient. However, the results of this study are obtained through three-node finite elements. In the analyses, n is the number of finite elements. According to this, it is observed that the finite element results have a great agreement. Normally, if two-node elements were used, the results would deviate slightly at lower finite element numbers, especially. Three-node elements eliminated these deviations. On the other hand, from a nanomechanical perspective, it is understood that the increment of atomic parameter increases the displacement. Therefore, the effect of atomic size is considered an indispensable factor at the nano scale. Due to the success of three-node finite elements, $n = 10$ finite elements are used in analyses performed from this point onwards.

Table 1. Comparisons of nonlocal maximum nondimensional deflections of simply supported nanobeam

$(e_0a)^2$	Ref. [4]	Ref. [24]	NL-FEM Results (This Study)		
$(\mathrm{nm})^2$			$n = 10$	$n = 4$	$n = 2$
0	1.3218	1.3102	1.3102	1.3102	1.3102
0.5	1.3909	1.3727	1.3727	1.3727	1.3727
1.0	1.4600	1.4352	1.4352	1.4352	1.4352
1.5	1.5290	1.4977	1.4977	1.4977	1.4977
2.0	1.5981	1.5602	1.5602	1.5602	1.5602
2.5	1.6671	1.6227	1.6227	1.6227	1.6227

Table 2. Nonlocal maximum nondimensional deflections of nanobeams resting on Winkler foundation

Nanobeam	e_0a/L	S-S			C-C		
Kinematics		$K_W = 0$	$K_W = 10$	$K_W = 100$	$K_W = 0$	$K_W = 10$	$K_W = 100$
EBBT	0	1.3021	1.1797	0.6305	0.2604	0.2552	0.2163
	0.1	1.4271	1.2807	0.6638	0.2604	0.2546	0.2117
	0.2	1.8021	1.5726	0.7271	0.2604	0.2527	0.1992
TBT	0	1.3102	1.1870	0.6418	0.2604	0.2552	0.2163
	0.1	1.4352	1.2879	0.6671	0.2604	0.2546	0.2116
	0.2	1.8102	1.5792	0.7284	0.2604	0.2526	0.1987

Table 2 lists the maximum nondimensional displacements of nanobeams resting on Winkler foundation for different nondimensional atomic parameter values. According to this, the results based on Euler-Bernoulli beam theory that neglects shear deformation are compared with the results of analyses considering shear deformation (Timoshenko beam theory). It is observed that the maximum displacements more increase with increasing atomic parameter values. As the stiffness of Winkler foundation increases, the equivalent stiffness of nanostructure increases and thus the deflection values decrease. C-C nanobeam is seen to deform less than S-S nanobeam because C-C boundary condition is more rigid. Also, it is noted that the atomic parameter and shear deformation have no effect on the displacements in the case without an elastic foundation. Additionally, it is an interesting result that the displacements of C-C nanobeams resting elastic foundation decrease with the increment of atomic parameter. Moreover, when the foundation stiffness is high, it is understood that the atomic parameter less increases the maximum deflection values. Finally, it can be added that the atomic parameter is more effective in the S-S nanobeam.

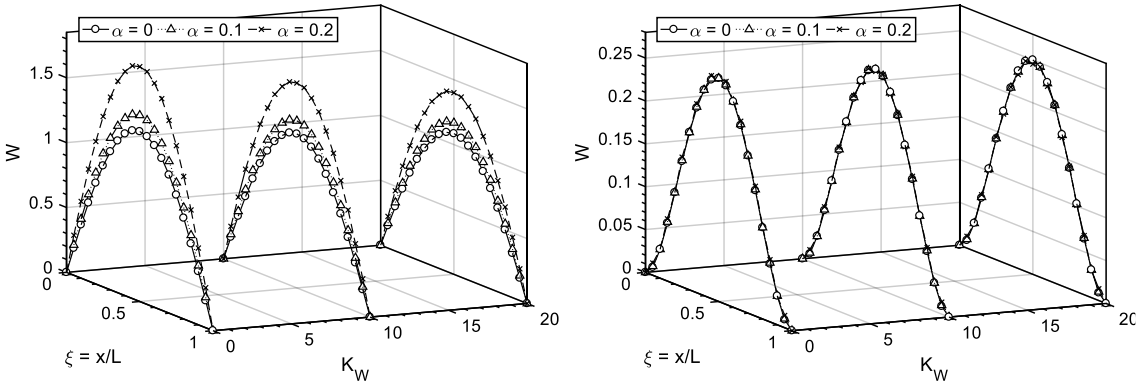

Figure 3. Nonlocal nondimensional elastic curves of nanobeams resting on Winkler foundation

The elastic curves of S-S and C-C nanobeams lying on Winkler foundation are plotted according to different atomic parameters in Figure 3. Accordingly, elastic curves are presented for $K_W = 0, 10, 20$. Similar conclusions to those made in Table 2 can be mentioned here as well. It is also understood from the figure that the atomic parameter and the elastic foundation parameter have almost no effect on the displacement behavior.

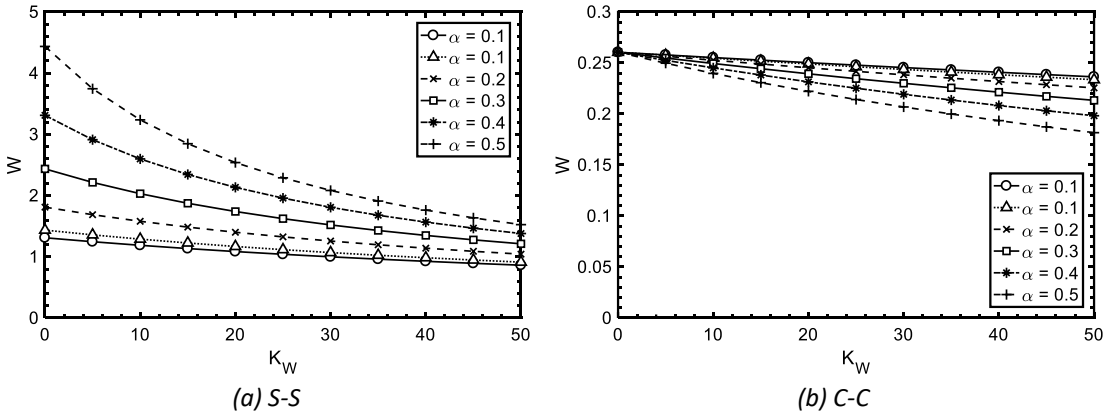

Figure 4. Nonlocal maximum nondimensional deflections of nanobeams according to the increment of nondimensional foundation stiffness

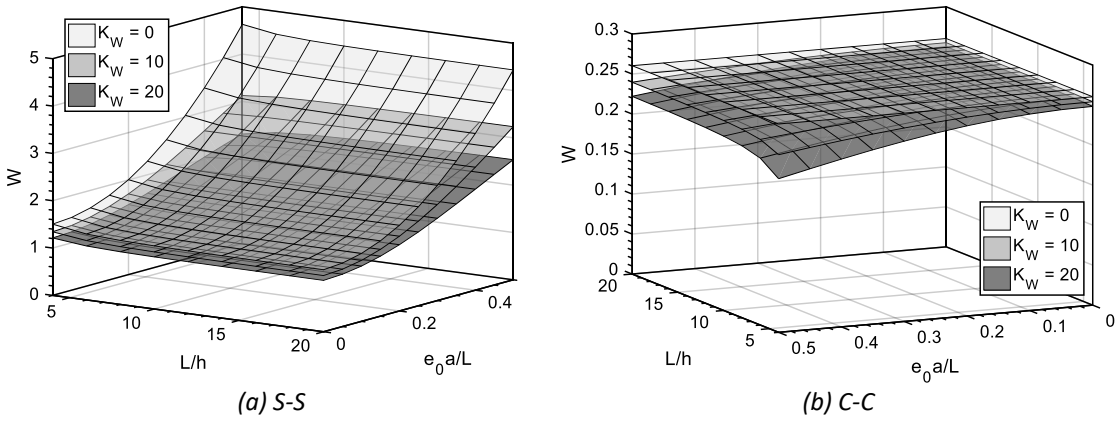

Figure 5. Nonlocal maximum nondimensional deflections of nanobeams according to the increments of nondimensional nonlocal parameter and length-to-height ratio (a) S-S (b) C-C

The changes in the nonlocal frequencies of the nanobeams in response to the increase in the elastic foundation parameter are presented in Figure 4. For S-S nanobeam, it is observed that the rate of increase in the displacements rises as the atomic parameter increases. In this case, Winkler foundation more reduces the displacements. In the C-C nanobeam, Winkler foundation is also more effective for high atomic parameters, but the decrease in displacements with increment of atomic parameters is a finding contrary to S-S and the general phenomenon of nonlocality. These results suggest that it may be more beneficial to consider C-C nanobeam within the context of paradoxical solutions.

The surfaces illustrating the effect of length-to-height ratio and nondimensional atomic parameter on the nonlocal maximum displacements are depicted in Figure 5. In these analyses, while the section height $h = 1$ nm is constant, the length is variable. Firstly, as it can be understood from the S-S boundary condition, when L/h ratio decreases, the displacements rises because the shear effect is more pronounced in short-span beams. On the other hand, the effect of atomic parameter becomes more pronounced as the nonlocal parameter and the stiffness of Winkler foundation increase. Moreover, in the C-C nanobeam, while L/h ratio does not affect displacements in the classical case, L/h ratio interestingly reduces displacements in the nanobeams resting on elastic foundation. Furthermore, this effect becomes more evident as the nonlocal parameter increases. Finally, as L/h ratio rises, the effect of nonlocal parameter decreases because the dimensions of structure move away from the atomic scale.

5. Conclusions

This study focuses on the nonlocal static analysis of shear deformable nanobeams resting on Winkler elastic foundation. First, the differential equation for bending is derived. Since the equation cannot be solved by integration, a finite element solution is developed. Additionally, due to the presence of higher-order derivatives in the differential equation, the finite element solution is formulated according to a higher-order shape function. Then the deflection values of S-S and C-C nanobeams are calculated by using this formulation. Also, the findings of static analysis are discussed in detail, and following conclusions are reached based on this discussion:

- Nonlocal parameters are a factor that increases displacements. Therefore, nonlocal parameters are an indispensable in the mechanical analysis of nanostructures.
- Shear deformation generally increases the displacements of nanobeams.
- Nonlocal parameters have a greater effect on the displacements when shear deformation is evident.
- Nanobeams resting on Winkler foundation generally have lower displacement values.
- The effect of nonlocal parameter on the displacement is reduced in the nanobeams resting on Winkler foundation.

- Nonlocal finite element solution based on three-node - six-degree-of-freedom shape function yields appropriate results for the static analysis of nanobeams.
- Due to displacement results that contradict nonlocal elasticity in the C-C nanobeam, it is suggested that this boundary condition be examined with paradox solutions.

It can be stated that these results can provide insights into the mechanical behavior and accurate design of structural elements that may be NEMS components and modelled as beams.

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Development and Characterization of Biomimetic Material Imitating the Optical Spectra of Natural Leaves Through the Sol-Gel Method

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ABSTRACT

Natural leaves exhibit highly ordered optical and thermal behavior, making them exceptional models for hyperspectral camouflage. As the importance of hyperspectral imaging as a detection method grows, so does the need for sophisticated camouflage technology. This study presents a novel biomimetic thin film composed of polyvinyl alcohol (PVA), calcium chloride ($CaCl_2$), and chromium oxide (Cr_2O_3), fabricated through controlled mixing, doctor-blade casting, and low- temperature drying. Systematic formulation testing identified 10 wt.% PVA as the optimal concentration for minimizing swelling, improving mechanical stability, and ensuring uniform pigment dispersion. The resulting films exhibit a uniform, defect-free surface with a green spectral appearance, thermal properties, and solar spectrum reflection, resembling natural leaves. These findings demonstrate the potential of PVA-$CaCl_2$-Cr_2O_3 composites as promising candidates for hyperspectral camouflage.

Keywords: Biomimetic leaf, solar spectrum reflection, thermal effect, thin film organic bionic membrane

1. Introduction

Modern surveillance and detection technologies particularly hyperspectral and multispectral imaging pose significant challenges for conventional camouflage systems, which typically fail to reproduce the complex optical and thermal responses of natural vegetation [1] [2]. Natural leaves exhibit finely tuned interactions with ultraviolet, visible, and near-infrared radiation, enabling them to regulate light absorption, scatter NIR wavelengths, modulate surface temperature, and dynamically adjust their reflectance under varying environmental conditions [3] [4]. These characteristics make foliage an essential biological model for developing advanced biomimetic materials intended for concealment in real outdoor environments. Recent research has explored the integration of polymeric matrices with pigments and hygroscopic salts as a promising route to replicate specific optical features of leaves [5]. Although such systems have demonstrated progress, many still depend on expensive or environmentally sensitive additives, such as lithium-based salts, which limit large-scale applicability and long-term field deployment [6]. Therefore, there is a growing need for sustainable, cost-effective materials capable of accurately mimicking leaf-like spectral signatures across the UV–Vis–NIR range. Chromium oxide (Cr_2O_3), a durable and chemically stable green pigment, has been widely recognized for its ability to reproduce the characteristic absorption and reflectance behavior of vegetation due to its strong spectral features in the visible and NIR regions [7]. In parallel, hygroscopic salts such as calcium chloride ($CaCl_2$) offer thermal and moisture-responsive behavior, enabling evaporative cooling and humidity-dependent spectral shifts similar to those observed in natural leaves [8] [9]. When combined within polymer films, these components can introduce dynamic optical and thermal modulation crucial for multispectral camouflage applications.

The present study aims to develop a biomimetic thin film designed to replicate the spectral and thermal characteristics of natural foliage using a polyvinyl alcohol (PVA)–based sol–gel composite incorporating $CaCl_2$ and Cr_2O_3. PVA provides a mechanically stable and transparent matrix suitable for controlled pigment and salt dispersion, while the additives introduce key optical and thermal functionalities. The fabricated films were systematically characterized using X-ray diffraction (XRD), ATR-FTIR spectroscopy, SEM–EDS, contact angle analysis, UV–Vis–NIR spectroscopy, and thermal radiation measurements to evaluate structural uniformity, chemical interactions, optical characteristics, and temperature responsiveness. The results demonstrate that incorporating $CaCl_2$ and Cr_2O_3 into the PVA matrix enhances moisture sensitivity, modifies absorption across critical vegetation-related wavelengths, and produces spectral signatures closely resembling those of natural leaves. These outcomes highlight the potential of the developed composite as a sustainable, low-cost candidate for multispectral camouflage and other biomimetic applications.

2. Materials and Method

2.1 Materials

Polyvinyl alcohol (PVA) powder, calcium chloride ($CaCl_2$), and chromium oxide (Cr_2O_3) pigment were used as the primary raw materials for the fabrication of biomimetic films. PVA was selected due to its film-forming ability and hydrophilicity, $CaCl_2$ (analytical grade) was incorporated to enhance hygroscopic behavior, and Cr_2O_3 pigment (particle size 54–250 nm) provided the green coloration. Distilled water served as the solvent throughout the process. The fabrication setup consisted of a hotplate magnetic stirrer, beakers, glass plates, PTFE sheets, a doctor blade, a micrometer-adjustable film applicator, and an ultrasonic bath. The base PVA membrane was prepared using a standard solution-casting approach. PVA powder was gradually added to distilled water and heated to 90 °C while stirring at 1000 rpm for 90 minutes until a clear, homogeneous solution was obtained. This PVA solution served as the polymeric matrix for all subsequent formulations. After membrane preparation, $CaCl_2$ and Cr_2O_3 were incorporated into the solution. $CaCl_2$ was added first and stirred for 90 minutes to promote ionic interactions and improve moisture absorption. Cr_2O_3 powder was dispersed by pre-sonication in water to enhance uniformity before being introduced into the PVA–$CaCl_2$ mixture. Multiple formulations were produced by varying the ratios of PVA, $CaCl_2$, and Cr_2O_3 to optimize viscosity, homogeneity, flexibility, and pigment distribution. These were designated with experimental codes as summarized in Table 1. Samples were evaluated based on texture, dispersion quality, swelling behavior, flexibility, and uniformity. Among the initial formulations, sample F0 showed the best performance, prompting further optimization of pigment concentration in samples F1–F3.

Table 1. The Composition of different samples

Sample	Water (ml)	PVA (grams)	$CaCl_2$ (grams)	Cr_2O_3 (grams)	Pigment Size
Sample A	100%	15%	4%	3%	54 nm
Sample B	100%	12%	1%	1.6%	54 nm
Sample C	100%	10%	4%	4%	54 nm
Sample D	100%	10%	2%	3%	54 nm
Sample E	100%	10%	2%	5%	54 nm
Sample F_0	100%	10%	1%	2.016%	54 nm
Sample F_1	100%	10%	1%	2.016%	225 nm
Sample F_2	100%	10%	1%	2.016%	230 nm
Sample F_3	100%	10%	1%	2.016%	250 nm

The prepared casting solutions were then poured onto glass or PTFE substrates and spread using a doctor blade. To achieve improved control of film thickness, later samples were cast using a micrometer-adjustable film applicator. The films were dried in an oven at 60 °C to ensure uniform

solvent evaporation and proper polymer network formation. Both air-drying and vacuum-drying methods were investigated, with vacuum-dried samples exhibiting superior flexibility and stretchability due to more efficient moisture removal under controlled conditions. A schematic representation of the fabrication process is shown in Figure 1.

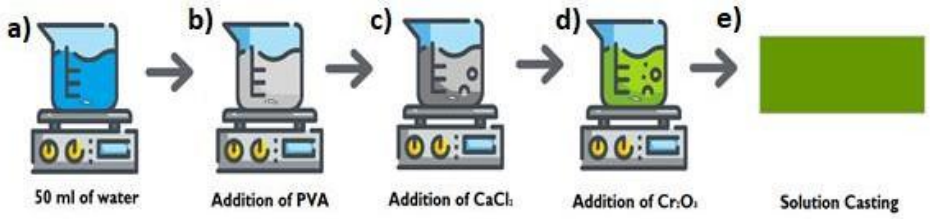

Figure 1. Diagrammatic representation of the biomimetic material's preparation steps, involving the addition of PVA, CaCl2, and Cr2O3 followed by solution casting.

3. Results and Discussion

3.1 Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM-EDS)

The SEM imaging results, shown in Figure 2, reveal a well-defined structure with uniform porosity across the biomimetic membrane. EDS analysis of Spectrum 1 confirms the successful incorporation of Cr_2O_3, PVA, and $CaCl_2$, with major elemental contributions from Cr (44.90%), C (19.86%), O (9.87%), Cl (9.87%), and Ca (5.78%). The consistent elemental distribution indicates effective material integration during synthesis.

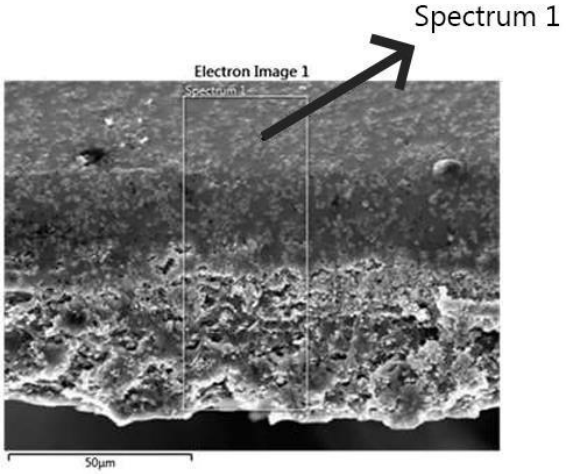

Figure 2. SEM Cross-sectional Image Showing Spectrum 1 + EDS Spectrum 1 with Element Weight Percentages

Further cross-sectional analysis, shown in Figure 3, highlights compositional variations across the internal layers. The Spectrum 18 and 19 also show balanced proportions of C (26.20%), O (22.23%), Cl (11.18%), Ca (7.08%), and Cr (32.79%), demonstrating a well-mixed region and confirming the stability of the composite throughout the membrane's depth. Collectively, the SEM-EDS results validate the structural uniformity, successful elemental incorporation, and controlled layering of the material, enhancing the functional performance and reliability of the developed biomimetic membrane.

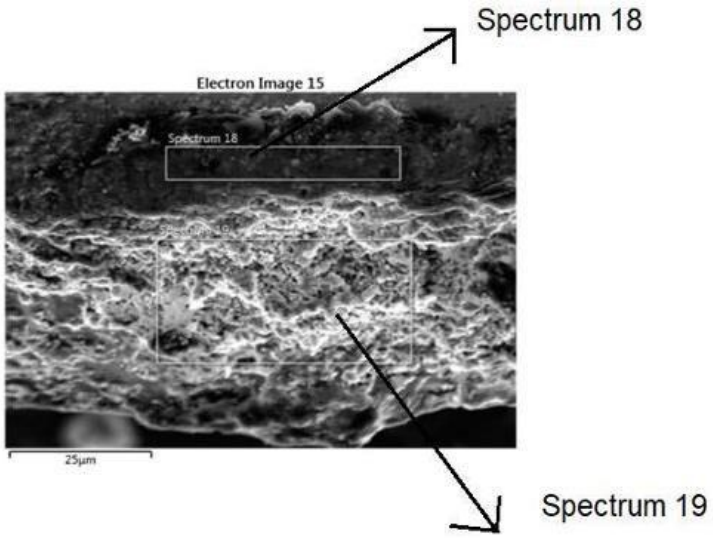

Figure 3. SEM Cross-sectional Image Showing Spectrum 18 AND 19 + EDS Results with Element Weight Percentages

3.2 X-Ray Diffraction (XRD)

The XRD spectra of PVA Powder (S1), PVA and $CaCl_2$ (S2), and the biomimetic sheet (F_3) are presented in Figure 4. The characteristic diffraction peak at 19.2° in S1 confirms the semi- crystalline structure of native PVA. Upon incorporation of $CaCl_2$, (S2) the reduced intensity of the peak indicates the loss of crystallinity, reflecting the disruption of interchain ordering.

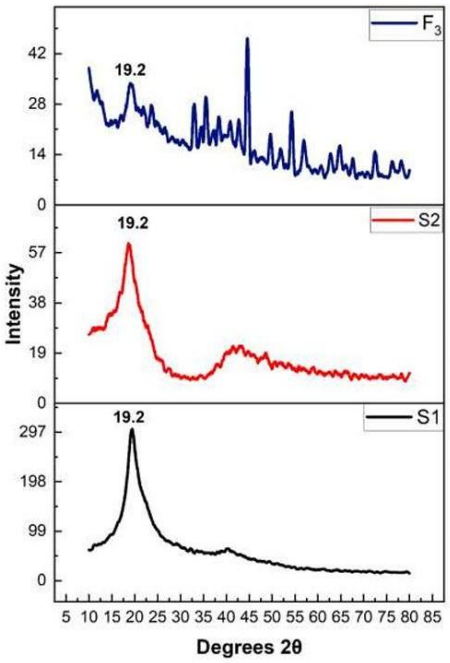

Figure 4. The XRD Spectra of PVA Powder (S1), PVA + $CaCl_2$ (S2), and the Biomimetic Sheet (F_3)

Finally, the biomimetic sheet (F_3) shows the disappearance of the sharp, characteristic peak at 19.2° found in the PVA sheet. The reason was concluded to be that the introduction of $CaCl_2$ disrupted PVA's

hydrogen-bonding network, resulting in a predominantly amorphous and flexible structure[13][14]. This structural transition directly enhances the mechanical pliability of the biomimetic material.

3.3 Hydrophobicity Test

The hydrophobicity of the PVA membranes was measured using a standard contact angle meter. Table 2 shows the contact angles of Sample F1, F2, and F3, wherein the average contact angles are 59.183°, 61.404°, and 72.114°, respectively, indicating the behavior of the three PVA membranes.

Table 2: The Contact Angles of Sample F_1, F_2, and F_3

No.	Sample	Contact Angle
1.	Sample 'F_1'	59.183°
2.	Sample 'F_2'	61.404°
3.	Sample 'F_3'	72.114°

Although the fabricated biomimetic sheets are not fully hydrophobic ($\theta > 90°$), they exhibit significantly increased water angles compared to fully wettable surfaces ($\theta < 30°$). In addition, while pure PVA shows a contact angle of 45.5°, the biomimetic sheets, modified with $CaCl_2$ and Cr_2O_3, demonstrated contact angles between 60° and 72°. These values increased with decreasing chromium oxide particle size, particularly between 250 and 225 nm, indicating a promising shift toward hydrophobicity and the real-time usability of the bionic membrane. Further, while the surfaces fall within the moderately hydrophilic range, the outcomes match the intermediate wetting phenomena observed in natural leaves [15]. It also provides critical insight into how material choice and surface micro-structuring affect wettability.

3.4 Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR)

The ATR-FTIR spectra for samples F_1 (Figure 5), F_2 (Figure 6), and F_3 (Figure 7) confirm the successful formation of PVA-$CaCl_2$-Cr_2O_3 composites and show how Cr_2O_3 particle size affects molecular interactions within the matrix. The first sample (Sample F_1) showcases a broad -OH stretching band at 3355 cm^{-1}, indicating extensive hydrogen bonding in the PVA–$CaCl_2$ network, slightly shifted compared to F_3, suggesting stronger PVA–Ca^{2+} interactions or higher moisture content. Peaks at 3006 cm^{-1} (C–H stretching) and 1413/1015 cm^{-1} (C–H bending and C–O stretching) confirm preservation of the PVA backbone. CO_2-related absorptions at 2355 and 2167 cm^{-1} indicate ambient CO_2 interaction. The 1699 cm^{-1} band reflects strong hydrogen-bond formation.

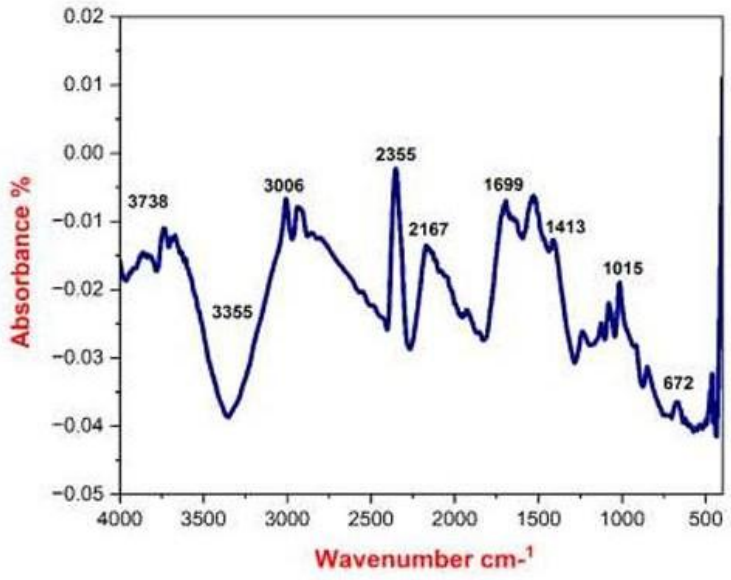

Figure 5. The ATR-FTIR of sample 'F₁'

In comparison, sample F_2 exhibits dual –OH absorptions at 3668 and 3354 cm^{-1}, revealing partial disruption of PVA–PVA hydrogen bonding and the emergence of weakly bound –OH groups, attributed to Ca^{2+} coordination and vacuum drying. Further peaks at 2998 cm^{-1} (C–H stretching) and 1404 cm^{-1} (CH_2 bending) confirm structural stability of PVA, whereas minor C=O features at 2739 and 1985 cm^{-1} suggest slight oxidation. Lastly, the 1593 cm^{-1} and 1077 cm^{-1} bands indicate Ca^{2+}–oxygen interactions and modified C–O stretching.

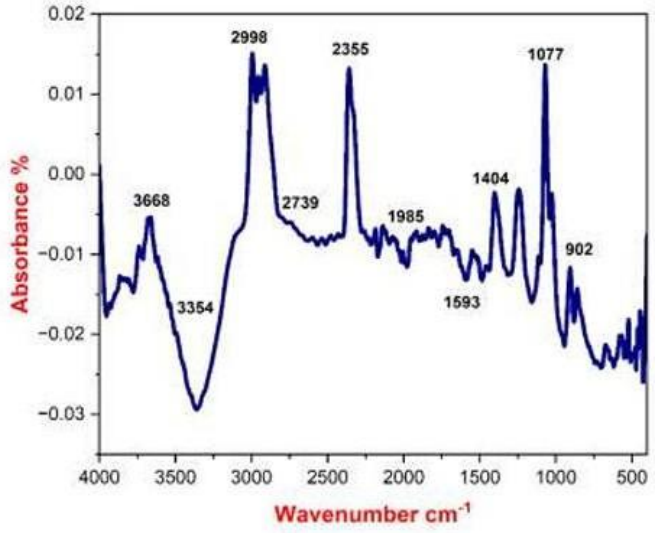

Figure 6. The ATR-FTIR of sample 'F₂'

Finally, sample F_3 exhibits a strong -OH band at 3368 cm^{-1}, indicating substantial hydrogen bonding within the PVA-$CaCl_2$ matrix. C-H stretching at 2977 cm^{-1} confirms preservation of the polymer backbone. A small C=O signal at 1720 cm^{-1} and COO^- signal at 1524 cm^{-1} suggest limited oxidation and minor carboxylate formation via Ca^{2+} coordination. Bands at 1259 and 1064 cm^{-1} correspond to secondary alcohol groups of PVA, confirming chemical integrity.

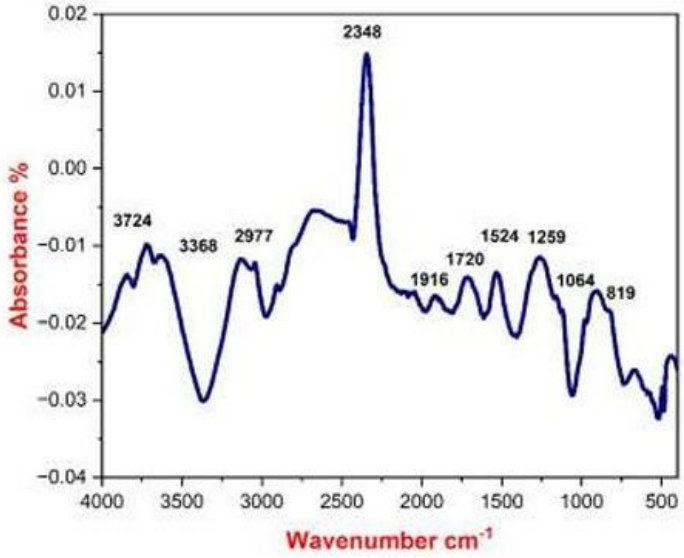

Figure 7. The ATR-FTIR of sample 'F3'

Thus, across all samples, the dominant -OH band at 3368 cm^{-1} confirms hydrophilicity; however, variations in peak intensity indicate that Cr_2O_3 particle size directly influences hydrogen-bonding density and matrix polarity. Moreover, F_2 exhibits slightly reduced –OH absorbance, implying a temporary reduction in surface –OH availability during nanoparticle dispersion. The F_3 sample shows higher C–H absorbance, indicating enhanced structural stability and possible molecular reordering with larger particles. Lastly, absorbance trends within the carbonyl region (1720 cm^{-1}) decrease slightly from F1 to F3, suggesting reduced carbonyl exposure and improved molecular packing as nanoparticle size increases—consistent with a more compact, less polar, and potentially less water-affinitive matrix.

3.5 Radiation Temperature Test

Infrared thermography was used to evaluate the thermal behavior of the biomimetic and natural leaves (Ficus Benjamina) at 11:00 AM, 2:00 PM, and 6:00 PM under similar environmental conditions. The biomimetic sample was positioned adjacent to the natural leaf to ensure direct comparability. As summarised in Table 3, the average surface temperature differences between the two samples were: 0.05°C at 11:00 AM, 0.60°C at 2:00 PM, and 0.25°C at 6:00 PM.

Table 3. The Radiative Temperature Difference between the Biomimetic & Natural Leaf

Time	Natural Max (°C)	Natural Min (°C)	Biomimetic Max (°C)	Biomimetic Min (°C)	Average Temperature Difference (°C)
11:00 AM	37.4	30.0	36.8	30.7	0.05
2:00 PM	36.4	30.3	37	30.9	0.60
6:00 PM	36.2	30.0	36.4	30.3	0.25

These small deviations demonstrate that the biomimetic material closely reproduces the thermal radiation characteristics of natural foliage across varying daytime conditions. The slightly elevated temperature observed at 2:00 PM is consistent with the absence of a biological cooling mechanism (e.g., transpiration) in synthetic materials.

Overall, the infrared results validate the biomimetic leaf's ability to emulate natural radiative cooling behavior, confirming its potential for applications requiring thermal mimicry and bioinspired energy regulation.

3.6 Absorbance & Reflectance Analysis

The absorbance spectrum of the natural leaf (Ficus Benjamina) in Figure 8 shows the characteristic absorbance in the blue region (400-500 nm) and red region (600-700 nm) bands with a pronounced dip near 550 nm (the 'green apex'), where green light is reflected due to chlorophyll. A clear drop in absorbance after 680 nm marks the onset of the red edge, reflecting reduced chlorophyll absorption and increased near-infrared scattering.

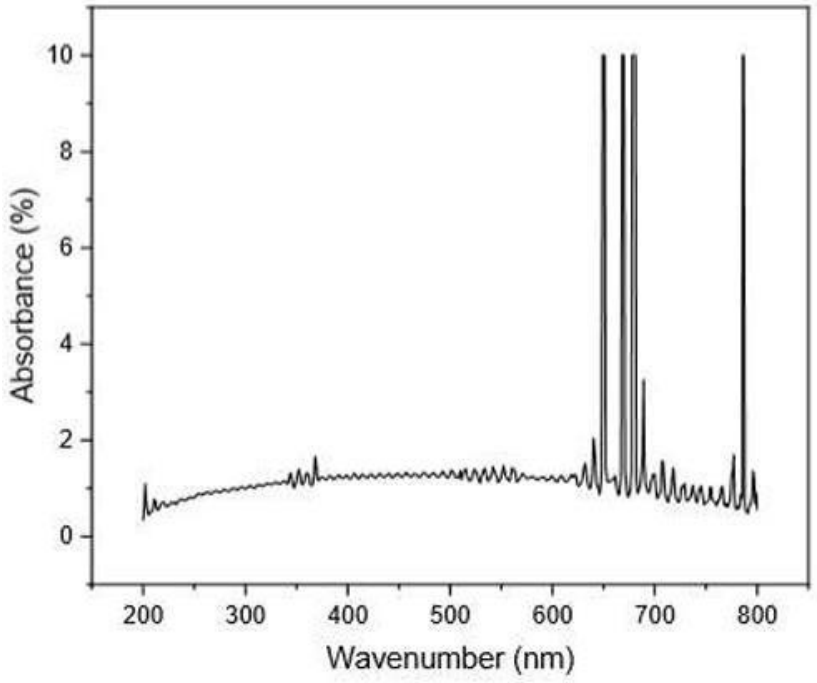

Figure 8. Shows the Wavenumber vs Absorbance Graph of Natural Leaf

In contrast, the Biomimetic material (Figure 9) exhibited broadly low, relatively flat absorbance across 300-700 nm (0.5-1.2 AU). The incorporation of Cr_2O_3 imparts absorption in the blue and red and produces a modest dip near 550 nm, indicating partial green reflectance, while only a faint, gradual red-edge is observed above 680 nm, indicating a partial but encouraging imitation of natural spectral response. The sharp features near 200 nm and between 650-750 nm are likely instrumental artefacts or interference rather than intrinsic material responses. Thus, the biomimetic film reproduces key spectral motifs of the natural leaf while maintaining lower, more uniform absorbance, demonstrating controlled optical tuning via pigment and matrix selection. Although the red-edge response is attenuated compared with Ficus benjamina, the partial spectral mimicry confirms that our composite can emulate essential leaf optical behavior.

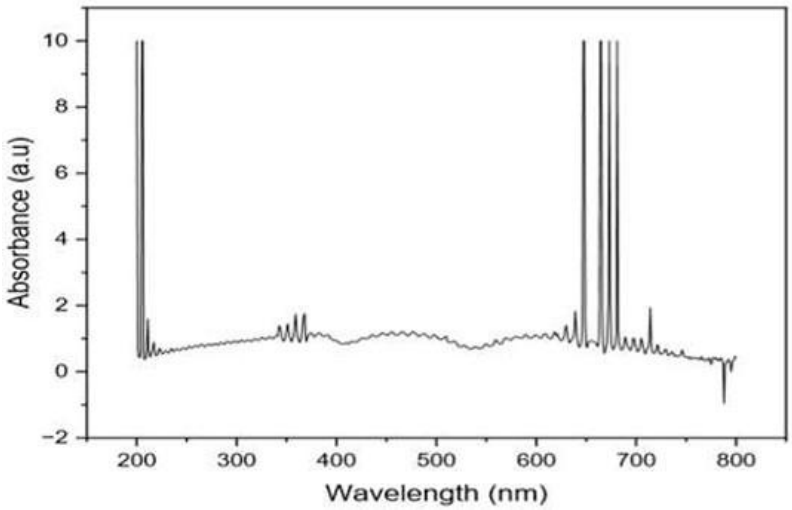

Figure 9. Shows the Wavenumber vs Absorbance Graph of Biomimetic Leaf

The reflectance profile Figure 10, shows the characteristic behavior of healthy green vegetation with low reflectance across the visible range (400-700 nm), particularly in the blue and red regions where chlorophyll strongly absorbs. A rise near 550 nm marks the 'green apex,' responsible for the leaf's green appearance. Beyond 680 nm, a sharp increase in reflectance signals the onset of the red edge, driven by reduced chlorophyll absorption and enhanced near-infrared scattering.

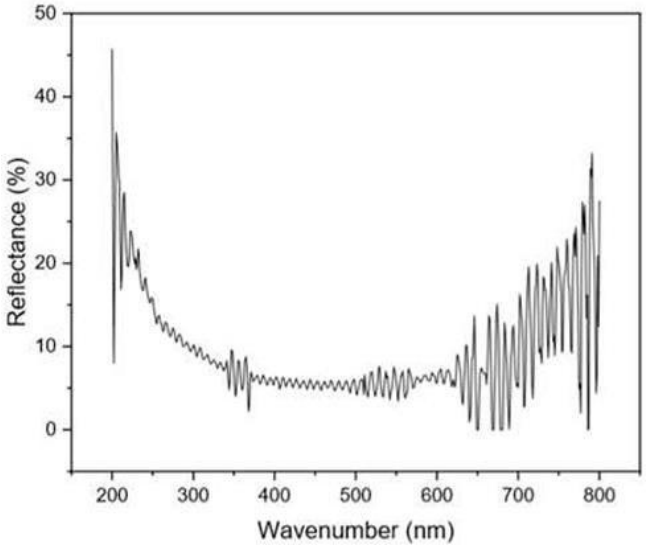

Figure 10. Shows the Wavelength vs Reflectance Graph of Natural Leaf

On the contrary, the biomimetic leaf Figure 11, displays uniformly low reflectance across 200-700 nm, indicating strong absorption in the visible region, consistent with Cr_2O_3 as a green-selective pigment. A mild reflectance rise near 550 nm suggests partial replication of the green apex, though less pronounced than the natural leaf. In the >700 nm region, reflectance shows an abrupt peak near 800 nm attributed to instrumental noise rather than true material behavior, and no smooth red-edge transition is observed. The results demonstrate that the biomimetic membrane successfully reproduces fundamental optical features of natural foliage, validating the effectiveness of pigment selection and composite design. Although the red-edge response is not fully captured, this limitation is likely due to measurement-range constraints rather than material formulation.

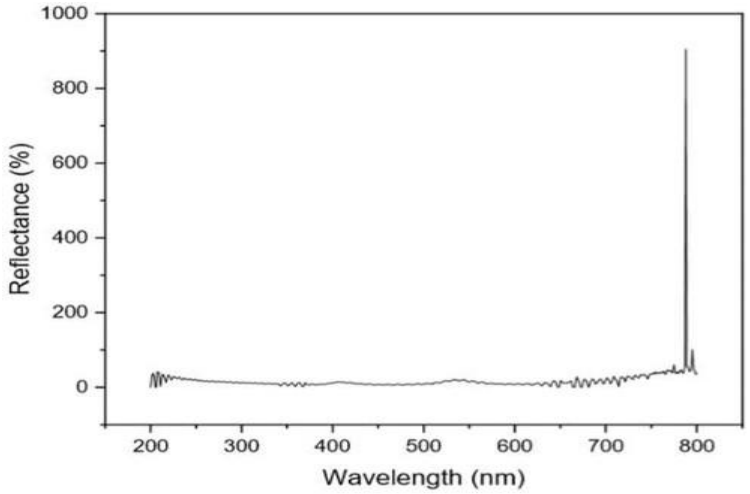

Figure 11. Shows the Wavelength vs Reflectance Graph of Biomimetic Leaf

4. Conclusions

This study successfully developed and characterized biomimetic thin films that mimic the optical spectra of natural leaves, with potential applications in hyperspectral camouflage. In this work, different compositions were synthesized by combining PVA, $CaCl_2$, and Cr_2O_3 via the solution-casting method. Among the samples, the composition with Cr_2O_3 particle size of 250 nm (Sample F3) exhibited optimal hydrophobicity, mechanical flexibility, and green coloration closely resembling natural leaves.

Systematic variation of PVA, $CaCl_2$, and Cr_2O_3 content identified 10 wt.% PVA as the optimal concentration, providing reduced swelling, enhanced mechanical performance, and improved compatibility with $CaCl_2$. Controlled temperature processing conditions, such as 90 °C during stirring and 60 °C during drying, lead to the development of films with near uniformity, minimal bubbles, and brittleness. Nanoparticles in the 230–250 nm range demonstrated superior structural mimicry and optical properties.

Detailed characterization proved the performance of the material: XRD showed that the addition of $CaCl_2$ reduced the crystallinity of PVA, enhancing the flexibility of the membrane.ATR-FTIR spectra showed strong hydrogen bonding and confirmed that the chemical structure was stable, proving that the interactions between Ca^{2+} and PVA were effective. The contact angle measurements proved that hydrophobicity was improved, with Sample F3 reaching up to 72.11°, resembling natural leaf behavior. SEM and EDS mapping showed consistent surface morphologies and homogeneous elemental distributions to prove homogeneity in the film. Thermal emissivity tests proved its resemblance to natural leaves, which could be used in infrared camouflage applications, while UV-vis spectroscopy confirmed that the films' optical properties matched the natural leaf spectra.

Overall, replacing lithium chloride with the more affordable and locally available calcium chloride produced biomimetic films with near-natural properties, offering a cost-effective, environmentally friendly alternative for applications in camouflage and leaf-mimicking materials.

5. Acknowledge

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Green-Synthesized CeO2 and CeO2-TiO2 Nanoparticles for Hydrophobic, Corrosion-Resistant, and Antifungal Surface Coatings

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ABSTRACT

This study reports the green synthesis of cerium oxide (CeO_2) and ceria-doped titanium dioxide (CeO_2– TiO_2) nanoparticles using plant extracts and their application in multifunctional protective coatings. CeO_2 and TiO_2 nanoparticles were synthesized using neem and jasmine extracts, respectively, and subsequently doped to form CeO_2–TiO_2 nanocomposites. The nanoparticles were incorporated into a chitosan matrix and applied onto mild steel and glass substrates via spin coating. Structural, optical, mechanical, and functional properties were evaluated using XRD, UV–Vis spectroscopy, SEM-EDX, contact angle measurements, scratch and Calo testing, linear polarization resistance, and antifungal analysis. Results showed enhanced crystallinity, surface morphology, adhesion, wear resistance, and corrosion protection with increasing nanoparticle content. CeO_2-based coatings exhibited improved hydrophobicity, while CeO_2–TiO_2 coatings showed superior mechanical and corrosion performance, demonstrating their potential for environmentally friendly surface protection applications.

Keywords: Antifungal coatings; Cerium oxide; Corrosion resistance; Green synthesis; Hydrophobicity

1. Introduction

The demand for durable and environmentally friendly surface protection technologies has increased due to growing concerns over corrosion, moisture degradation, and microbial contamination. Conventional coating systems often rely on toxic chemicals and energy-intensive processes, raising environmental and health concerns. Nanotechnology provides an effective route to engineer multifunctional coatings with improved surface wettability, corrosion resistance, and durability through nanoscale material control [1,2].

Cerium oxide (CeO_2) nanoparticles are of particular interest because of their reversible Ce^{3+}/Ce^{4+} redox behavior, high oxygen storage capacity, and thermal stability. These properties enable CeO_2 to form protective oxide layers that enhance corrosion resistance and impart intrinsic hydrophobicity [3,4]. Titanium dioxide (TiO_2) is widely used in surface coatings due to its chemical stability, UV-shielding ability, and photocatalytic properties [5]. When combined, ceria-doped titania (CeO_2–TiO_2) systems exhibit synergistic effects, including improved coating adhesion, charge transfer, and corrosion protection compared to individual oxides [6,7]. Recent attention has shifted toward green synthesis of nanoparticles as a sustainable alternative to conventional chemical routes. Plant-extract-mediated synthesis utilizes naturally occurring phytochemicals as reducing and stabilizing agents, minimizing the use of hazardous chemicals while producing nanoparticles with comparable functional performance [8,9]. In parallel, biopolymers such as chitosan are increasingly employed as coating binders due to their biodegradability, film-forming ability, and strong adhesion to metallic and glass substrates [10].

Despite these advances, limited studies have comprehensively evaluated green-synthesized CeO_2 and CeO_2–TiO_2 nano coatings for combined hydrophobic, corrosion-resistant, and antifungal performance on both metal and glass substrates.

The objective of this study is to synthesize CeO_2 and CeO_2–TiO_2 nanoparticles using green routes and to develop chitosan-based nanocoating via spin coating. The coatings are systematically evaluated for hydrophobicity, corrosion resistance, mechanical durability, and antifungal behavior, aiming to demonstrate their potential as sustainable multifunctional protective coatings.

2. Materials and Method

2.1.Materials

The raw materials used in the green synthesis of NPs (i.e., CeO2, TiO2, and CeO2–TiO2), the preparation of coating solutions, and in the antifungal tests, are as follows: Neem leaves, Jasmine flowers, Distilled Water, Cerium (III) Nitrate Hexahydrate ($Ce(NO3)3{\cdot}6H2O$; 99% purity; Sigma-Aldrich), Titanium Tetra Isopropoxide (TTIP; $C_{12}H_{28}O_4Ti$; 97% purity; Sigma-Aldrich), Acetic Acid ($CH3CO2H$; 99.8% purity; Sigma-Aldrich), Chitosan (CS; low molecular weight; ≥75% deacetylated; Sigma-Aldrich), Agar-agar powder (microbiological grade; Sigma-Aldrich), and Saccharomyces cerevisiae (commercially available as Rossmoor Instant Yeast).

2.2.Method

2.2.1 Green Synthesis of CeO2 NPs using Neem Leaves

The green synthesis of CeO_2 nanoparticles was carried out using neem extract, following a previously reported method with slight modifications [11]. For neem extract, fresh neem leaves were thoroughly cleaned with distilled water to remove any contaminants, and then dried at room temperature. The dried leaves were crushed into a fine powder, and 2g of this powder was added to 100 mL of distilled water. The mixture was heated to 80°C for 2.5 hours with constant stirring, to extract the active ingredients. This mixture was then filtered to obtain a clear neem extract.

The precursor solution was prepared by dissolving 1.2 g of cerium nitrate hexahydrate (CNH) in 25 mL of distilled water. This solution was then mixed with the neem extract, and the resulting reaction mixture was heated to 60°C for 2 hours while stirring. Precipitates formation was observed throughout the reaction, indicating the successful synthesis of CeO_2 NPs. The crystal settled at the bottom of the beaker were collected and transferred to a ceramic crucible. They were dried at 150°C for 6 hours in a drying oven, followed by calcination at 500°C for 3 hours in a muffle furnace. This process resulted in the successful formation of cerium oxide nanoparticles. A schematic representation of the synthesis process is provided in Figure 1.

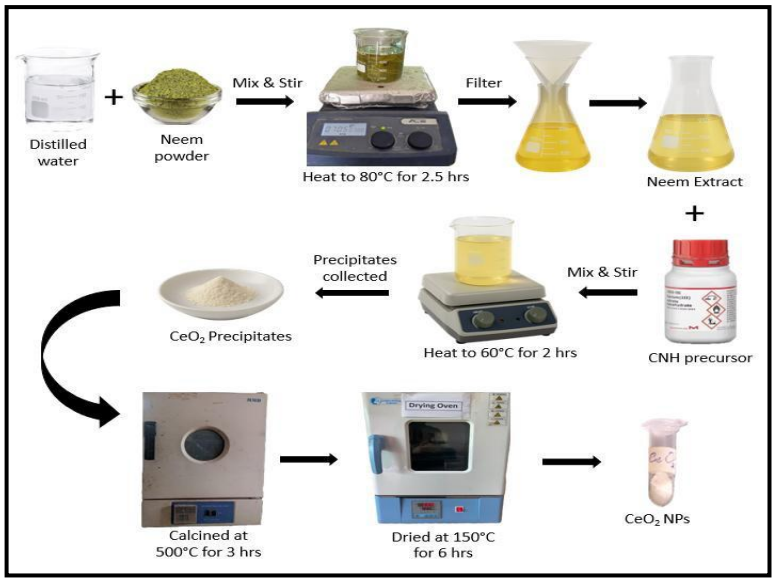

Figure 1. Schematic representation of CeO_2 NPs synthesis using neem.

2.2.2 Green Synthesis of TiO_2 NPs using Jasmine flowers

The green synthesis of TiO_2 nanoparticles was carried out using jasmine extract, adapted with slight modifications as demonstrated in [12]. For jasmine extract, 50g of fresh jasmine flowers were collected and mixed with 100 mL of distilled water in a 1:2 (w/v) ratio. The mixture was heated to 100°C for 30 minutes to extract the active plant components. This mixture was then filtered to obtain a pale colored jasmine extract.

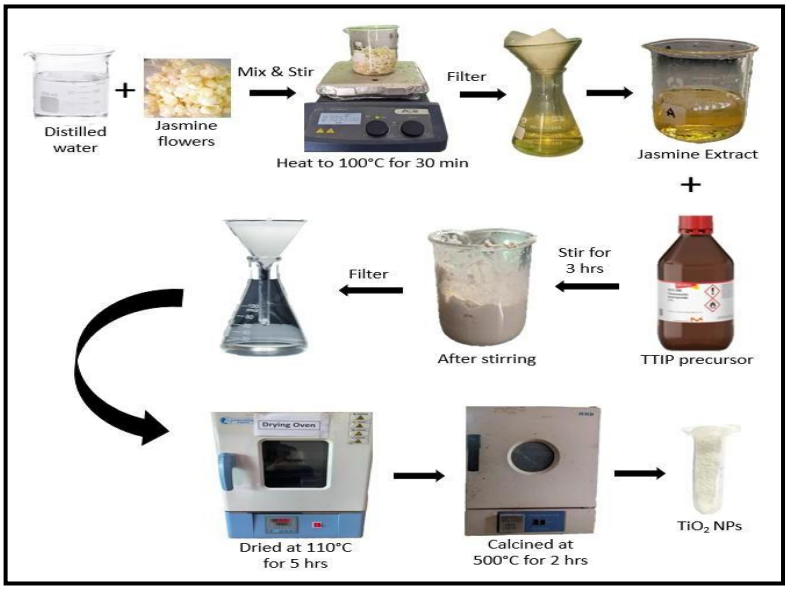

Figure 2. Schematic representation of TiO_2 NPs synthesis using jasmine.

50 mL of Titanium Tetra Isopropoxide (TTIP) was taken as the precursor solution and 20 mL of the prepared jasmine extract was added to it dropwise under continuous stirring at room temperature for 3 hours. During this period, a gradual color change was observed from white to yellowish grey, indicating the formation of TiO_2 NPs. The resulting reaction mixture was filtered to eliminate residual impurities and the filtrate was transferred to a petri dish which was dried at 110°C for 5 hours in a drying oven, followed

by calcination at 500°C for 2 hours in a muffle furnace. This process resulted in the successful formation of TiO_2 nanoparticles. A schematic representation of the synthesis process is provided in Figure 2.

2.2.3 Synthesis of CeO2 – doped TiO2 NPs

For the preparation of CeO2–doped TiO_2 nanoparticles, equal masses (50:50 ratio by weight) of the green-synthesized CeO_2 and TiO_2 nano powders were dispersed in 30 mL of distilled water. The suspension was ultrasonicated for 20 minutes to ensure uniform dispersion and intimate mixing. The resulting composite mixture was filtered and dried at 80 °C for 12 hours. The composite was successfully obtained using a method adapted from [13]. A schematic representation of the synthesis process is provided in Figure 3.

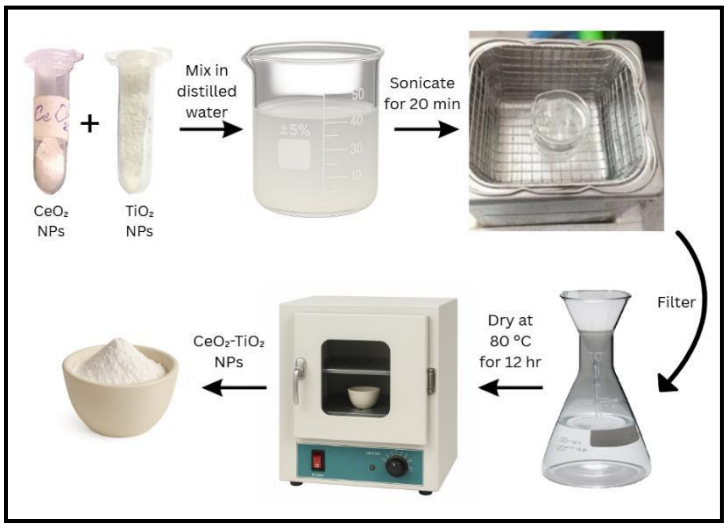

Figure 3. Schematic representation of CeO_2-TiO_2 NPs synthesis.

2.2.4 Preparation of Coating Solution

To prepare the chitosan solution, 75 mL of a 1% acetic acid was heated to 50 °C and 2 grams of chitosan was gradually added. This was stirred continuously for about 9 hours to allow the chitosan to fully dissolve. Once the solution became uniform, it was filtered to remove any remaining undissolved particles. This process resulted in a homogenous chitosan solution suitable for nanoparticle dispersion.

Four different types of nanoparticle dispersions were prepared by dispersing the synthesized nanoparticles in distilled water. These included: 1% CeO_2, 2% CeO_2, 1% CeO_2-TiO_2, and 2% CeO_2-TiO_2. Each nanoparticle type was dispersed in 2 mL of distilled water and were sonicated for a period of 30 minutes to ensure uniform dispersion and prevent agglomeration.

After sonication, 2 mL of each nanoparticle dispersion was mixed with 6 mL of the previously prepared chitosan solution. This yielded a total of five coating formulations: Chitosan only, 1% CeO2-chitosan, 2% CeO2-chitosan, 1% CeO_2-TiO_2-chitosan, and 2% CeO_2-TiO_2-chitosan.

2.2.5 Spin Coating

The prepared coating solutions were deposited on glass and mild steel substrates using a spin coater, where the solution was spread uniformly by centrifugal force and the solvent evaporated during spinning to form a solid film. Spin coating was carried out at a speed of 150 rpm for 30 s with an acceleration (ramp) rate of 100 rpm/s.

Each type of coating was applied to both mild steel substrates and glass, as shown in Figure 4 and Figure 5. A total of six samples were prepared for each substrate type: Uncoated, Chitosan coated, 1% CeO2- chitosan coated, 2% CeO2-chitosan coated, 1% CeO_2-TiO_2-chitosan coated, and 2% CeO_2-TiO_2-chitosan coated.

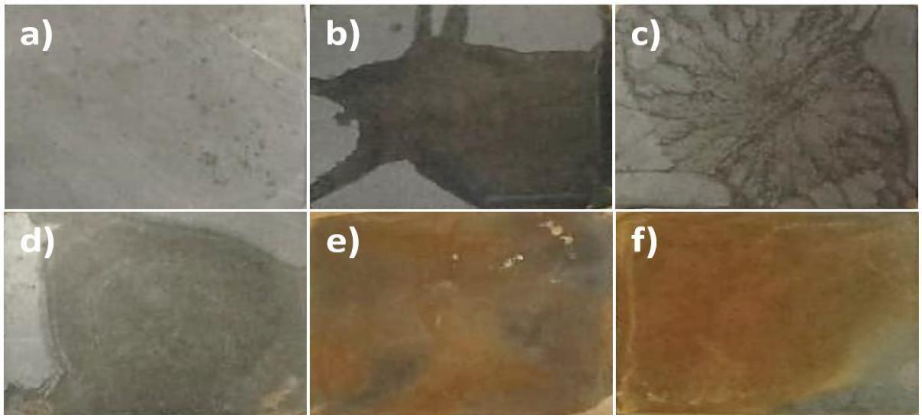

Figure 4. Spin coated mild steel samples: (a) Uncoated, (b) Chitosan only, (c) 1% CeO_2- chitosan, (d) 2% CeO_2-chitosan, (e) 1% CeO_2-TiO_2-chitosan, (f) 2% CeO_2-TiO_2-chitosan.

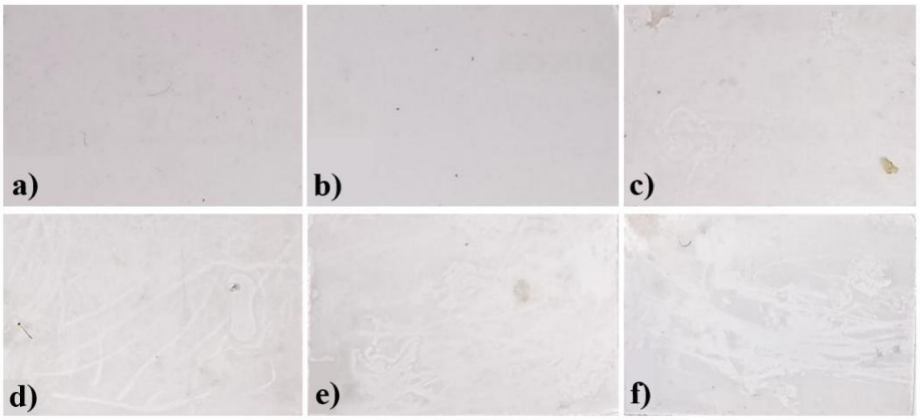

Figure 5. Spin coated glass samples: (a) Uncoated, (b) Chitosan only, (c) 1% CeO_2-chitosan, (d) 2% CeO_2-chitosan, (e) 1% CeO_2-TiO_2-chitosan, (f) 2% CeO_2-TiO_2-chitosan.

2.3 Characterization Techniques

X-ray diffraction (XRD) was used to examine the crystal structure, phase purity, and average crystallite size of the synthesized CeO_2 NPs and their coated samples, with crystallite size estimated using the Scherrer equation. UV–Visible spectroscopy was employed to confirm CeO_2 nanoparticle formation and evaluate their optical properties through characteristic absorption peaks.

Energy-dispersive X-ray (EDX) analysis was used to determine the elemental composition of CeO_2–chitosan coatings on mild steel substrates, while scanning electron microscopy (SEM) was employed to examine surface morphology at different magnifications for varying nanoparticle concentrations.

Calo and scratch tests were conducted to characterize CeO_2 and CeO_2–TiO_2 nanoparticle coatings deposited on substrates. The calo test measured coating thickness based on the geometry of the wear

crater formed during testing, while scratch testing assessed the mechanical durability and adhesion strength of the coatings.

Linear Polarization Resistance (LPR) measurements were performed to evaluate the corrosion behavior of mild steel surfaces coated with CeO_2 and CeO_2–TiO_2 nanoparticle-reinforced chitosan films. A small overpotential (±10–20 mV) was applied around the open circuit potential (OCP), and the resulting current response was used to determine the polarization resistance (R_p). Coated samples were tested electrochemically in 3.5 wt% NaCl solution to assess corrosion performance.

The hydrophobicity of CeO_2 and CeO_2–TiO_2 nanoparticle coatings in a chitosan matrix on glass substrates was evaluated using contact angle measurements via the sessile drop method. A 2–5 µL water droplet was placed on the coated surface, and the contact angle (θ) was measured using image analysis software such as ImageJ.

The antifungal activity of CeO_2 and CeO_2-TiO_2 nanoparticle coatings in a chitosan matrix was evaluated using the standard agar diffusion method. Yeast or fungal cultures were spread on agar plates, and coated glass slides were placed face-down on the surface. Plates were incubated at room temperature for 24–48 hours to assess potential inhibition of fungal growth.

3. Results and Discussion

3.1 XRD

The X-ray diffraction (XRD) pattern of the synthesized cerium dioxide (CeO_2) nanoparticles, as seen in Figure 6, exhibits distinct peaks at 2θ values of 28.5°, 33.1°, 47.5°, 56.3°, 59.1°, and 69.4°, corresponding to the (111), (200), (220), (311), (222), and (400) planes, respectively [14]. The presence of these sharp and defined peaks confirms the successful formation of a single-phase crystalline structure [15]. Moreover, the broadness of the peaks indicates a nanocrystalline nature of the particles.

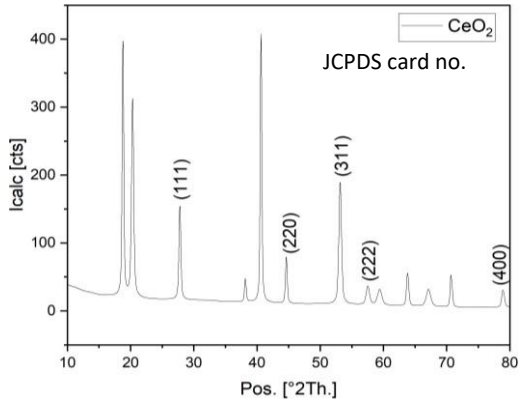

Figure 6. XRD spectrum of CeO_2 nanoparticles.

Table 1 presents the calculation of particle size for the synthesized CeO2 nanoparticles. Based on the data, the average crystallite size was calculated to be around ~10.95 nm, further supporting the nanoparticulate form of the material [16]. The calculations were done by using the Debye–Scherrer formula, which is given by:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (4.1)$$

where D is the crystallite size, K is the shape factor (typically ~0.9), λ is the X-ray wavelength (λ = 1.540), β is the full width at half maximum (FWHM) of the diffraction peak in radians, and θ is the Bragg angle.

Table 1. Particle size calculation.

β (radians)	2θ (degrees)	D (nm)
0.787	28.05	10.5
0.787	39.651	10.8
0.787	44.685	11.0
0.787	55.267	11.5

In addition to the main peaks, a few minor peaks appear at other 2θ values that are not assigned in the standard CeO_2 pattern. These may result from surface defects, residual stress within the crystal lattice, or slight preferred orientation effects during sample preparation [17]. It is also possible that these minor peaks are due to trace impurities or intermediate by-products not completely removed during the synthesis and annealing process. However, the intensity of these unmatched peaks is very low and does not significantly affect the overall phase identification. The dominance of the major peaks confirms the purity and crystallinity of the CeO_2 nanoparticles, indicating that the microwave-assisted route effectively produces nanocrystalline ceria with a well-defined fluorite structure [18].

The XRD analysis of coated samples of CeO2 and CeO2-TiO_2 and chitosan coating on mild steel substrates reveals distinct variations in phase composition and crystallinity, as shown in Figure 7, influenced by dopant type and concentration [19] [20].

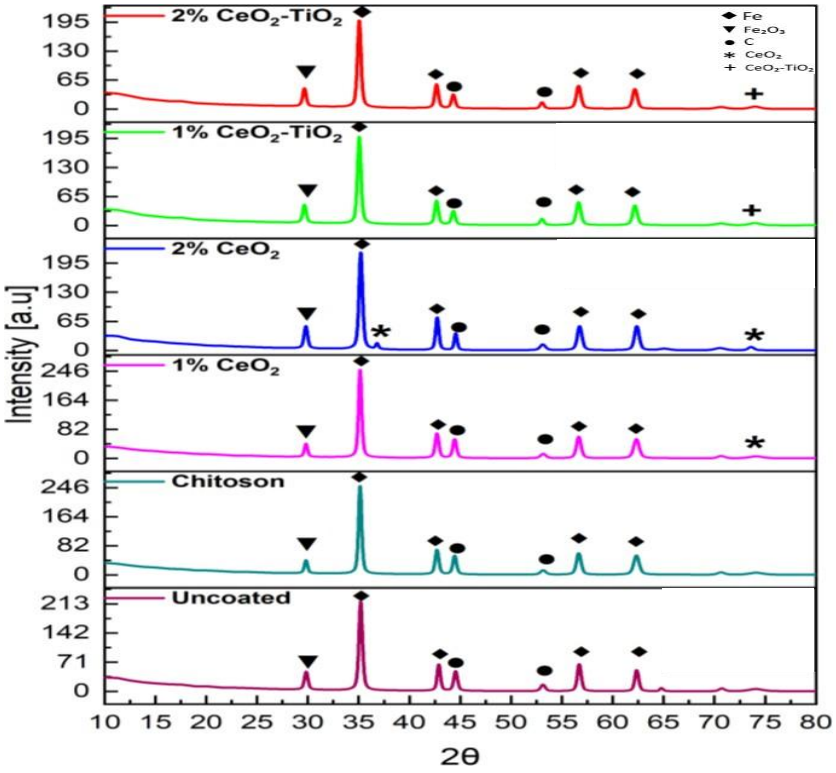

Figure 7. XRD spectrums of uncoated, chitosan coated, and coatings containing 1% CeO_2, 2% CeO_2, 1% CeO_2-TiO_2, and 2% CeO_2-TiO_2 nanoparticles.

The uncoated mild steel substrate exhibits prominent diffraction peaks for elemental iron and iron oxide phases, consistent with typical ferritic steel structures. These peaks remain visible in all samples, suggesting that the underlying substrate contributes significantly to the overall diffraction pattern. The chitosan- coated steel shows the presence of iron peaks along with minor carbon, indicating the organic nature of the biopolymer but lacking any crystalline oxide phases, which confirms the amorphous nature of chitosan on its own [21].

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However, upon doping with cerium oxide, the XRD patterns change noticeably. The 1% CeO_2 coating shows dominant peaks of iron and Fe_2O_3 but only a weak or almost absent CeO_2 (∗) peak, indicating poor crystallinity or low concentration of cerium oxide in the film, insufficient for distinct phase detection [22]. The 2% CeO_2 coating, by contrast, displays identifiable CeO_2 peaks, particularly near $2\theta \approx 28°$ and 47°, suggesting that increased concentration promotes better crystal growth and phase stability. The higher CeO2 loading enhanced crystalline oxide visibility due to improved nucleation during synthesis [23].

Similarly, the 1% and 2% CeO_2-TiO_2 doped coatings show further evolution in structure. At 1% CeO2-TiO2, peaks are not significantly visible, resembling the behavior of 1% CeO_2, and dominated again by iron and oxide peaks. However, the 2% CeO2-TiO2 coating distinctly shows CeO2-TiO2 associated peaks along with more prominent CeO_2 peaks, indicating successful incorporation and crystal formation of doped phases at higher concentration (Mikaeili et al., 2018). The emergence of CeO2-TiO2 peaks at lower intensity

confirms improved dopant diffusion and compound formation within the matrix [24]. By increasing ceria content and calcination enhances crystallite formation and peak resolution due to the formation of fluorite-structured CeO_2 and its doped variants. Additionally, the sharpening of CeO_2 peaks in the 2% samples suggests a transition toward more ordered, crystalline structures as particle agglomeration and growth occur with increased dopant mass. These results suggest that 2% doped coatings not only improve crystalline definition but may also contribute to better coating performance in terms of thermal stability and redox activity, consistent with previous observations in ceria-based catalytic and protective films [25].

3.2 UV-Visible Spectroscopy

The UV-Visible absorption spectrum presented in Figure 8, shows a prominent peak at 310 nm, which is a characteristic feature of cerium oxide (CeO_2) nanoparticles. This sharp absorption peak indicates a successful synthesis of CeO_2 NPs and aligns precisely with the peak reported in the reference study by [26], where green-synthesized CeO_2 NPs using neem extract exhibited a peak at the same wavelength. The origin of this peak lies in the charge transfer transition from the O^{2-} valence band to Ce^{4+} conduction band.

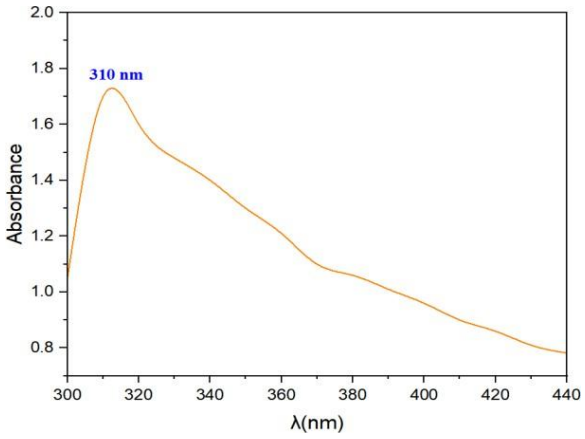

Figure 8. UV-absorption spectrum of CeO_2 nanoparticles.

The sharpness of the peak and its location in the UV region further suggest a high degree of crystallinity and narrow particle size distribution. The gradual decline in absorbance beyond the peak indicates the tailing of the absorption edge, which reflects the semiconducting nature of the nanoparticles. Such behaviour is typically observed in nanoparticles with oxygen vacancies and band gap narrowing effects, which enhance their photoactivity under UV light.

The absorbance at 310 nm confirms the expected optical behaviour of nanoscale CeO_2. This UV absorption is critical for photocatalytic applications, as demonstrated in the reference study by [27], where the CeO_2 NPs achieved a 97.3% degradation of sunset yellow dye under UV irradiation. The presence of oxygen vacancies, confirmed by the reduced band gap of 2.91 eV in the original work, likely plays a significant role in the observed absorbance and reactivity. Additionally, the observed spectrum supports the potential application of these NPs in biomedical fields, as the same optical properties contribute to reactive oxygen species (ROS) generation, enhancing cytotoxic effects against cancer cells. Thus, the UV-Vis result not only confirms successful synthesis but also correlates well with enhanced photocatalytic and biological properties documented in previous studies.

3.3 EDX

The elemental composition of coated samples was analyzed using Energy Dispersive X-ray Spectroscopy (EDX), with results presented for coatings containing different concentrations of CeO_2 nanoparticles.

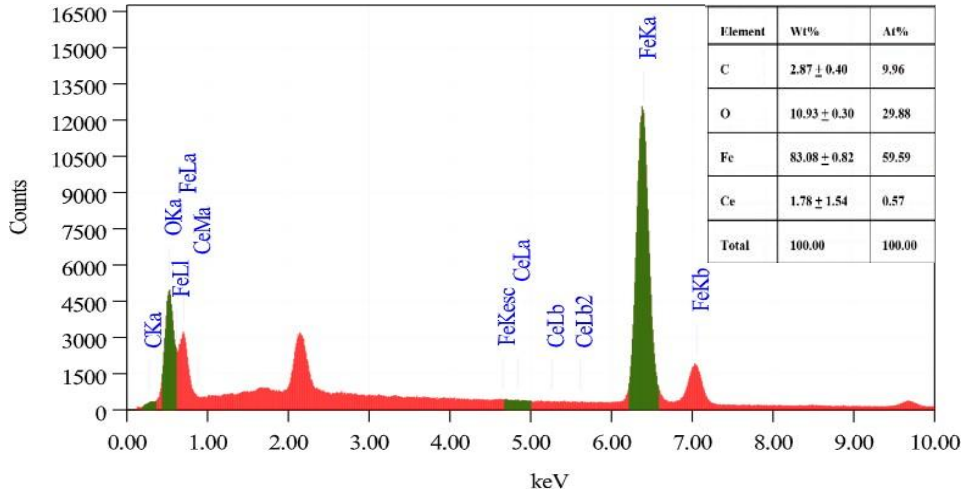

Figure 9. EDX spectrum of 1% CeO_2 NPs coated mild steel sample. The inset table (top right) shows the atomic and weight percentages of the detected

In the EDX analysis of the 1% CeO_2-coated steel sample, the primary elements detected were iron (Fe), oxygen (O), carbon (C), and cerium (Ce), as evidenced by Figure 9. Iron showed a dominant weight percentage of 83.08% and an atomic percentage of 59.59%, reflecting the underlying steel substrate. Oxygen was present at 10.93 wt% and 29.88 at%, indicating the successful formation of metal oxides, mainly CeO_2. The carbon content, attributed to the chitosan matrix, was 2.87 wt% and 9.96 at%, confirming the presence of the biopolymer layer that supports the nanoparticle dispersion. The cerium peak appeared at 1.78 wt% and 0.57 at%, confirming the incorporation of CeO_2 nanoparticles at the intended 1% concentration. These results validate that the chitosan-CeO_2 composite was effectively coated on the steel surface, with a uniform distribution of elements and no foreign impurities [28].

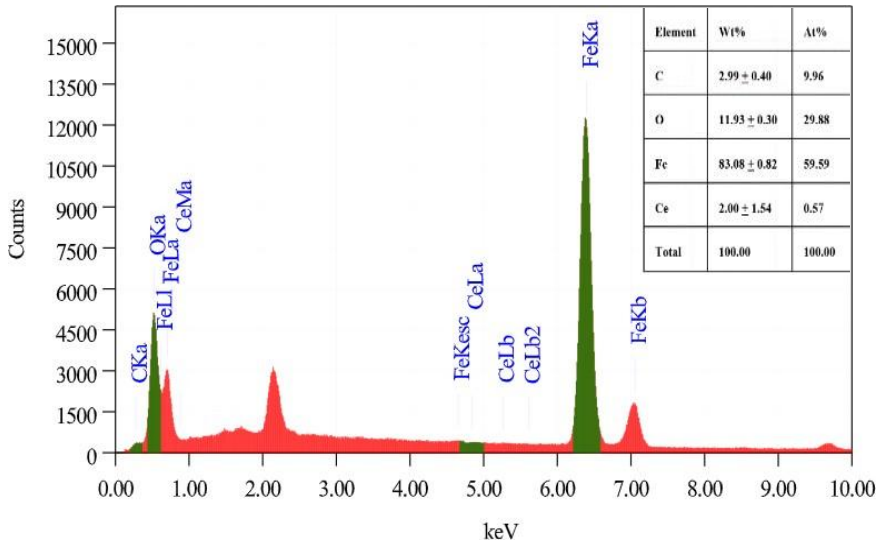

Figure 10. EDX spectrum of 2% CeO2 NPs coated mild steel sample. The inset table (top right) shows the atomic and weight percentages of the sample

For the 2% CeO_2-coated sample, similar elemental peaks were observed, but with slight changes in composition, as depicted in Figure 10. The cerium weight percentage increased to 2.00%, while the atomic percentage remained at 0.57%, indicating an enhanced loading of CeO_2 nanoparticles without significantly altering the atomic distribution due to their small particle size. Oxygen content rose slightly to 11.93 wt%, maintaining the same atomic percentage (29.88%) as in the 1% sample, suggesting consistent oxidation levels. Carbon content also showed a slight increase to 2.99 wt% (9.96 at%), reinforcing the uniform presence of the chitosan layer. Iron content remained unchanged at 83.08 wt% and 59.59 at%. The increase in CeO2 content between the two samples confirms the successful adjustment of nanoparticle concentration, and the consistent elemental profile across both spectra indicates that the chitosan matrix effectively stabilizes and distributes the CeO_2 nanoparticles at different doping levels [29].

3.4 SEM

The SEM analysis of CeO_2–chitosan coatings on mild steel reveals significant differences in morphology and structural integrity depending on ceria concentration and magnification. At lower concentrations (1% CeO2), as shown in Figure 11 (a to c), the coating exhibits visible nanoceria agglomerates and a relatively rough surface with clear signs of porosity and delamination. Cracks are evident, particularly in the cross-sectional image (c), indicating mechanical instability of the coating. The observed delamination may be attributed to poor adhesion between the coating and the substrate, possibly due to internal stresses or insufficient binding from the chitosan matrix. The non-uniform thickness and presence of voids suggest that low CeO_2 content may not sufficiently reinforce the chitosan film, leading to weak barrier performance and potential failure under stress or corrosion environments.

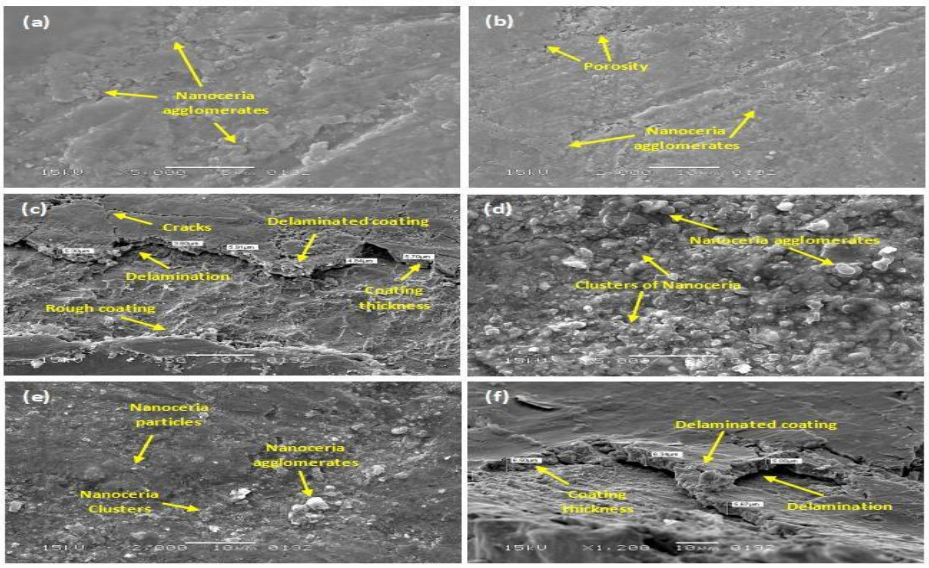

Figure 11. SEM images of nanoceria coating on mild steel substrate at varying magnifications: (a–c) 1% CeO_2 coating at 5000X, 2000X, and 950X; (d–f) 2% CeO_2 coating at 5000X, 2000X, and 1200X

In contrast, the SEM images of 2% CeO_2 coatings (d, e, f) demonstrate more frequent clustering and denser agglomeration of nanoceria particles. While these clusters may enhance localized redox activity beneficial for catalytic applications, they can also contribute to stress concentrations within the film, resulting in cracks and delaminated zones as seen in image (f). The coating remains porous, and while the higher nanoparticle content increases active surface area, it also exacerbates the formation of defects when not properly dispersed. The interface between the coating and steel substrate in both concentrations shows signs of mechanical failure, indicating that optimal ceria loading and improved dispersion strategies are necessary. These morphological features align with findings in the referenced study, where chitosan-

templated CeO_2 materials showed excellent catalytic potential due to high surface area and porosity, but required controlled synthesis conditions to prevent sintering and preserve structural uniformity [30].

3.5 Calo Test

The thickness of the coated samples was calculated using the Calo test method, based on the geometry of the wear crater produced during testing. The coating thickness (t) was determined using the following formula:

$$t = \frac{XY}{Diameter\ of\ ball} \quad (4.2)$$

where;

where;

X = 2C2- 2C1,

Y = 2C1 + X, and

Diameter of ball = 25 mm

This formula allows for an accurate estimation of the coating thickness by accounting for the spherical geometry of the crater formed. The calculated thickness values for all coated samples are summarized in Table 2, showing unidirectional growth in coating thickness over the samples.

The trend is clear that the addition of cerium and titanium to chitosan-based coatings greatly increases the film thickness, possibly due to a higher rate of deposition efficiency and material build-up. These increases in coating thickness can enhance barrier function and durability, which are essential for such applications as biomedical implants. These results support previous research that has proven the advantages of composite coatings in improving mechanical and protective features [31].

Table 2. Coating thickness of different coatings.

Coating Type	**Thickness (µm)**
Chitosan	0.8
CeO_2 (1%)	9.3
CeO_2 (2%)	13.6
CeO_2-TiO_2 (1%)	19.61
CeO_2-TiO_2 (2%)	22.23

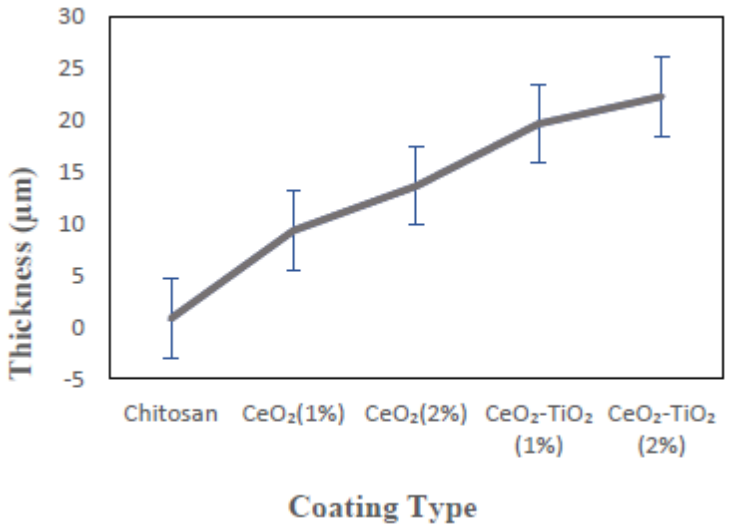

Figure 12 . Comparison of coating thickness across different

The graph in Figure 12, displays the coating thickness obtained from the Calo test for different coating types. Thickness generally correlates with the amount of material deposited and can impact the durability and protective performance of the coating. Pure chitosan has the thinnest layer, while the addition of 1% and 2% ceria progressively increases the coating thickness, indicating that ceria contributes to a better build-up of the layer. The inclusion of both ceria and titania (CeO2-TiO_2) further enhances the coating thickness, with CeO2-TiO_2 (2%) showing the highest value. This trend suggests that combining ceria and titania, especially at higher concentrations, promotes more efficient deposition and results in thicker, more robust coatings.

3.6 Scratch Test

The critical load (Lc) was calculated based on the applied force at which coating failure occurred during the scratch test, and is calculated using the following formula;

$$L_c = (L_2 - L_1) \times \left(\frac{load}{distance\ ratio}\right) + \text{initial load} \qquad (4.3)$$

where;

Lc = Critical Load,

L2 - L1 = Edge Chipping Failure

= 10 N/mm

Initial Load = 10.4 N

The results are summarized in Table 3.

Table 3. Scratch test results: failure initiation length (Lfail), total scratch length (LTotal), and critical load (Lc) for each coating types.

Coating Type	L_{fail} (mm)	L_{Total} (mm)	L_c (N)
Chitosan	2.286	2.292	10.46
CeO_2 (1%)	1.329	2.338	20.49
CeO_2 (2%)	0.939	2.259	23.6
CeO_2-TiO_2 (1%)	0.800	2.246	24.86
CeO_2-TiO_2 (2%)	0.748	2.348	26.2

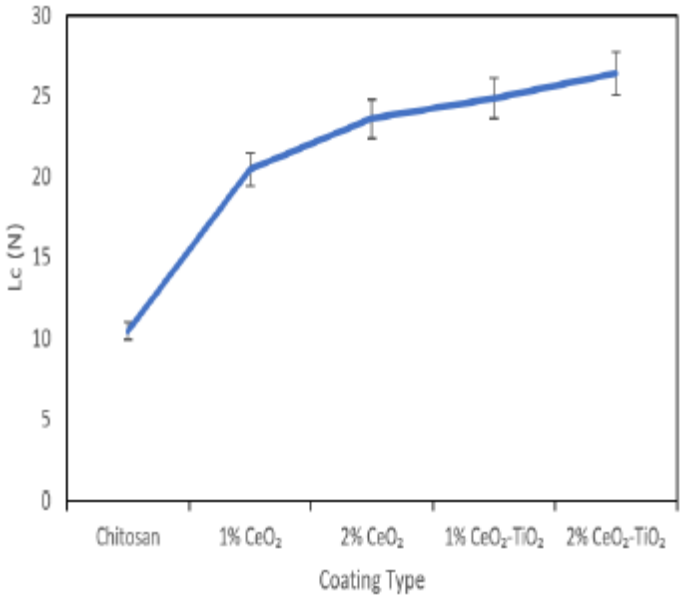

Figure 13 . Graphical comparison of critical load (Lc) and coating type.

Scratch test results indicate varied mechanical performance for the coatings. Chitosan has the lowest critical load (Lc = 10.46 N) and good adhesion to the substrate, though it starts failing relatively early. CeO2 only coatings (1% and 2%) have average performance — CeO2 (1%) resists initial failure for a longer duration (Lfail = 1.329 mm) but has the lower Lc (20.49 N), while CeO2 (2%) shows relatively early failure (Lfail = 0.939 mm) but better adhesion (Lc = 23.6 N), indicating that increased content of CeO2 increases the bonding strength. CeO2-TiO2 (1%) coating has the latest failure occurrence (Lfail = 0.800 mm),

indicating excellent scratch propagation resistance; however, it has the good adhesion strength (Lc = 24.86 N), thus being prone to delamination at lower loads. CeO2-TiO2 (2%) has improved overall performance, with high adhesion (Lc = 26.4 N) and acceptable scratch resistance (Lfail = 0.748 mm), thus being a balanced but strong contender. Overall, though Chitosan has the maximum adhesion and CeO2-TiO2 (1%) has the maximum scratch length resistance, CeO2-TiO2 (2%) is the strongest candidate coating for its overall strong adhesion, cohesive integrity, and well-balanced mechanical strength.

The graph in Figure 13 represents the results of the scratch test, which measures the critical load (Lc) required to initiate failure in the coating, such as cracking or delamination. A higher Lc value indicates better adhesion strength and scratch resistance of the coating. In this graph, pure chitosan shows the lowest critical load, suggesting weak initial adhesion. When 1% ceria (CeO2) is added, the critical load increases significantly, indicating improved bonding or coating uniformity. At 2% CeO2, the critical load further increases, suggesting that a higher concentration of ceria continues to reinforce the coating. Interestingly, the CeO2-TiO_2 (1%) sample exhibits a slightly higher critical load than CeO2 (2%), pointing to enhanced adhesion, possibly due to the synergistic effect of ceria and titania. CeO2-TiO_2 (2%) shows the highest critical load overall, implying that increasing the CeO2-TiO_2 content significantly boosts the mechanical strength and scratch resistance of the coating.

3.7 LPR Corrosion Test

The linear polarization resistance (LPR) test was conducted on six steel samples coated with varying compositions of CeO_2 and CeO_2-TiO_2 at different concentrations to evaluate their corrosion resistance in a 3.5 wt% NaCl solution. The polarization curves were analysed to assess the slope of each sample, as displayed in Figure 14, with a flatter slope indicating a higher polarization resistance (Rp) and hence better corrosion protection.

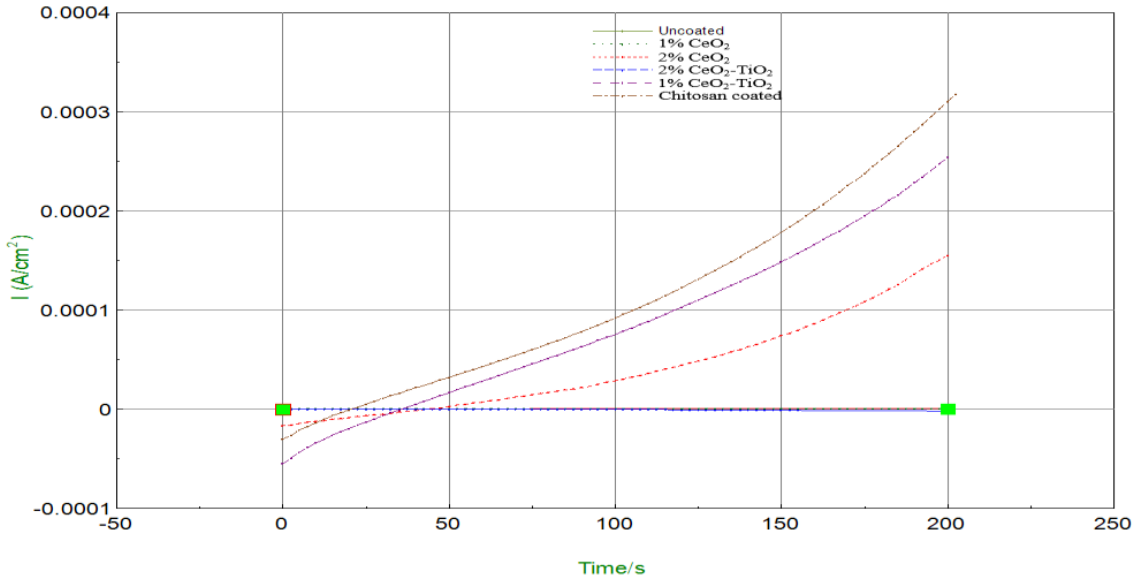

Figure 14. LPR of different coated samples.

The sample coated with 2% CeO_2–TiO_2, displays the flattest slope in the LPR test, protection among all tested coatings. This exceptional performance is attributed to the synergistic interaction between cerium and titanium oxides. The CeO_2 provides mixed-type inhibition through the formation of a redox-stable passive layer, while TiO_2 enhances film compactness and stability. This dual-action mechanism limits both anodic metal dissolution and cathodic reactions, aligning well with literature that shows CeO_2–TiO_2

nanocomposites improve passivation and corrosion resistance through cooperative oxide film formation [32].

The 1% CeO_2–TiO_2, shows a slightly steeper slope than its 2% counterpart but still significantly flatter than the CeO_2-only coatings. This indicates moderate corrosion resistance, suggesting that even at lower concentrations, the CeO_2–TiO_2 composite provides a protective barrier. However, reduced particle loading may result in thinner or more porous films, which offer less uniform coverage.

The sample coated with 2% CeO_2, demonstrates a moderately flat slope, suggesting reasonable corrosion protection. This supports results from Brito-Franco et al., 2024, who found that CeO_2 at 600 ppm significantly reduces corrosion current by forming a stable, adsorbed oxide-hydroxide layer. Though effective, CeO_2 alone lacks the physical reinforcement provided by TiO_2, which explains why this sample underperforms slightly compared to the CeO_2–TiO_2 combination.

The 1% CeO_2, has a noticeably steeper slope, reflecting lower corrosion resistance. At this concentration, CeO_2 nanoparticles are likely insufficient to form a continuous, adherent film on the steel surface, resulting in partial exposure and susceptibility to localized corrosion.

Two other samples, likely represented by the orange and pink curves, show almost straight LPR slopes, which may misleadingly appear as excellent corrosion resistance. However, this behaviour is most likely the result of experimental error, particularly due to improper soldering or weak electrical contact, especially common with very thin or poorly connected samples. Such artifacts can suppress the current response, producing unnaturally flat polarization curves [33].

In summary, the CeO_2–TiO_2 nanocomposite coatings outperformed CeO_2-only films, with 2% CeO_2–TiO_2 delivering the most robust corrosion protection. The role of TiO_2 in enhancing oxide film compactness, in combination with the redox activity of CeO_2, creates a strong passive barrier against corrosion. These findings reinforce the importance of coating composition and nanoparticle synergy in developing high-performance, environmentally friendly corrosion inhibitors.

3.8. Contact Angle (CA) Measurement

Representative water droplet images for the six different glass slide samples are shown in Figure 16, and the corresponding contact angle (CA) results are presented in Figure 15.

The uncoated glass slide, exhibited a low contact angle of 33°, indicating strong hydrophilicity. The chitosan-coated slide showed a slightly reduced hydrophilicity with a contact angle of 25°.

Notably, the introduction of ceria nanoparticles had a significant impact on surface hydrophobicity. The slides coated with 1% and 2% ceria nanoparticles showed contact angles of 87° and 91°, later respectively, with the latter surpassing the hydrophobic threshold of 90°. This indicates that the surface energy was effectively reduced by ceria incorporation, particularly at higher concentrations.

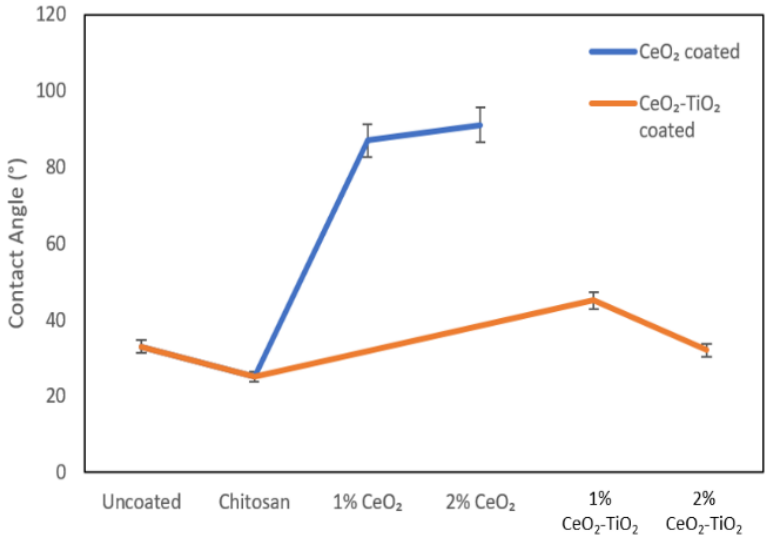

Figure 15. Contact Angle Graph.

Further enhancement was attempted with ceria-titania composite coatings. The 1% CeO_2-TiO_2 coated slide exhibited a moderate contact angle of 45°, whereas 2% CeO_2-TiO_2 yielded a slightly lower angle of 32°. These results suggest that while the addition of titania altered surface behavior, it may have reduced the hydrophobic effect observed with ceria alone. According to studies, nanoceria based coatings exhibit hydrophobicity [34], while CeO_2-doped TiO2 nanoparticle coatings exhibit hydrophilicity [35], which is consistent with the results observed in this work

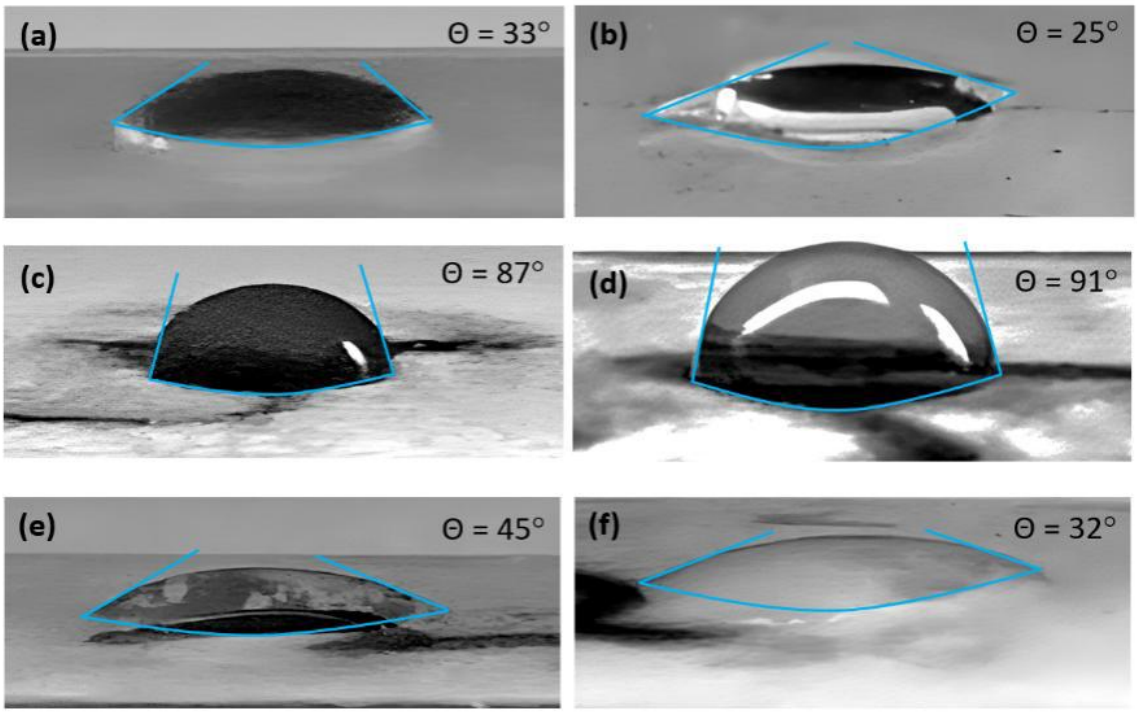

Figure 16 . Contact angle images: (a) uncoate d, (b) chitosan coated, (c) 1% CeO 2 coated, (d) 2% CeO 2 coated, (e) 1% CeO 2 TiO 2 coated, (f) 2% CeO 2 TiO 2 coated

3.9. Antifungal Test

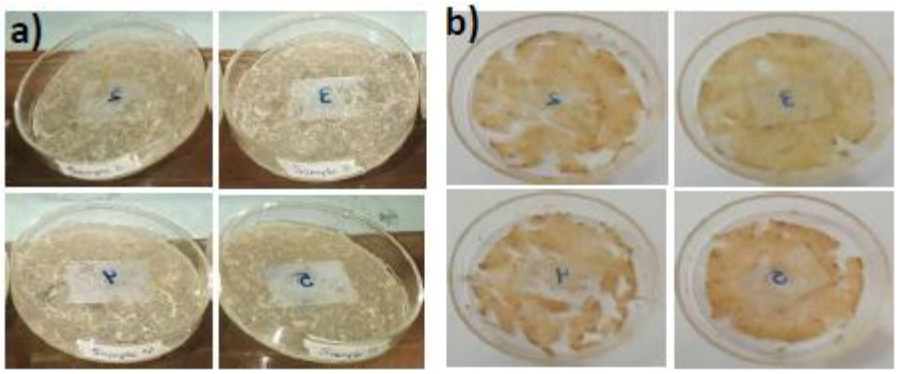

Figure 17 . Yeast inoculated agar plate (a) before, and (b) after incubation.

The antifungal test was carried out using an agar–yeast setup to evaluate the bioactivity of coated glass slides prepared with different nanoparticle compositions. As shown in Figure 17, which presents images of the yeast-inoculated agar plate before and after incubation, no clear zones of inhibition were observed around any of the samples. This indicates a lack of antifungal activity under the given conditions. The absence of inhibition may be attributed to insufficient antifungal properties of the coatings or suboptimal environmental conditions for antifungal action during the test.

4. Conclusions

This research successfully produced CeO_2 and CeO_2–TiO_2 nanoparticles though green synthesis routes, to develop eco-friendly protective coatings with enhancement of hydrophobicity and corrosion resistance for mild steel substrates. Through a range of characterization techniques, including XRD, UV-Vis spectroscopy, SEM, EDX, hydrophobicity measurements, mechanical testing (scratch and calo tests), and linear polarization resistance (LPR), the study offered a comprehensive assessment of structural, optical, mechanical, and electrochemical behavior of the coatings.

X-ray Diffraction (XRD) confirmed that CeO_2 nanoparticles possess a cubic fluorite crystal structure. Crystallinity improved with increasing CeO_2 concentration, as evident from sharper in the higher concentration samples, whereas 1% coatings showed weak or absent CeO_2 and CeO2-TiO2 peaks, indicating insufficient dopant incorporation at low concentrations. SEM imaging revealed that lower concentration of CeO_2 coating were porous, with cracks and weak adhesion. On the other hand, by increasing the concentration of coating demonstrated improved film continuity and particle coverage, although some agglomeration remained an issue. EDX confirmed the presence of elements in appropriate ratios, with increased CeO2 loading in 2% samples.

Optical analysis using UV-Vis spectroscopy identified a characteristic of good absorption in CeO_2 nanoparticles, and the bandgap suggests semiconductor properties suitable for photocatalytic applications. Hydrophobicity testing showed a significant rise in contact angle for higher concentration CeO_2 coatings, crossing the hydrophobic threshold, while CeO2-TiO2 coatings exhibited hydrophilic, consistent with previous studies indicating that TiO_2 increases surface wettability.

Similarly, scratch and calo tests highlighted superior mechanical performance in CeO2-TiO2-doped coatings, especially by increasing concentration. The critical load (Lc) and coating thickness were also increased by increasing CeO2-TiO2 concentration respectively, confirming enhanced adhesion and wear resistance. Electrochemical tests demonstrated that increased concentration of CeO2-TiO2 on steel substrate offered the best corrosion protection, with the flattest LPR slope, indicating higher polarization

resistance due to the formation of a compact CeO2-TiO2 oxide film. Antifungal testing showed no inhibition, indicating insufficient bioactivity of current formulations under the test conditions.

In summary, by increasing the concentration of CeO2-TiO2 nanoparticles embedded in chitosan provided the best combination of crystallinity, mechanical durability, hydrophobicity, and corrosion protection. However, further optimization is necessary to address agglomeration and explore potential multifunctional applications.

Moreover, the applications are to develop eco-friendly nanoparticle coatings, especially 2% CeO2-TiO2 in chitosan, offer great potential for use in protective layers on mild steel and glass surfaces in industrial and biomedical applications, where enhanced corrosion resistance, mechanical stability, and hydrophobicity are desired.

5. Acknowledge

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