



ENGINEERING MATERIALS AND INNOVATIVE TECHNOLOGIES

EDITED BY
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Engineering Materials and Innovative Technologies

Edited by
Prof. Chafic-Touma Salame
Prof. Yuyuan Zhao
Prof. Omar S. Es-Said
Dr. Omar S. Dahham

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Edited by

**Prof. Chafic-Touma Salame, Prof. Yuyuan Zhao,
Prof. Omar S. Es-Said and Dr. Omar S. Dahham**

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Preface

This edition presents the latest research results and innovative solutions in materials science and technologies for materials synthesis and processing.

The topics of this issue are modern biomaterials for implantation, some technologies for metal processing including rotary friction welding and electron beam brazing, thin films and nanocomposites for electronic and energy storage applications, technologies of fuel production, latest technologies and procedures of wastewater treatment and waste recycling, some innovative building materials.

The issue will be interesting and helpful to engineers whose activities relate to biomedicine, the mechanical engineering industry, chemical production and construction.

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CHAPTER 1:

Biomaterials in Implantation

Investigation Some Characteristics of Biocomposites Coating for Biomedical Implants

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Keywords: Implant; coating; bio composite; stainless steel 316L; chitosan; alginate.

Abstract. The surface has a vital function in the tissue's response to the presence of foreign material in the field of body implants. Surface modification with coatings can be adjusted to provide the highest service performance at the lowest cost. Coatings can increase corrosion resistance by reducing metal ion and corrosion product migration in the body. We fabricated polymer based bio-composite coatings by blending chitosan (Chi), alginate (Alg) and nanoparticles ((TiO₂, Nb₂O₅) by dip coating onto a 316L stainless steel substrate. The coatings' surface morphology and phases were studied using FESEM and FTIR analysis. The wettability behavior of the coated samples was also studied by investigating their contact wetting attributes. The antibacterial activity of the functionalized coatings was determined too. The FTIR results showed that the blending of Chi-Alg and nanoparticles was excellent, and no obvious differences in the spectra or any changes in the structures of the polymer matrices were observed. The SEM results demonstrated that the coating layers were uniform, homogeneous, and crack-free on the 316L Stainless steel substrate when using TiO₂-Nb₂O₅ nano particles. The contact angle results showed the highly hydrophilic properties of the pure chitosan-alginate blend. As well, coatings containing nano particles showed the same antibacterial effect of chitosan-alginate blend coating.

1. Introduction

A bone plate is one way of restoring broken bones that can be used during implantation. This bone plate is a component that aids in the healing of fractured or cracked bones. This approach employs metal as an implant substrate, which is still being refined in response to the growing demand for artificial bone in people. Titanium alloys, stainless steel, and Cr-Co alloys are all extensively utilized as bone plates [1].

Metals, on the other hand, become a limitation in terms of biocompatibility with their interacting media, as they cannot regenerate new bone, limit organ function, or alter bioactivity in the body. Corrosion products will also have an impact on the human body, resulting in implant failure. Coating the metal surface with particular biomaterials is one way to increase the biocompatibility, fixation, and longevity of implant materials. Biomaterials or bioceramics, such as titania, hydroxyapatite, and others, can be used to modify coatings to induce bone formation and cell development [1, 2].

The most crucial condition for the long-term effectiveness of skeleton implants, such as knee joints or artificial hips, is a stable compound between the surrounding tissue and the biomaterial. The implant surface, with its structure and composition, plays a critical role in achieving strong cell adherence to the biomaterial [3].

Joint replacement pieces and fracture repair devices are frequently made of stainless steel (316L). Stainless steel, in comparison to other metallic implants, has a low cost, good formability, and high mechanical properties, making it an ideal metallic implant material [4, 5].

Chitosan is a cationic polymer that offers various advantages over other wound dressing materials, including strong biocompatibility, antibacterial activity, and chemical stability [6]. The natural polymer chitosan (CS) is used with nanoparticles to enhance antimicrobial biomaterial properties, such as biocompatibility and antimicrobial efficiency, for medical applications [7].

Alginate is an anionic natural polymer that has attracted a lot of attention in the field of tissue engineering. Its biocompatibility, biodegradability, and hydrophilic characteristics are well-known [8].

Titanium oxide (TiO_2) is available in the form of high-surface-area nanocrystals. Titanium oxide has antibacterial and antiseptic properties, according to certain researchers [9]. Some researchers have also suggested that TiO_2 can be employed as a useful filler material in biodegradable polymers because it promotes cell proliferation and attachment [10]. It has medicinal and health applications due to its inert nature.

Niobium oxide (Nb_2O_5) has the potential to be used as an oxide coating for metallic implants due to its strong corrosion resistance and thermodynamic stability [11]. Many simple and direct methods can be used for modifying implant surfaces by the application of a bio coating layer consisting of an appropriate material, such as dip coating, and electrophoretic deposition, have been used, which have distinct advantages and disadvantages that affect coating properties [12].

The properties of the material's surface can be changed using coating techniques without affecting the implant's overall properties [13, 14]. In this study, we employed these two types of polymer to create a blend by chemical binding. The aim of this study is to develop a new type of chitosan and alginate based coating on 316L stainless steel substrates incorporating nano-titanium dioxide (TiO_2) and nano-niobium (V) oxide as reinforcing materials to form a bio-composite layer by the dip coating method.

2. Materials and Methods

2.1 Materials Used

The materials that were utilised are Chiton (from shrimp shells/HIMEDIA-high molecular weight), Sodium alginate (HIMEDIA) as the matrix, titanium dioxide (TiO_2) (from BDH as laboratory reagents), Niobium oxide (ZHANUN/China) as the reinforcements, and Acetic Acid 99-100% extra pure (glacial/ Riedel-de-Haën) used as a dissolving solution.

2.2 Methods

2.2.1 Preparation of chitosan/alginate/nanoparticles bio-composite coating

The bio-composite coating contains chitosan (Chi), alginate (Alg), nano-titanium dioxide (TiO_2), nano-niobium oxide (Nb_2O_5), which examination by particle size analysis testing, the average particle size was 26.5 nm for (Nb_2O_5), while the average particle size was 79.9 nm for (TiO_2), as shown in Fig. (1,2). In the initial step, the matrix was prepared, Chitosan solution is made by dissolving chitosan powder in 1 % (v/v) acetic acid. Secondly, dissolved alginate in distilled water, 99% was added to the above chitosan solution as (75% Alginate + 25% Chitosan) and stirred for 1 hour at room temperature until a homogeneous blend was obtained. After a homogeneous solution had been formed, the matrix was separated into four 100-ml beakers. Then the reinforcements were added (TiO_2 and Nb_2O_5) and stirred for an additional 15-20 min. After the solutions are prepared, the substrate samples (316L Stainless Steel) are immersed vertically in the prepared solution (as mentioned above) for 15 minutes by dip coating, after which they are left to dry for 24 hours. The dip coating method was used in depositing a composite coating layer of Chi-Alg based biocomposite coatings and with different reinforced materials, as shown in Table 1.

Brookhaven Instruments Corp.
90Plus Particle Sizing Software Ver. 5.34
Sample ID 232-0 (Combined)
Operator ID 1
Notes

Date: Nov 28, 2021
Time: 02:11:30
Batch: 0

Measurement Parameters:			
Temperature	= 25.0 deg. C	Runs Completed	= 3
Liquid	= Water	Run Duration	= 00:00:30
Viscosity	= 0.890 cP	Total Elapsed Time	= 00:01:30
Ref.Index Fluid	= 1.330	Average Count Rate	= 434.7 kcps
Angle	= 90.00	Ref.Index Real	= 1.590
Wavelength	= 660.0 nm	Ref.Index Imag	= 0.000
Baseline	= Auto (Slope Analysis)	Dust Filter Setting	= 30.00

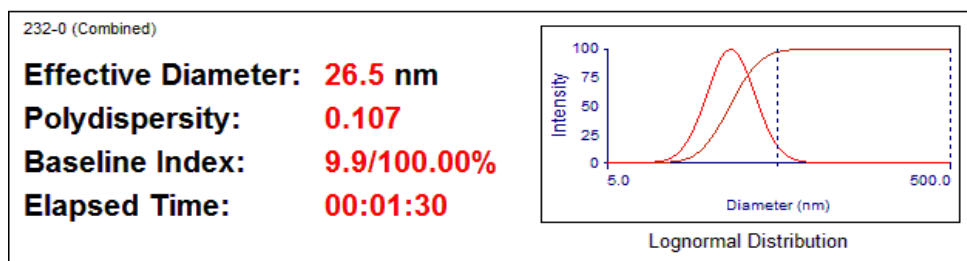


Fig. 1: Particle size analysis for niobium oxide (Nb_2O_5) powders.

Brookhaven Instruments Corp.
90Plus Particle Sizing Software Ver. 5.34
Sample ID 219-0 (Combined)
Operator ID 1
Notes

Date: Nov 16, 2021
Time: 23:22:26
Batch: 0

Measurement Parameters:			
Temperature	= 25.0 deg. C	Runs Completed	= 2
Liquid	= Water	Run Duration	= 00:00:30
Viscosity	= 0.890 cP	Total Elapsed Time	= 00:01:00
Ref.Index Fluid	= 1.330	Average Count Rate	= 543.7 kcps
Angle	= 15.00	Ref.Index Real	= 1.590
Wavelength	= 660.0 nm	Ref.Index Imag	= 0.000
Baseline	= Auto (Slope Analysis)	Dust Filter Setting	= 30.00

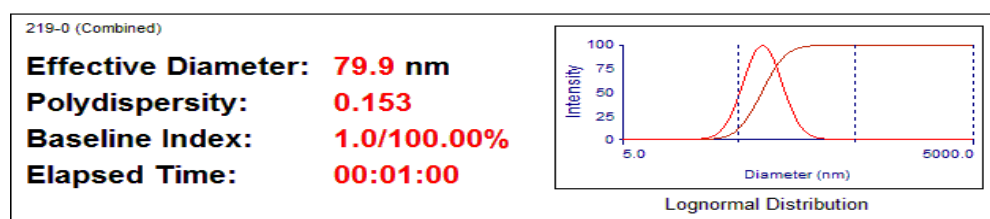


Fig. 2: Particle size analysis for titanium dioxide (TiO_2) powders.

Table 1: Samples coating composition on stainless steel 316L substrate.

Sample No.	Composition of Coating Layer
1	Pure matrix (25% chitosan + 75% alginate)
2	Pure matrix with 6% wt. of TiO_2
3	Pure matrix with 6% wt. of Nb_2O_5
4	Pure matrix with 3% wt. of TiO_2 + 3% wt. Nb_2O_5

Several characterization methods were used; the FTIR was utilized to determine the intermolecular interactions between the components in the bio-composite coating that had been created. FTIR also provides information on the existence of various chemical or functional groups in the materials. The Field Emission Scanning Electron Microscope (FE-SEM, TESCAN) has provided details on the surface morphology and porosity. Performance properties such as wettability (wettability was examined by measuring contact angles) and antibacterial behavior by the Drug Sensitivity Test (Kirby-Bauer) method.

3. Results and Discussion

3.1 FTIR Analysis

In a polymer study, Fourier Transform Infrared Resonance (FTIR) was used to classify polymers and visualize group ends as well as chain branching [15]. A distinctive band of the amino group $[-NH_2]$ was seen in the chitosan spectra (Fig. 3) at 1590.06 cm^{-1} . The partial N-deacetylation of chitin correlates to the strength of the amide peak for chitosan [16]. The $[-CH_2]$ and $[-CH_3]$ groups stretching vibrations were assigned to the 2873.63 and 2921.63 cm^{-1} peaks, respectively, while the C–H bending vibration was attributed to the 1418.23 cm^{-1} peak [17]. The typical alginate peaks were found at 1597.46 and 1417.04 cm^{-1} in (Fig 3), which correspond to two carboxyl groups $[-COOH]$ in the molecular chain.

The amide (II) peak (1558.91 cm^{-1}) was significantly intensified in the chitosan-alginate spectrum (Fig. 3), while the amino group (1590.06 cm^{-1}) and carboxyl group (1597.46 cm^{-1}) peaks were absent. These alterations revealed that the ionic-interaction between the carboxyl group (negatively charged) $[-COO^-]$ of alginate and the amino group $[-NH_3^+]$ (positively charged) of chitosan was responsible for the creation of the chitosan-alginate blend.

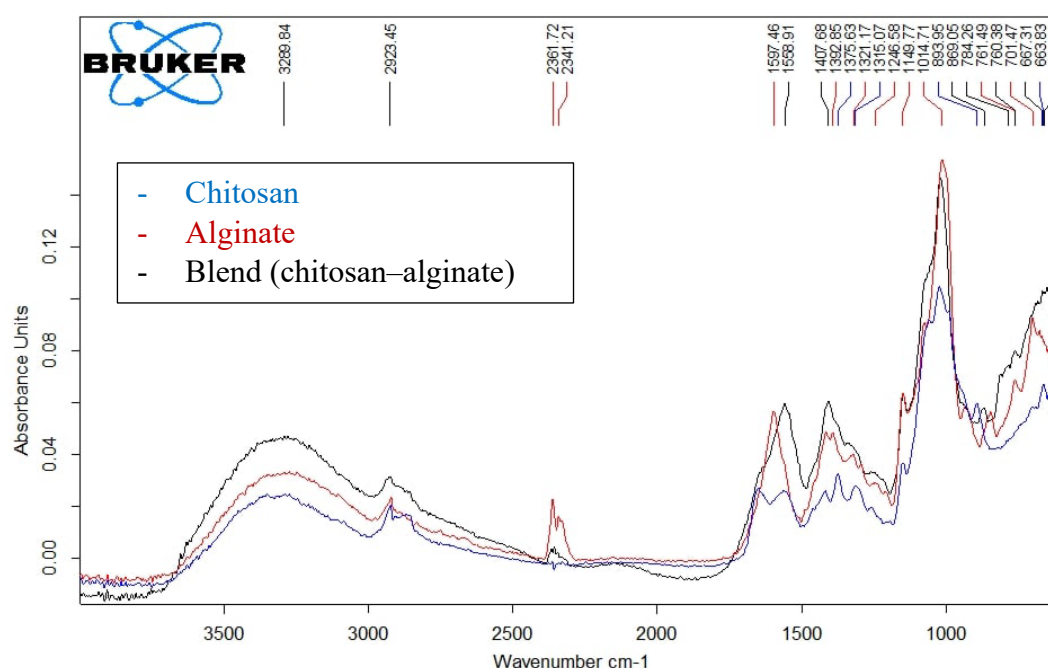


Fig. 3. Fourier Transform Infrared spectra of (a) chitosan, (b) alginate, and (c) blend (chitosan-alginate).

The same peak appeared in the FTIR spectra when adding TiO_2 or Nb_2O_5 nano particles to the Chi-Alg blend, as shown in Fig. (4). No obvious difference was found among the spectra, and the composite coating showed no change in its structural polymer matrix. There were no new peaks discovered for the Chi-Alg biocomposite specimens with the addition of TiO_2/Nb_2O_5 nano particles. The lack of crosslinking and physical bonding in the specimens accounts for this [18]. The intensity of the peaks and shifting changes with the addition of nano particles because of the dual effect of

reinforcements on the composition of the Chi-Alg matrix. The absence of a chemical reaction among the components indicated a development in the miscibility state and the absence of by-products that might cause toxic and allergic effects inside the human body [19].

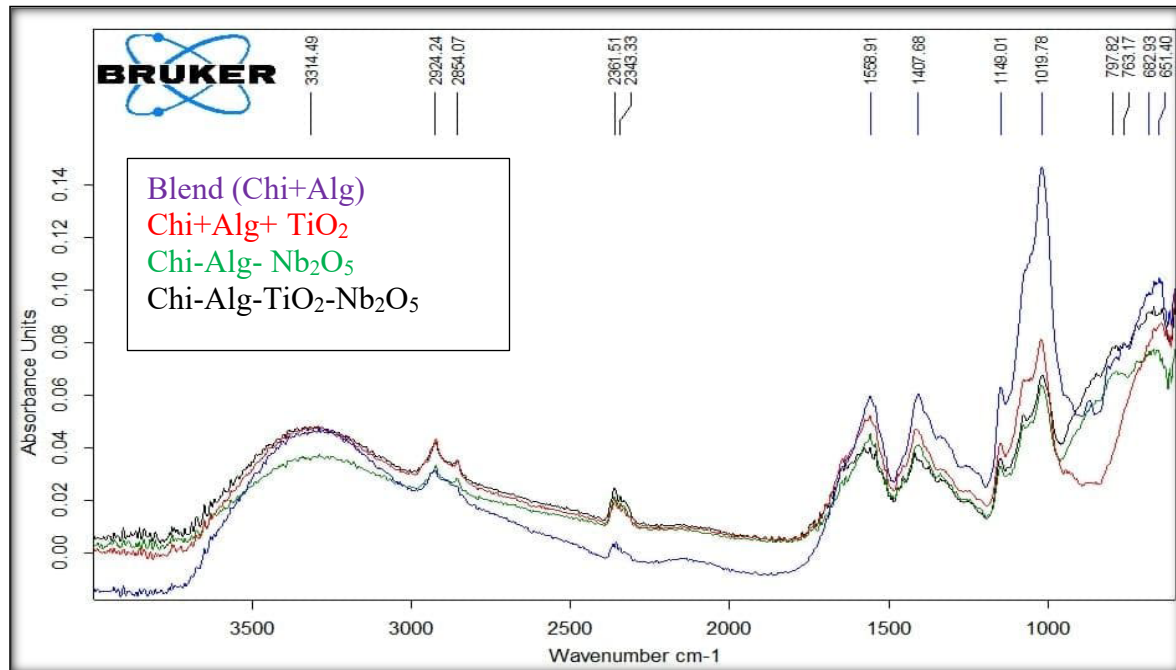


Fig. 4: FTIR spectrum of Chi-Alg biocomposite coatings.

3.2 Scanning Electron Microscopy

The microstructures of the composite coating samples were characterized through FE-SEM, and the effect of nano particle addition (TiO_2 and Nb_2O_5) to the Chi-Alg matrix on surface texture was examined. A uniform coating of Chi-Alg was produced on the whole stainless steel surface, as shown in (Fig. 5 a). There were no well-defined pores on the rough surface. The addition of TiO_2 to Chi-Alg shows that, also at the micrometric level, the coating is homogeneous all over the surface (Fig. 5 b) with well-distributed clusters. The coating layers exhibit a consistent distribution of Nb_2O_5 particles within the polymer, a homogeneous deposition of the coating, and a modest level of porosity, as shown in (Fig. 5 c).

A closer look at one of the clusters (Fig. 5 d) shows that they are composed of a mixture of TiO_2 and Nb_2O_5 particles. The addition of TiO_2 and Nb_2O_5 resulted in a uniform and homogeneous finishing surface, a fine grain structure with excellent integration, and a distribution of the reinforced particles throughout the natural polymer matrix of the coating. The pore structure of Chi-Alg with TiO_2 - Nb_2O_5 coating was clearly defined and interconnected, whereas the addition of TiO_2 or Nb_2O_5 nanoparticles to the Chi-Alg biocomposite resulted in a reduced pore structure. No density gradients of models will be detected at cross segments analyses by SEM for all types of polymer composites, as shown in all homogeneous microstructure cases [20].

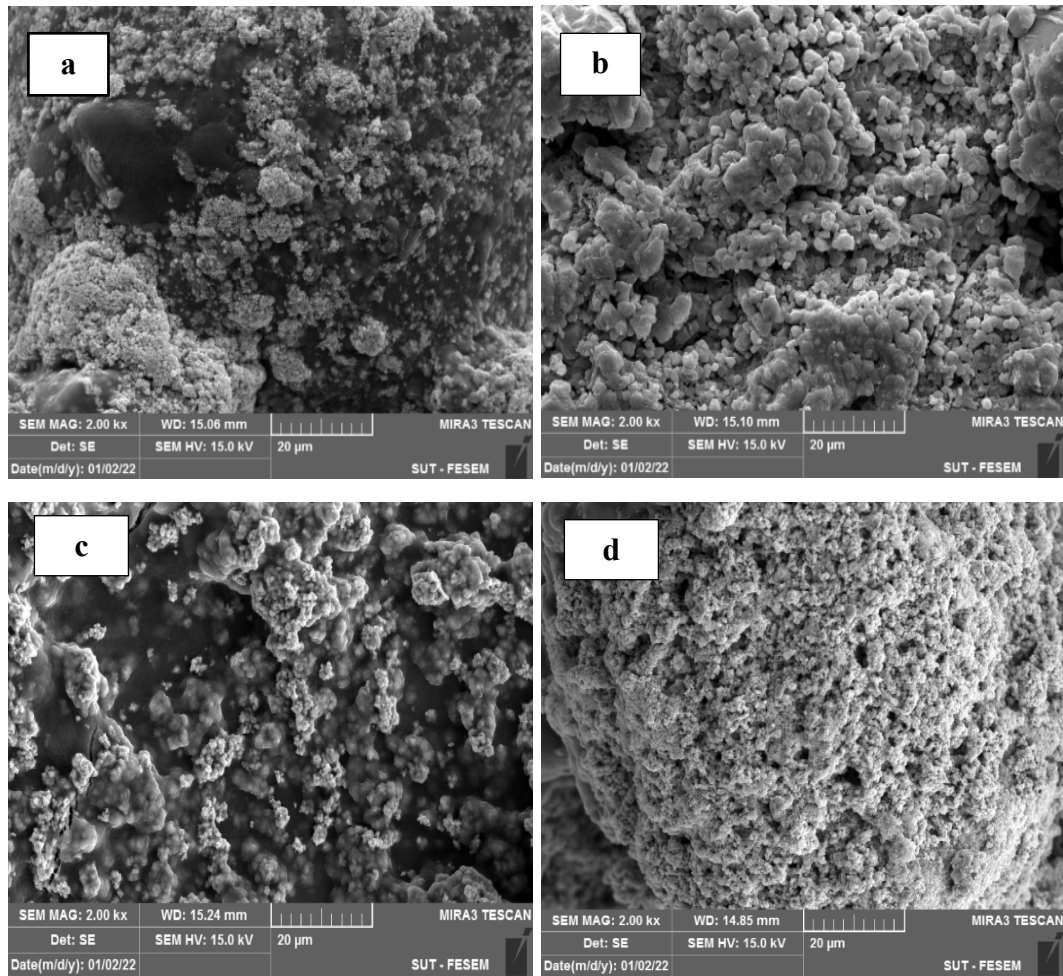


Fig. 5: FE-SEM images of Chi-Alg composite coated on 316LSS: a) Blend (Chi-Alg), b) Chi-Alg-TiO₂, c) Chi-Alg-Nb₂O₅, and d) Chi-Alg-TiO₂-Nb₂O₅.

3.3 Wettability Test

The contact angle is the angle formed when a liquid interface makes contact with a material surface. Contact angle was used to measure surface hydrophilicity at the moment of water droplet contact with a surface coating. It is an important feature that considerably influences biological responses to implants. Surface hydrophilicity is important in the early stages of proliferation, cell migration, and bone formation. Understanding the surface phenomena of composite coatings requires wettability analyses. Fig. (6) shows the contact angles of all the coated specimens.

The contact angles of all samples were less than 90 degrees, indicating that they were hydrophilic. The addition of TiO₂ to the blend, the contact angle increased to (52.55°) as well as with the addition of Nb₂O₅ which reached (74.58°). With the introduction of both nanoparticles TiO₂-Nb₂O₅ to the blend, the contact angle significantly increased from 19.47° (Chi-Alg) to 84.39°, demonstrating that the hydrophilicity of the blend Chi-Alg is significantly more than Chi-Alg with TiO₂-Nb₂O₅ nanoparticles. Cell affinity is influenced by the hydrophobic or hydrophilic properties of a biomaterial surface. In most circumstances, a hydrophilic surface has a higher capability for proliferation and cell attachment than a hydrophobic one [21]. The coatings with the Chi-Alg-TiO₂ composite have a small contact angle when compared with the Chi-Alg-Nb₂O₅.

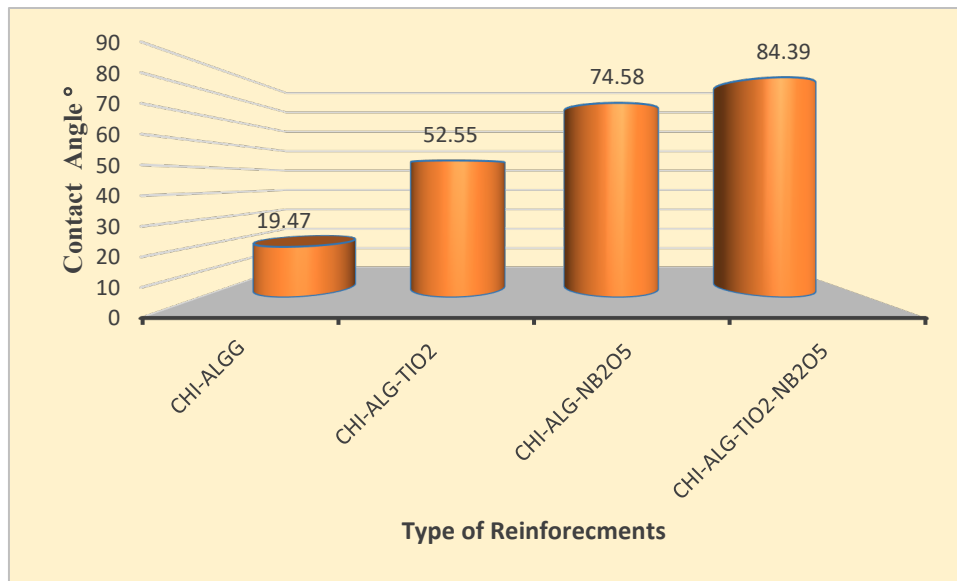


Fig. 6: Contact angle values of all samples.

3.4 Antibacterial Activity Test

The anti-bacterial behavior of composite materials with different particulate reinforcements (Titanium dioxide, Niobium oxide) was performed by using two different types of bacteria (*Staphylococcus aureus* and *Escherichia coli* bacteria). In the current study, stainless steel 316L coated with the blend of chitosan and alginate, blend/TiO₂, blend/Nb₂O₅, and blend with TiO₂/Nb₂O₅ composites were tested for antibacterial activity. Figs. (7,8) show the inhibition zone diameter (mm) of all samples against *Escherichia coli*, and *Staphylococcus aureus* bacteria used in this study. The addition of both particles as reinforcing materials to the chitosan-alginate polymer matrix leads to enhanced anti-bacterial behavior for whole composites by limiting the activity of bacteria proliferation and growth processes at composite surface. The results showed that the inhibitory effect of composite coating (Chi-Alg-nanoparticles) was the same as compared with coating (Chi-Alg), where the inhibition zone of the Chi-Alg-nanoparticles sample against *Staphylococcus aureus*, and *Escherichia coli* was about 10,10 mm, respectively.

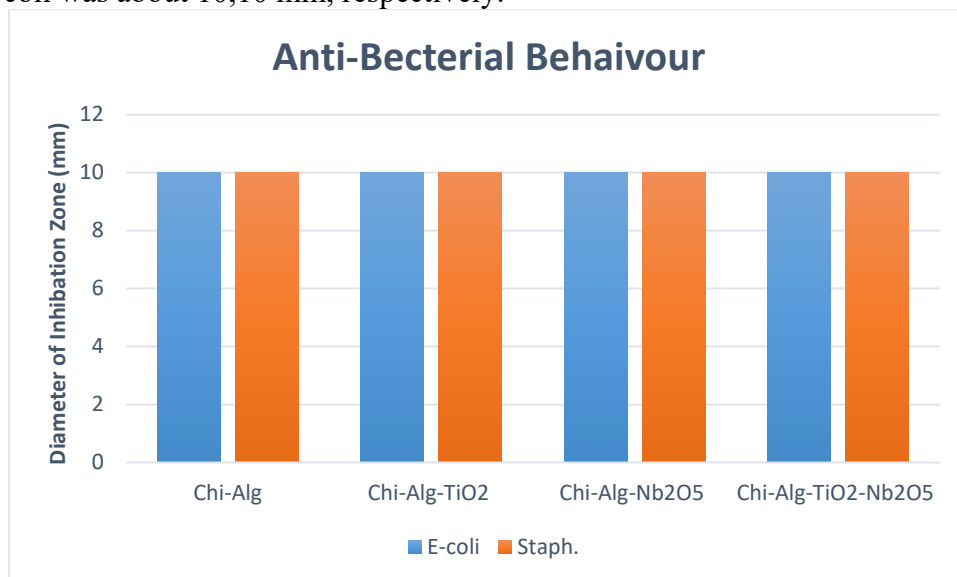


Fig. 7: Anti- bacterial behavior of all samples.



Fig. 8: The inhibition zone diameter (mm) of all sample against (a) *Escherichia coli*, and (b) *Staphylococcus aureus*.

4. Conclusions

In conclusion, the strong ionic-interaction between the amino groups of chitosan and the carboxyl groups of alginate was used to create a natural polymer-based chitosan-alginate blend. A new nanocomposite coating based on Chi-Alg with TiO_2 , Nb_2O_5 nano particles was used successfully for the coating of a 316L stainless steel substrate by using a simple and cheap dip coating method. FTIR results showed the same peak appears in the FTIR spectra of the coating groups (Chi-Alg-nano particles) compared with pure Chi-Alg coating. No obvious difference in the spectra of the rover and composite coating was found, and no change in the structural polymer matrix. The SEM images indicated homogeneous adhesion between the Chi-Alg based composite coating reinforced with TiO_2 , Nb_2O_5 and TiO_2 - Nb_2O_5 nanoparticles and the 316L stainless steel substrate, confirming the suitability of the dip coating technique. From contact angle results, the hydrophilicity of the surface decreases with the addition of nano particles to the blend. And decreasing activity of *Staphylococcus aureus*, and *Escherichia coli* bacteria for all type of nano particle which attack the bacteria preventing cell growth and enhancing the antimicrobial behavior of composite material.

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Enhanced the Structure of Ophthalmic Implants (Rigid Contact Lenses) by Aloe Vera Addition

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Keywords: Rigid contact lens, PMMA, natural materials, Aloe Vera, OH content.

Abstract. More than 125 million people in the world use contact lenses for ophthalmic treatments across the globe. There has been a recent surge in interest in researching and developing new materials for contact lenses (CLs). With the advancement of associated biomaterials, such as drug delivery, these materials will continue to grow in importance in the future. If you're looking to buy contact lenses, you'll most likely find them made out of polymer or silicone hydrogel. To meet the ever-increasing needs for contact lenses and the ever-increasing number of contact lens users, this work aims to study the effect of adding aloe Vera gel to contact lenses, antibacterial behavior, surface texture, and wettability. Results show the addition of aloe Vera natural materials to rigid PMMA contact lenses aid to promote the performance of contact lenses by changing the internal structure of PMMA, especially when using (0.1%, 0.2%, and 0.3%) of aloe Vera due to the increasing in OH content as well as the increasing in the uniformity of microstructure. addition of (0.4% and 0.5 %) of aloe Vera make a reverse effect on the structure due to the saturation of PMMA chain with OH leading to destroying the connections between bonds, therefore, weakening PMMA lenses also using aloe Vera gel act to soften the lenses by increasing the OH content in PMMA structure lead to improving the lens wettability at about (0.2-0.3) % after these percentage large drop in whole properties will occur.

1. Introduction

According to the Food and Drug Administration of the United States, contact lenses are now classified into two basic categories based on their physical properties and chemical composition: hydrophilic (soft) and hydrophobic (hard) contact lenses [1].

Hydrogels that are used to make soft contact lenses are flexible and have a moderate amount of cross-linking. They are capable of absorbing and retaining huge amounts of water (more than 35 percent water by weight), which oxygen may dissolve and distribute into the cornea. They are also capable of dissolving and absorbing oxygen. Acrylic polymers with very hydrophilic side chains and agents (NVP, MAA, AA) that connect the polymer molecules in three dimensions are used in their construction.

Therefore, hydrophilic groups encourage water absorption into the polymer, while hydrophobic bonds restrict it; therefore, the hydration of a hydrogel may be adjusted by modifying the degree of chain cross-linking [2][3][4]. On the other hand, hydrophobic lenses are incapable of regulating the amount of water that they contain. PMMA, the principal component of hard contact lenses, has excellent transparency, stability, and nontoxicity; nevertheless, due to its low water content, it is impermeable to oxygen, making it exceedingly difficult to mold into contact lenses.

PMMA poly (methyl methacrylate) — often known as Plexiglas or acrylic — was formerly thought to be the greatest material for contact lenses due to its flexibility and clarity. The first mass-market contact lenses were produced in the 1940s, and they were all constructed of this stiff, nonporous PMMA material, which is being used today.

The market share of PMMA CLs is less than 1%, they serve as an excellent starting point for understanding CLs materials and the properties of polymers that make them acceptable for eyewear by giving a practical example. One of the major disadvantages of PMMA is low to non-existent

oxygen permeability. This is because polymer chains are rigid, preventing oxygen from passing through or the usage of internal water to mediate the flow of oxygen, respectively. This happens in PMMA as a result of the shared intermolecular interactions connecting polymer chains, including dipole-dipole attraction and physical entanglement. The negatively charged (electrochemically negative) oxygen atoms form the dipoles, not the surrounding positively charged (electrochemically positive) carbon and hydrogen atoms. As a result, nearby polymer chains can interact, maintaining the polymer's thermodynamic stability. PMMA has a limited free volume (the amount of space between polymer chains) as a result of these intermolecular tensions, which implies that the chains do not rotate or move very readily. Additionally, PMMA is free of large pendant chains that might obstruct the interaction of neighboring chains. All of these ingredients operate in concert to keep oxygen out of the polymer. However, if done, functionalization of the PMMA surface might increase hydrophilicity [2][3][4][5], which would benefit these CLs. From an ophthalmological standpoint, When a PMMA contact lens is put into the eye, the unstable balance between the tear film and the lens causes a "crack" in the cornea. Because contact lenses are largely used to treat ametropic disorders, the number of people who use them regularly is growing at an increased pace and is expected to overtake the number of people who wear traditional eyeglasses in the not-too-distant future. However, frequent contact lens wearers have a non-negligible risk of developing corneal erosion and infections, which are thought to afflict around 25% of all cases in the United States, according to current estimates. Numerous problems connected with long-term contact lens wear may be traced back to interactions that occur between the contact lens material and the Components of tear fluid [6].

PMMA has frequently been used as standard reference material in studies looking at the eye's response to various CLs [7][8][9][10]. Astigmatism [7] strabismus [11], and Blepharoptosis [8]. are just a few of the eye conditions that have been shown to improve with the PMMA lens in previous studies. RGP lenses were shown to be the most successful in post-corneal refractive surgery patients [7]. According to Li et al., a new PMMA hybrid lens including zinc oxide quantum dots might be produced to reduce ultraviolet exposure. Reduced UV light transmission by 50% while maintaining the optical transparency predicted by a contact lens containing 0.017 wt. percent Zn O quantum dots. Nanophotonic lenses may have been the most important development in PMMA lens technology [12][13]. Chemically modified fullerenes (C60) were covalently bonded to poly (methyl methacrylate) (PMMA) to exploit the fullerene's photo- and electro-activities. On the other hand, SCL materials are now focused on Nanophotonic lenses [14]. In any case, van der Warp [15] emphasized the relevance of PMMA as scleral lenses, so it's not all terrible for PMMA. A prosthetic eye can be created by grafting PEG onto PMMA [16]. Overall, these are just a few of the many works that have been written about contact lenses.

Menicon is credited with developing the first contact lenses that have high oxygen transmissibility ($Dk = 175$) (Figure 2.2/h, i). These lenses were made of tris (trimethylsiloxy) silyl styrene and fluoromethacrylate. Menicon Z contact lenses are the only hard lenses that have gotten permission from the FDA for continuous usage for 30 days. This approval was granted in 2019.[17]

Researchers have revealed that Aloe Vera contains a wide range of biological activity in recent years, including anti-inflammatory, antioxidant, immunomodulatory, and cell growth-promoting capabilities [18], [19], and [20] properties. In aloe vera gel, water makes up the great majority of the components that are mentioned in Table 1 under the heading "Aloe Vera Compositions." Aside from a large amount of water present, approximately 1 percent of the plant's weight includes bioactive substances such as aloin (anthraquinones), flavonoids, saponin, and aloe-mannan, in addition to an assortment of amino acids and vitamins [23]. Aloe Vera is also rich in antioxidants, including flavonoids, saponin, and aloe-mannan. Aloe Vera also includes a range of amino acids and vitamins, which are beneficial to the body. The inclusion of these bioactive chemicals in aloe Vera gel substantially enhances the gel's antibacterial action. AV is a naturally occurring organic antibacterial agent that is produced by the presence of various bioactive components in the plant's structure.

Table 1 Aloe Vera Composition [21].

Composition of <i>Aloe vera</i>	Weight by weight (w/w%)
Water	96
Dry matter	4
Organic acid	22.8
Dietary fiber	18.8
Polysaccharide	8.8
Protein	4.7
Lipid	2.7
Ashes	16.0

2. Materials and Methods

The (Poly) methyl methacrylate((PMMA) (purity 95%)Linear Formula ($C_5O_2H_8$)_n with the density of 1.18 g/cm³ that was used in this study was supplied from (Sigma-Aldrich/USA) (sigmaaldrich.com).

Using a natural method, aloe Vera gel was harvested from a section of the plant by cutting it in a diagonal direction and then thoroughly washing the cut section to remove dust and grime, as well as the yellow dye that occurs as a result of the cut.

Sample preparation:

From Aldrich (95 percent purity), Sigma acquired PMMAs with molecular weight $M = 15,000$ g/mol. According to the instructions provided by the provider, this material has been kept. (Poly)methyl methacrylate (PMMA) was mixed with different proportions (0.1,0.2,0.3,0.4 and 0.5) ww% of aloe Vera gel using a magnetic stirrer at room temperature at medium speed for 1 hour under normal atmospheric pressure to give sufficient time to form polymeric chains and then poured. The mixture was placed in silicone molds and the mix was healed below 365 nm UV light for 5 minutes to dry. then the model was extracted from the mold and a silicone mold was used because it does not need to be lubricated and this is better to prevent the protein content from increasing from the resulting lens.

The samples were sent for several tests, including the Fourier shift spectroscopic test Infrared (FTIR), which is used in the diagnosis of the registered polymer by knowing the active groups of the polymer and the bonding of some groups in a compound and revealing the type of bonds that bind the molecules of the material.

The contact angle test was used to measure the wettability of the samples. The antibacterial test is measured by estimating the number of bacteria in a small amount of a mixed sample after it has been placed on a microscope slide (lens bacterial culture dish) divided into squares of known dimensions and area. bacteria per 3 cm of a sample. the bacteria were used is staphylococcus Scanning electron microscopy (SEM) to obtain microscopic information about the surface or near-surface region of the sample (surface morphology).

EDX is an analytical method that may be used to determine the chemical composition of a substance.

3. Result and Discussions

3.1 Fourier Transformation Infrared Spectroscopy (FTIR)

The structure of prepared contact lenses was examined by utilizing Fourier Transformation Infrared Spectroscopy (FTIR) to identify the active functional group of the master sample (PMMA without Aloe Vera gel) and samples with different aloe Vera percentages. it was obvious that PMMA is the practical name for the synthetic polymer commonly known as acrylic which has the carboxylic acid functional group containing Both the O-H bond and the C=O bond. Figure (1) show the FTIR spectra of pure (PMMA), from the figure three main transmission bands of PMMA were observed. Stake-shaped C=O stretch band appears at 1723.4cm^{-1} , also the C-H band appears between 2949.57 cm^{-1} to 2990.67cm^{-1} . The third characteristic weak band of the O-H bond appears at 3415.41cm^{-1} indicating the successful preparation process of pure PMMA contact lenses without any unwanted bonds. presents the FTIR spectra of the PMMA sample with 0.1% of aloe Vera gel, from the figure it was clear that all three main bands appear at nearly the same frequency (cm^{-1}) indicating that the addition of aloe Vera has no bad effect on the structure of PMMA in addition to that there was a considerable increase in the intensity of O-H bond about 20% result from aloe Vera high water content gel indicating that increasing in OH content of PMMA structure. also when rising aloe Vera gel percentages. were 0.2%, and 0.3% same effect on PMMA structure was observed as shown in figures (1) which explain the strong effect of aloe Vera percentage on the intensity of O-H bond reacting to (75%,90%) for 0.2 and 0.3, present high OH content PMMA contact lenses. from FTIR spectra of another high aloe Vera percentage 0.4 and 0.5. it was obvious that the enhancement of PMMA structure by increasing the OH content due to aloe Vera additions ha as significant limitations. it was clear that the intensity of the OH bond band began to back off to 65% and 50% for 0.4 % and 0.5% respectively, also other main bands C=O and C-H began to change their frequencies and shape indicating the unwanted effect on the PMMA structure.

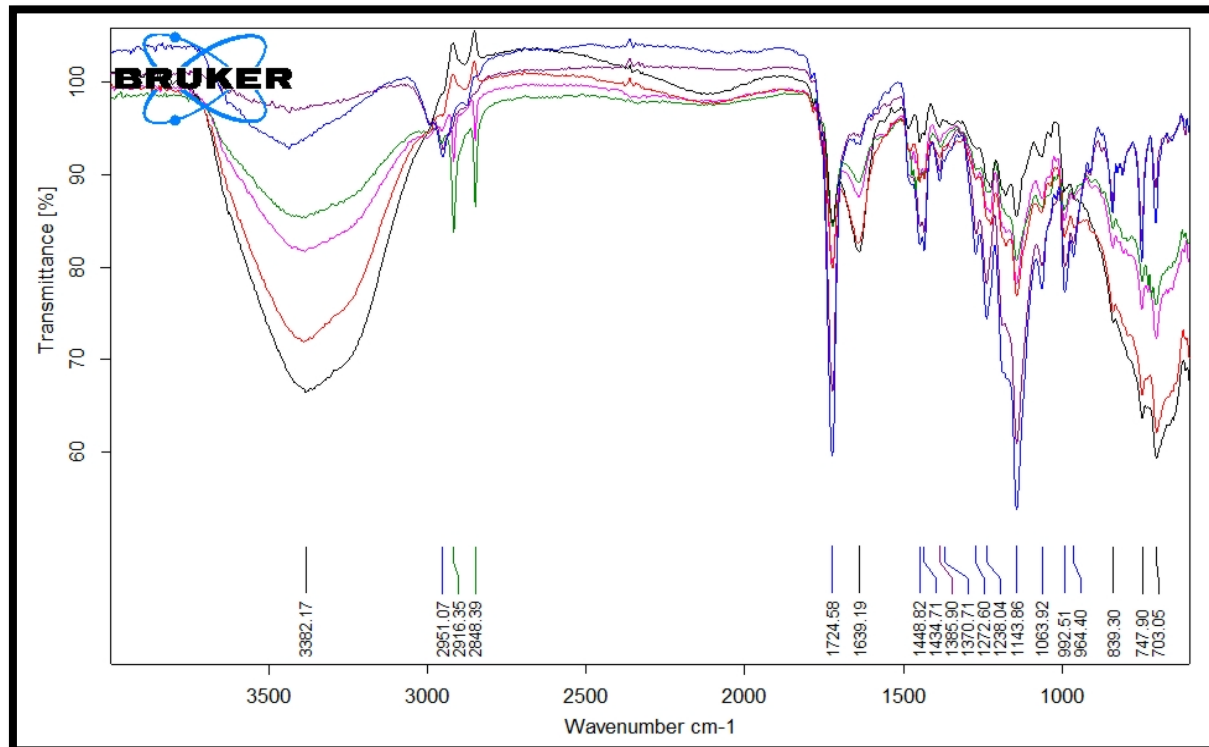


Fig. 1 [FTIR]spectra of PMMA with aloe Vera gel.

3.2 Microstructure observation (scanning electron microscopy (SEM))

Scanning electron microscopy was utilized to identify the microstructure of prepared contact lenses obtained from casting PMMA before and after aloe Vera addition with different percentages (0.1, 0.2, 0.3, 0.4, and 0.5) %. Figures (2,3) showed the SEM images of pure PMMA lens, the form figure's rough surface with Nanopore structure observed, and nothing of unwanted impurities or bubbles appears in the microstructure of pure PMMA. Additions of natural gel material such as aloe Vera rich in hydration to PMMA contact lenses result in increasing the microstructure homogeneity making it smoother than pure PMMA due to the effect of gel filling the Nanopore structure as shown in figures (4,5) which present the SEM images of PMMA contact lenses with 0.1 aloe Vera, high homogeneity with no pore – structure obtained. figures (6,7) showed the SEM images of PMMA with 0.2% aloe Vera gel, an increasing in aloe gel lead to increase inhomogeneity and present uniform structure with high scale porosity due to an increasing OH content in PMMA chain structure, figures (8,9) showed the SEM images of PMMA with 0.3 % aloe Vera gel, small cracks began appears in structure as aloe Vera percentage increased due to the increase in amount on O-H bond which produces PMMA chains saturated with OH. adding more amount of aloe Vera has to make bad effect on PMMA structure and microsegregation appears in the structure as in figures (10,11) of 0.4% aloe Vera then high structure separation occurs at 0.5% aloe Vera as mentioned in figures (12,13).

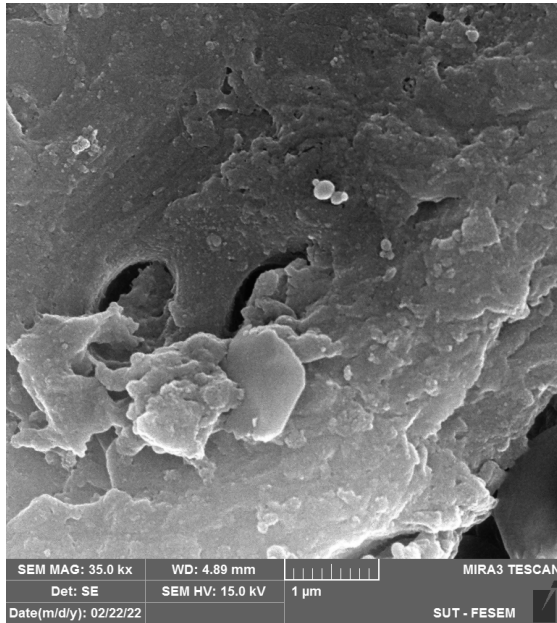


Fig. 2 SEM image of pure PMMA.

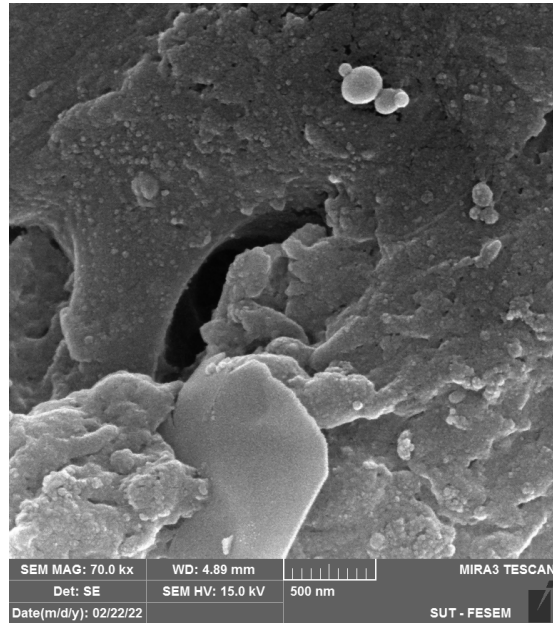


Fig. 3 SEM image of pure PMMA at 500nm.

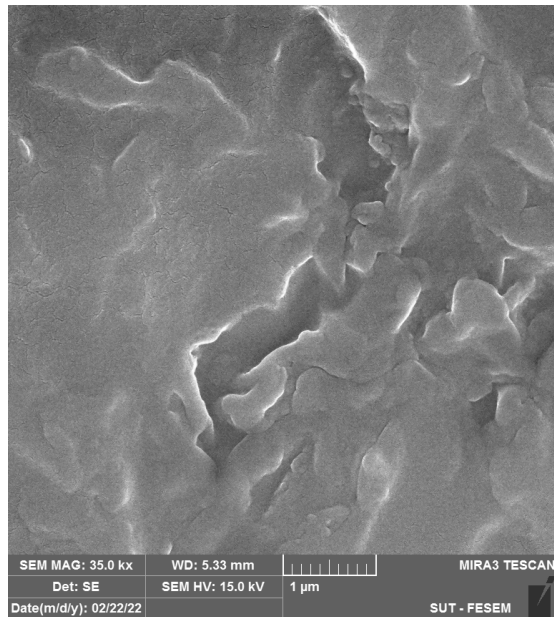


Fig. 4 SEM image of PMMA with 0.1% aloe vera.

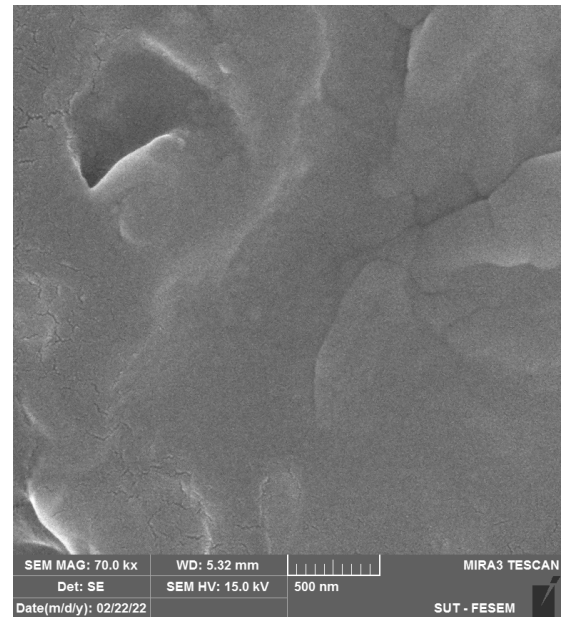


Fig. 5 SEM image of PMMA with 0.1% aloe Vera at 500nm.

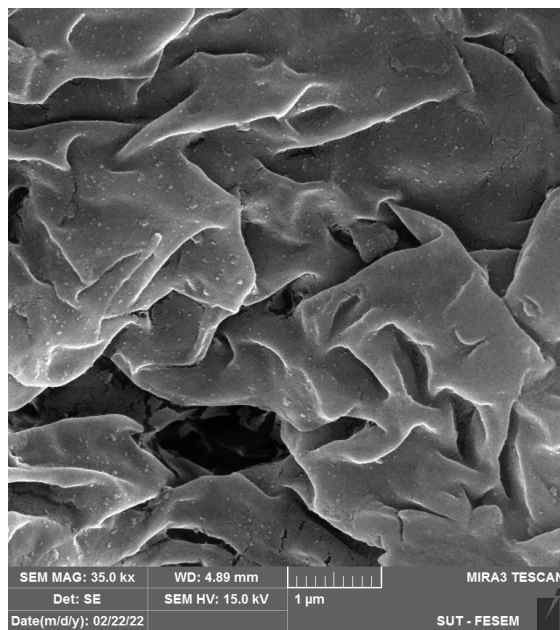


Fig. 6 SEM image of PMMA with 0.2% aloe vera.

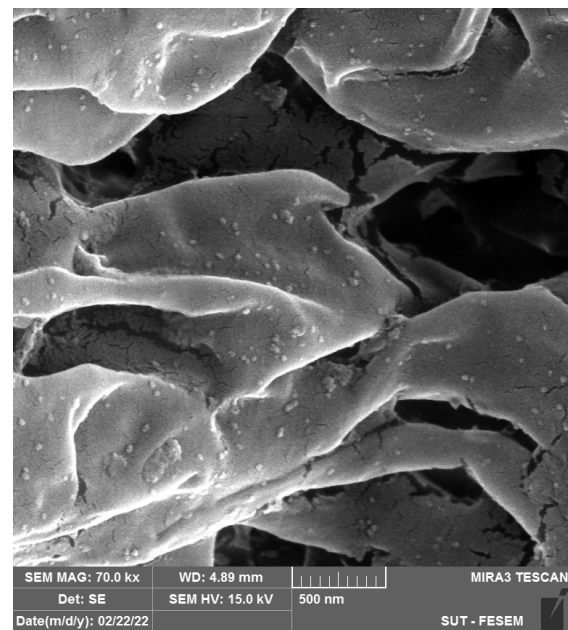


Fig. 7 SEM image of PMMA with 0.2% aloe Vera at 500nm.

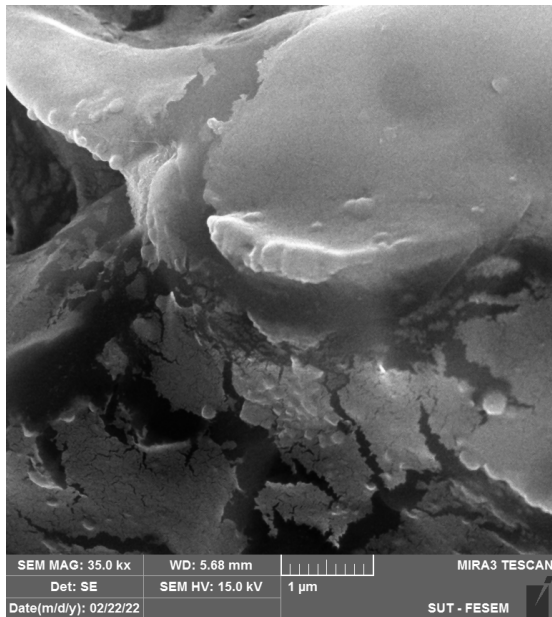


Fig. 8 SEM image of PMMA with 0.3% aloe Vera.

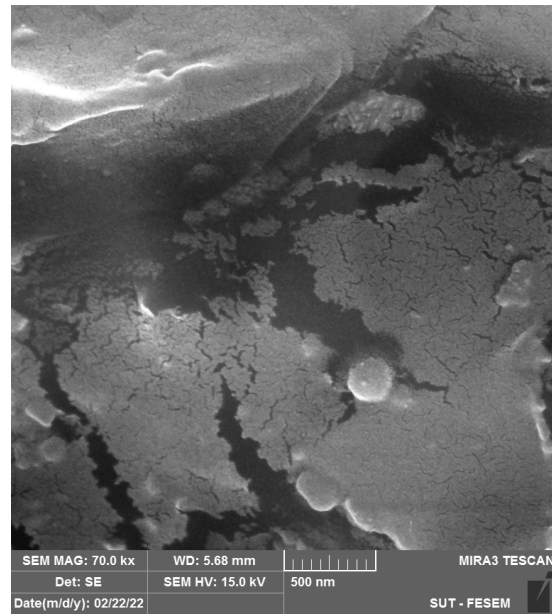


Fig. 9 SEM image of PMMA with 0.3% aloe Vera at 500nm.

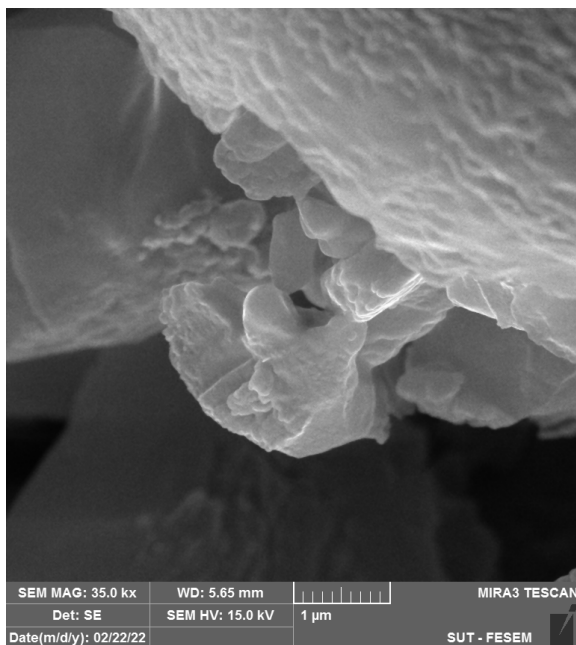


Fig. 10 SEM image of PMMA with 0.4% aloe Vera.

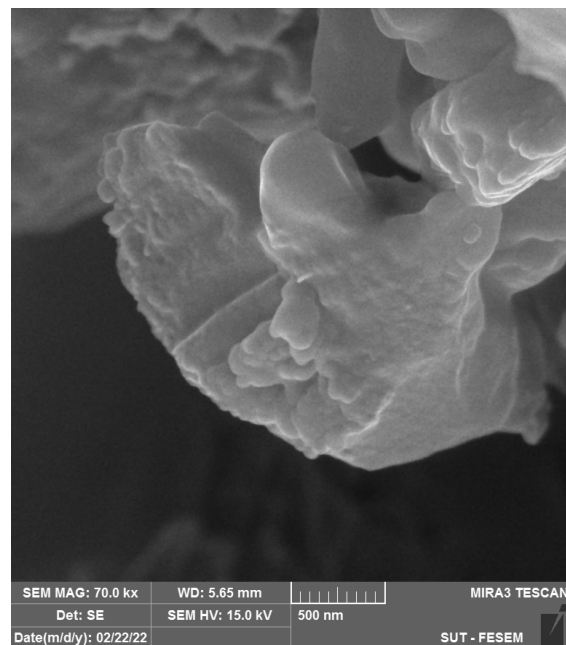


Fig. 11 SEM image of PMMA with 0.4% aloe Vera at 500nm.

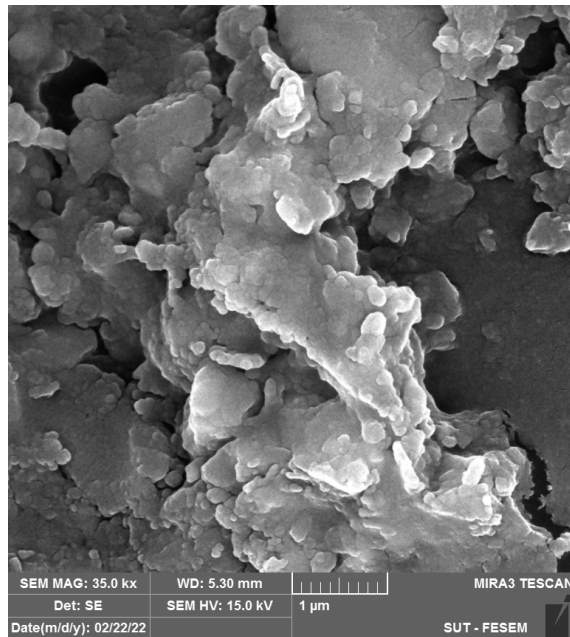


Fig. 12 SEM image of PMMA with 0.5% aloe Vera.

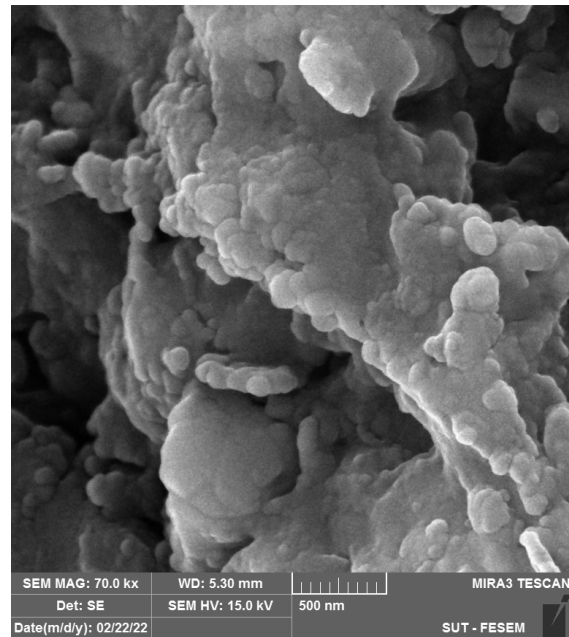


Fig. 13 SEM image of PMMA with 0.5% aloe Vera at 500nm.

3.3 Contact angle (wettability) test

Improvement of PMMA structure by aloe Vera gel addition has a considerable effect on many lens properties especially surface properties of contact lenses that serve a crucial function in lens performance, surface contact angle was examined using purified water droplet for pure PMMA and PMMA with different aloe Vera percentage. figure (14) showed the contact angle values of PMMA contact lens before and after aloe Vera gel addition, from the figure pure PMMS sample, expose hydrophobic surface than samples with aloe gel due to PMMA rigid structure makes the surface more hydrophobic than a structure with high OH content, the addition of 0.1% and 0.2% of aloe Vera to pure PMMA result in decreasing the contact angle value as shown in figure (14) make lenses more hydrophilic additionally increasing the aloe Vera percentage above 0.2% causing an increasing the contact angle as obtained with 0.3%,0.4%, and 0.5% due to many changes in internal structure which appears directly at the surface, finally using aloe Vera gel act to soften the lenses by increasing the OH content in PMMA structure lead to improving the lens wettability at about (0.2-0.3)% after these percentage large drop in whole properties will occur.

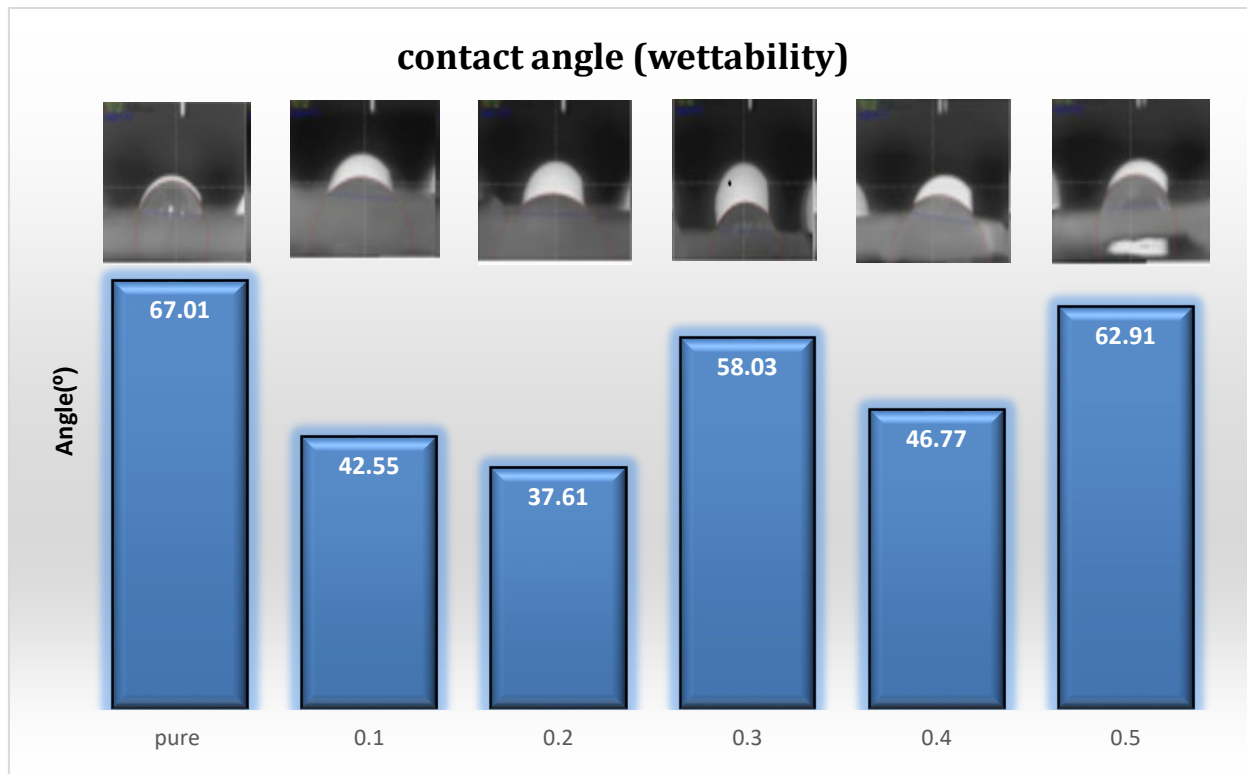


Fig. 14 Contact angles of PMMA samples.

3.4 Anti-bacterial test

Anti-microbial activity of prepared PMMA contact lenses before and after the addition of aloe Vera was accomplished using Kithy by–Bauer method in which *Staphylococcus* bacteria were cultivated for drug sensitivity by taking part of the colony and placing it in 0.85 NaCl medium until the bacterial suspension confirmed with 0.5 Mcf. Afterward, it was placed on a hot plate in the middle of Mueller Hinton agar. Then, pits were made and distributed at specific distances. The complex was added at the concentrations applied in the study. The plates were incubated for 24 hours at °C. subsequently, the halos (the area of inhibition) were observed around the pits, and measurements were compared in millimeters with a ruler by the National Standard Committee for Clinical Laboratory Standards. as shown in photographs of agar, figure (16) of all samples. Results showed that the addition of aloe Vera to pure PMMA rigid contact lenses enhanced the antibacterial behavior by increasing the value of the inhibition zone from 12 mm to 15 mm which means increasing the efficiency of lenses to resist the *staphylococcus* activity in the human eye when used this type of lenses.

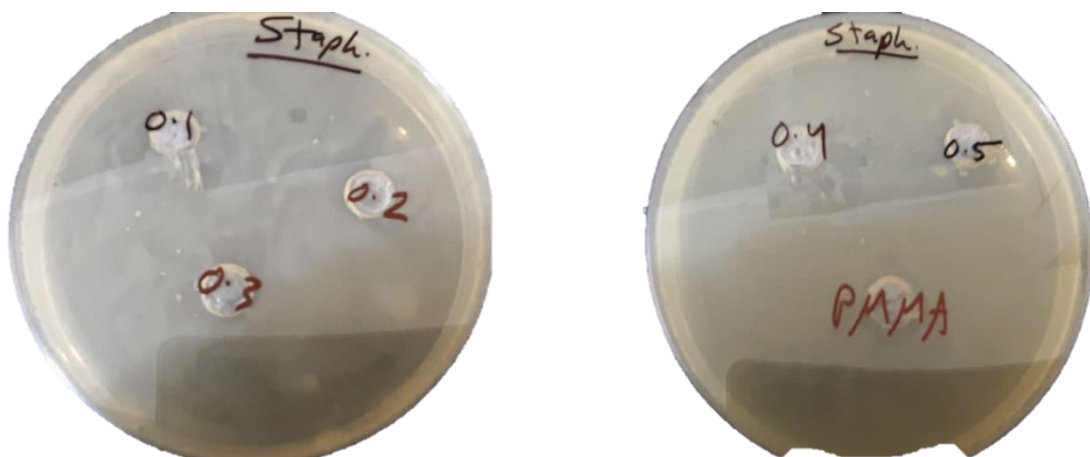


Fig. 15 Antibacterial *Staphylococcus* zone formation around PMMA contact lenses.

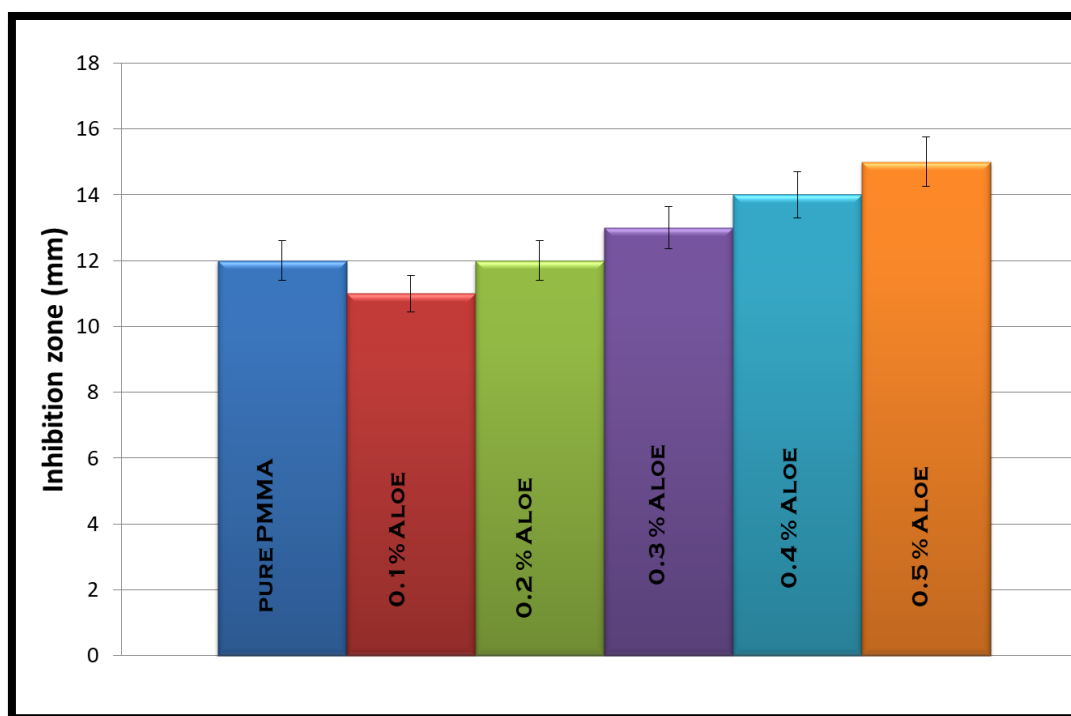


Fig. 16 Inhibition zone value (anti-bacterial test) of staphylococcus for PMMA contact lenses.

Conclusion

Addition of aloe Vera natural materials to rigid PMMA contact lenses aid to promote the performance of contact lenses by changing the internal structure of PMMA, especially when using (0.1%, 0.2%, and 0.3%) of aloe Vera due to the increase in OH content as well as the increasing in the uniformity of microstructure. Addition of (0.4% and 0.5%) of aloe Vera make a reverse effect on the structure due to the saturation of the PMMA chain with OH leading to destroying the connections between bonds there for weakening PMMA lenses.

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Effect of Zr Concentration on the Microstructure and Mechanical Performance of Porous Ti-Zr System by Powder Metallurgy

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Keywords: Powder metallurgy, binary alloys, space holder, general porosity.

Abstract. In this study, porous binary Ti-(x)Zr alloys of nominal Zr contents (x=10, 20 and 30 at. %) with differing porosities were manufactured, using powder metallurgy with compaction conducted under a pressure of 300MPa and sintering at 1200 °C for 6 h. A space holder agent was employed to control the general porosity. The microstructures were characterized by scanning electron microscopy and energy dispersed spectroscopy. The phase constitution was done by X-ray diffractometer. Uniaxial compressive tests were performed to determine the mechanical behaviours. Microstructural studies revealed macro/micro pores generated were mostly irregularly shaped with a uniform pore size distribution in all Ti-(x)Zr (at. %) alloys. The finer microstructure was obtained with increasing Zr contents. The mechanical performances of the porous Ti-(x)Zr (at. %) binary systems were strongly influenced by Zr and general porosity.

Introduction

Titanium (Ti) based alloys can be used in implantable devices owing to excellent corrosion resistances, acceptable mechanical performances, and outstanding biocompatibilities [1]. Normally, they can be classified as alpha (α), alpha (α) + beta (β) and beta (β) phase alloys, depending on the phase constituents of individual alloys [2]. Aluminium (Al) or interstitial atoms such as oxygen (O), carbon (C), nitrogen (N), and hydrogen (H) can be considered as α -stabilizer. On the other hand, most of other elements in the periodic table can be known as β stabilizer [3]. However, there are also some neutral elements or weak β stabilizer like zirconium (Zr), tin (Sn) or silicon (Si) since they do not critically shift α and β solvus line [4-7]. Ti-Zr binary systems exhibit a complete solid-solution and thus Zr can be added into the Ti matrix with a wide range of alloy composition, which improves the corrosion resistance and the mechanical properties of the alloy [8]. In addition, Ti-Zr binary alloys are good candidates for use as load-bearing implant materials due to a thermodynamically stable oxide layer formed on their surface [9-10]. To replace the currently used Ti-6Al-4V alloys, in which both Al and V have allergic effects as they have been found to cause adverse tissue-implant reactions, it is aimed to produce Al and V free-Ti based alloys as load bearing implant material in this study [11].

Ti based alloys used as load bearing implant have a mechanical mismatch problem. i.e., their elastic modulus is too high (>110GPa), compared to that of bones (<30GPa for cortical bones), which leads to non-uniform load transfer between implant and bone, termed *stress shielding effect*. Such a condition may cause a reduction in bone density (osteopenia) [12]. Powder metallurgy is widely used in implant applications due to adjustable mechanical properties, and high tolerance. This method also provides porous structure with a reduced elastic modulus, which can minimize the *stress shielding effect*. In addition, it facilitates adequate adherence between implant and tissue [13-15]. Therefore, for this study, powder metallurgy is selected in material production [16,17].

Material and Method

To fabricate porous Ti-(x)Zr binary alloys of nominal Zr contents ($x=10, 20$ and 30 at. %), Ti and Zr initial powders (>99 % wt. purity, Alfa Aesar) were employed in this study. The detailed chemical compositions and process parameters were given in Table 1.

Table 1. Chemical composition of Ti–Zr alloys and process parameters.

Group Number	Chemical Composition [at. %]	Mixing Time [h]	Compaction Pressure [MPa]	Sintering Temperatures [°C]	Sintering Time [h]
Group 1	Ti-10Zr	10	300	1200	6
	Ti-20Zr	10	300	1200	6
	Ti-30Zr	10	300	1200	6
Group 2	Ti-10Zr + 20 (wt. %) NH_4HCO_3	10	300	1200	6
	Ti-20Zr + 20 (wt. %) NH_4HCO_3	10	300	1200	6
	Ti-30Zr + 20 (wt. %) NH_4HCO_3	10	300	1200	6

Zr and Ti initial powders were prepared according to the chemical compositions given in Table 1. To begin with, the metal initial powders were mixed in a rotating container at 24 rpm for 10 h at room temperature. 20 (wt.%) ammonium bicarbonate (99% wt. purity, Fisher) was added to group 2 alloys as space holder. The powder mixtures were compacted under 300 MPa, in a steel die with 10 mm in diameter and 15 mm in height. Sintering procedure was done to the green compacts by using a digitally controlled Protherm furnace. To remove the space holder agent, group 2 alloys were firstly held at 180 °C for 2 h, and then all green compacts (group 1 and 2 alloys) were heated up to 1200 °C with 5 °C/min and kept for 6 h under argon atmosphere. In conclusion, group 1 and 2 alloys were cooled down 200 °C with 5 °C/min and then left to cool at room temperature.

Metallographic route was performed using conventional techniques. All alloys were chemically etched with Keller's solution; (190 ml H_2O , 5 ml HNO_3 , 3 ml HCl and 2 ml HF) for 5 sec [17]. The micrographs were taken by scanning electron microscopy (SEM) and energy dispersed analysis (EDS) (type JEOL 6000). Rigaku (Rad-B D-Max 2000) diffractometer using $\text{Cu-K}\alpha$ radiation and scanning from 30° to 80° was used to determine the phase constitutions. Uniaxial compressive tests were performed with a size of $\Phi 10$ mm $\times$ 15 mm by compressive test machine (Zwick/Roell Z600). Finally, general porosity was calculated using the following mathematical Eq. 1, 2 and 3 [18]. V , ε , ρ , and ρ_0 is volume (cm^3), general porosity (%), sintered density (g/cm^3) and theoretical density (g/cm), respectively.

$$\rho_{o=} (M_{Ti} + M_{Zr}) / (V_{Ti} + V_{Zr}) \quad \text{Eq. 1}$$

$$\rho = m / V. \quad \text{Eq. 2}$$

$$\varepsilon = (1 - \rho / \rho_0) * 100. \quad \text{Eq. 3}$$

Result and Discussion

General Porosity. Characterizations of Ti and Zr initial powders were performed by SEM and EDS. The corresponding SEM and EDS analysis were shown in Fig. 1. The average particle sizes for Ti and Zr initial powders specified in their SEM micrographs were 44 μm and 23 μm , respectively. The shapes of Ti and Zr initial powders were irregular and Zr initial powder aggregated more than Ti initial powder. Also, only EDS peaks of Ti and Zr elements were detected in the initial powders.

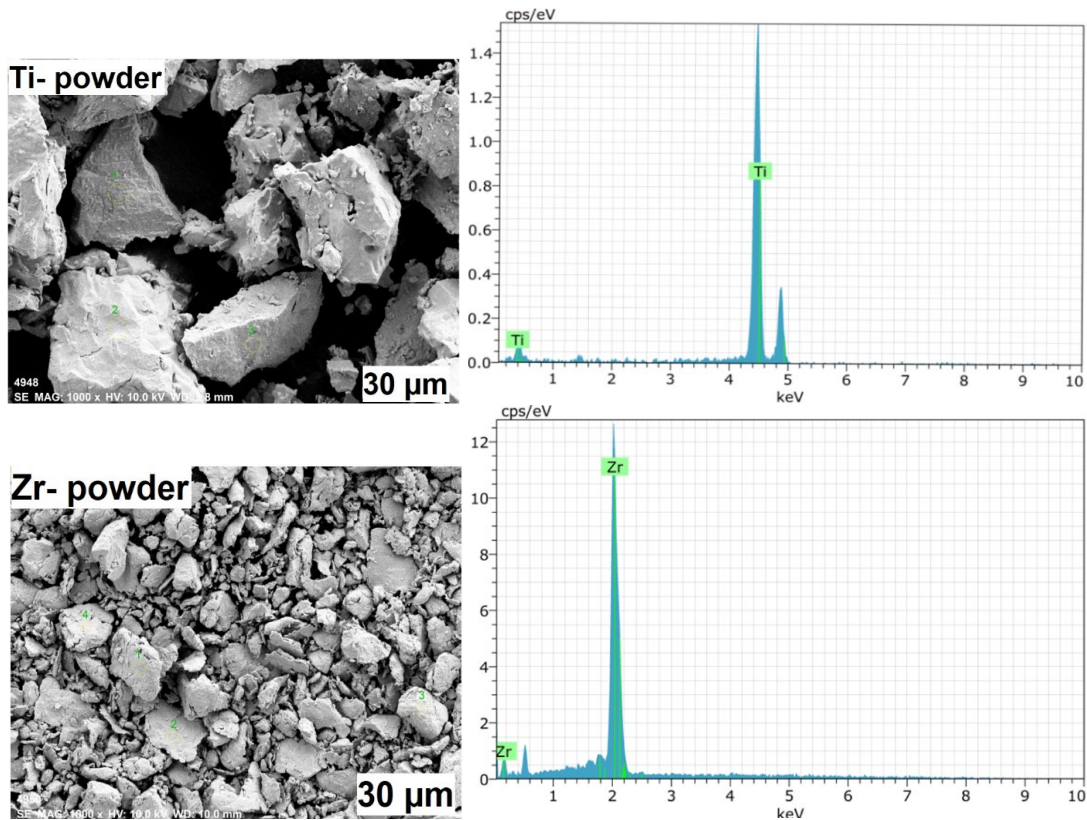


Fig. 1. SEM and EDS analysis of Ti and Zr initial powders.

To determine the general porosity (ϵ), alternative mathematical Eq. 1, 2 and 3 were used. Representative SEM micrographs showing macro and micro pores for group 1 and 2 alloys were given in Fig. 2. Results of the general porosity for group 1 and 2 alloys were depicted in Table 2. The general porosity values for group 1 alloys were in the range from 20.57 % to 21.17 % meanwhile these for group 2 alloys were in the range from 42.56 % to 44.98 %. Minimum general porosity for group 1 alloy was observed in Ti-10Zr (at. %) as 20.57% and that for group 2 alloy was determined in Ti-10Zr (at. %) +20 (wt. %) NH_4HCO_3 which was 42.56 %. Accordingly, Ti-(x)Zr alloys of nominal Zr contents ($x=10, 20$ and 30 at. %) had two ranges of general porosities since ammonium bicarbonates completely degraded to $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$ when heated up to 180°C and it was replaced by pores [18]. On the other hand, median pore diameter for group 1 alloys specified on SEM micrographs was about $78\ \mu\text{m}$. For the group 2 alloys, this value was recorded as approximately $141\ \mu\text{m}$. As foreseen, a significant increase in pore diameter occurred in group 2 alloys. Moreover, micro-macro pores of group 2 alloys were more interconnected than that of group 1 alloys due to reducing the thickness of the cell walls in group 2 alloys, which is a desired feature for bone ingrowth and transportation of body fluid because it provides the penetration of cells into the alloys effectively when implanted [19,20].

Table 2. The general porosity for Ti - (x)Zr (at. %) alloy series.

Chemical Composition [at. %]	Porosity Level [%]
Ti-10Zr	20.57
Ti-20Zr	21.04
Ti-30Zr	21.17
Ti-10Zr + 20 (wt. %) NH_4HCO_3	42.56
Ti-20Zr + 20 (wt. %) NH_4HCO_3	43.12
Ti-30Zr + 20 (wt. %) NH_4HCO_3	44.98

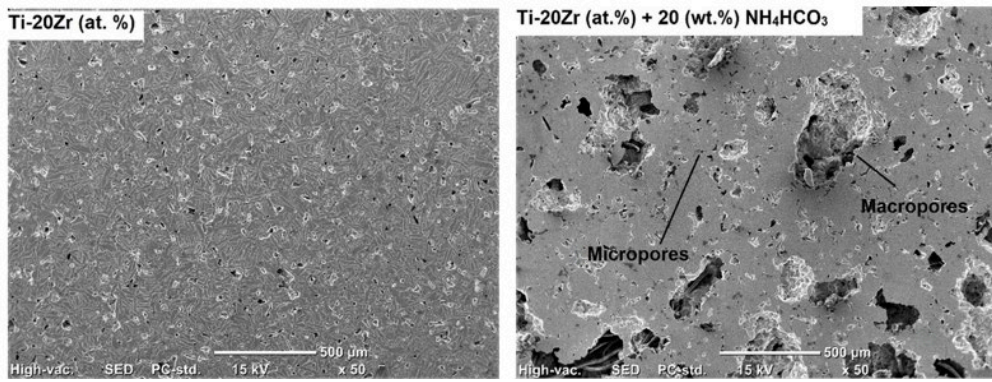


Fig. 2. SEM micrographs showing macro and micro-pores.

Microstructure Analysis. SEM micrographs for porous Ti-(x)Zr (at. %) binary alloys manufactured by powder metallurgy were given in Fig. 3. Microstructures generally showed complete solid solution, as understood from binary Ti-Zr phase diagram [10]. The lamellar shape with Widmanstatten patterns were observed in Ti–10Zr (at. %) alloys for group 1 and 2 alloys, which were the martensitic α' phase having a distorted hexagonal close-packed (hcp) and hcp α phase. Similar result was found by Kobayashi et al. They declared that when an alloying element affecting the martensite start temperature (M_s) is added to Ti matrix, martensitic α' phase may be formed in its microstructure [21]. Gray areas in the SEM correspond to α phase rich in Ti contents while light gray areas correspond to α' phase rich in Zr contents. With increasing Zr contents in Ti matrix, finer microstructures were determined in Ti-20Zr (at. %) for both group 1 and 2 alloys compared to Ti–10Zr (at. %) alloys for group 1 and 2 alloys. In addition, it was striking to determine a great number of needle-like structures replacing lamellar shape structure in Ti–30Zr (at. %) for group 1 and 2 alloys [21]. For this reason, reduction in M_s led to by Zr contents prevented the growth of α phase [14]. Thus, increasing Zr contents resulted in finer grains. It was concluded that microstructures of Ti-(x)Zr systems were strongly sensitive to Zr concentration [22].

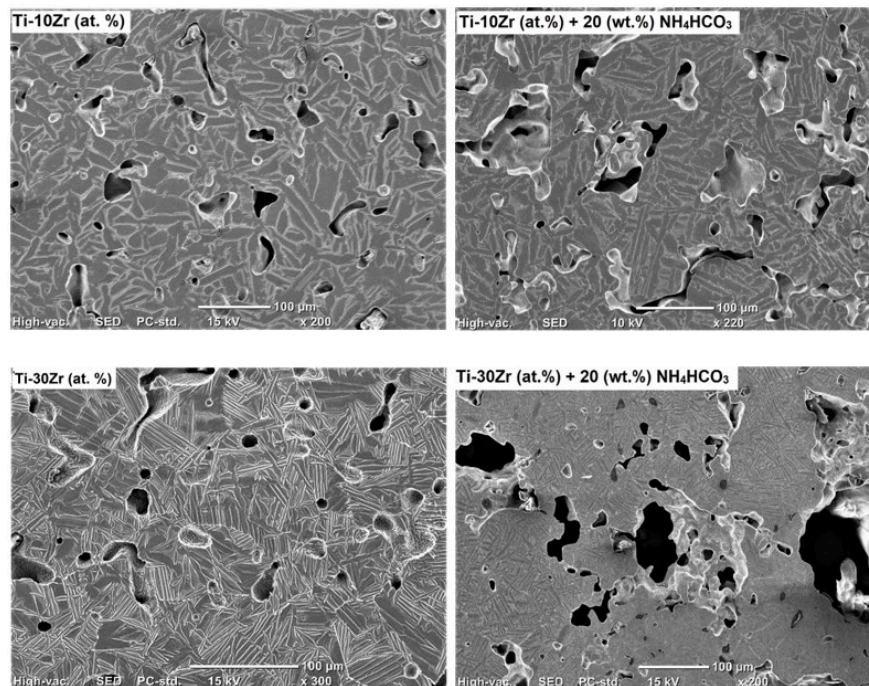


Fig. 3. SEM micrographs for porous Ti - (x)Zr (at. %) binary alloy.

Fig. 4 shows EDS analysis points in Ti - 20Zr (at. %) alloys for both group 1 and 2 alloys. No undissolved pure Zr was identified. EDS points values from 1 to 4 in Ti-10Zr (at. %) for group 1 alloy were Ti-29.34Zr (at. %), Ti-23.45 (at. %), Ti-18.98Zr (at. %) and Ti- 16.32 (at. %) respectively. Moreover, EDS point values from 1 to 2 in Ti-20Zr + 20 (wt. %) NH_4HCO_3 for group 2 alloy were

consisted of Ti-29.62 (at. %) and Ti-14.76 (at. %) respectively. According to the EDS results, Ti-20Zr (at. %) for group 1 alloy showed better match with the nominal composition compared to Ti-20Zr + 20 (wt. %) NH_4HCO_3 for group 2 alloy.

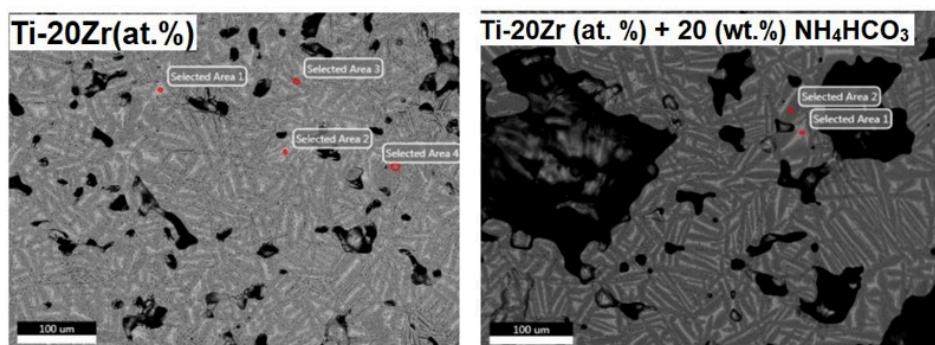


Fig. 4. SEM micrographs showing EDS analysis points.

XRD Analysis. XRD patterns for series of porous binary Ti-(x)Zr alloys with Zr contents up to 30 (at. %) in group 1 alloys were given in Fig. 5. The X-ray profiles showed that predominant hcp α phase and some distorted hcp α' phase were present. These results were similar to those of the binary Ti-Zr alloys reported by Wen et al [23]. They stated the presence of similar X-ray patterns in Ti-(x)Zr (x:5, 15, 25, 35, 45 wt. %) alloys produced by powder metallurgy. On the other hand, due to the difference in atomic radius between Ti (1.47 Å) and Zr (1.62 Å), it generated stress in the lattice parameters of hcp α and hcp α' phases, resulting in a shift in the XRD graphs depending on increasing Zr contents [23].

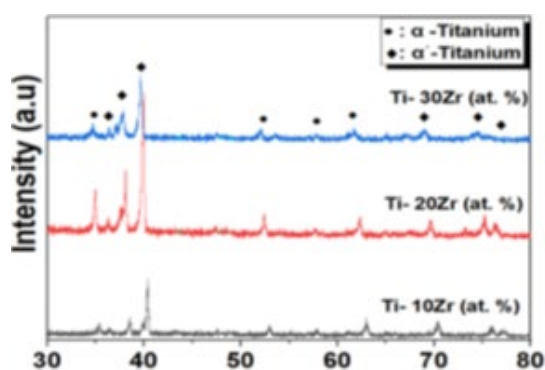


Fig. 5. XRD patterns for Ti-(x)Zr (at. %) master alloys.

Mechanical Performance. The compressive stress -strain curves for porous Ti-(x)Zr (at. %) binary alloys were summarized in Fig. 6 as a function of Zr concentration. Ultimate compressive strengths (UCS) for Ti-10Zr, Ti-20Zr and Ti-30Zr (at. %) in group 1 alloys were 1185 MPa, 1344 MPa and 1487 MPa whilst for group 2 alloys, they were determined as 261 MPa, 356 MPa and 382 MPa, respectively. There was an improvement in UCS values for both group 1 and group 2 alloys according to increasing Zr contents. This improvement was probably induced from two aspect. Former was the *solid solution mechanism*. Adding of Zr to Ti matrix generated *solid-solution strengthening* by distorting the crystalline lattice in the Ti-(x) Zr (at. %) master alloys, which lead to a great resistance to the slip system [23]. It was concluded that UCS were increased with increasing Zr concentration. This finding was consistent with previous studies cited by other researchers and some solid solution mechanism identified in general. Wang et al [14] also stated mechanical performances of Ti-Zr systems were strongly influenced by Zr contents. Latter was general porosity. With increasing general porosity, mechanical performances of the alloys decreased. Elastic modulus results calculated from stress-strain curves for Ti-(x) Zr master alloys with nominal Zr content (10, 20, and 30 at. %) were reduced from 46 GPa to 11 GPa, 59 GPa to 16 GPa, and 67 GPa to 18 GPa, respectively, which reveal that general porosity had great impudence on elastic modulus of Ti-(x)Zr

master alloys. This is because cracks preferentially occurred in the pores expanded with increasing the compressive strength, which resulted in a serious reduction in UCS for group 2 alloys. With increasing porosity, mechanical performance is close to human bone (10-32 GPa), reducing *stress shielding effect* for group 2 alloys [14]. Mechanical performances of group 2 alloys were closer to that of bone than group 1 alloys.

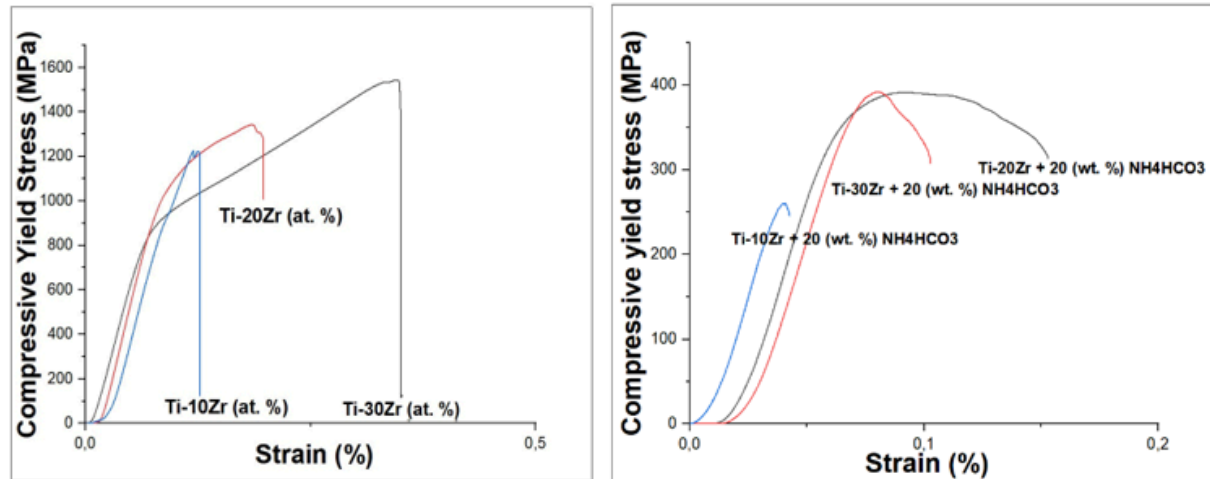


Fig. 6. Compressive yield stress-strain curves for Ti-(x) Zr (at. %) master alloys.

Conclusion

Porous binary Ti-(x) Zr alloys of nominal Zr contents ($x=10, 20$ and 30 at. %) were fabricated by powder metallurgy. Conclusions taken from the present study are given as below.

I. Pores structures showed irregular shapes but uniform pore size distribution for two range of pore sizes in all Ti- (x)Zr alloys investigated.

II. Porosity size and volume fraction could be adjusted by changing processing parameters without changing phase constitution.

III. Microstructure refinement occurred with increasing Zr content. At the highest Zr content in this work, i.e., the Ti-30Zr needle-like structures replaced the lamellar structures.

IV. Mechanical performances were highly sensitive to porosity level of the alloys.

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CHAPTER 2:
Metals Processing

Electron Beam Brazing of Titanium and Stainless Steel Dissimilar Joints with Ag-Based Filler

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Keywords: electron beam, brazing, soldering, austenitic, stainless steel, titanium, intermetallic compounds, IMCs, dissimilar joints.

Abstract. In this work, electron beam was used for butt brazing of austenitic stainless steel with grade 2 titanium. Due to its low solidus temperature and high silver content, AWS BAg-21 filler containing Ag, Cu, Sn and Ni was selected. The joints were brazed with a defocused oscillating beam using offset. The resulting brazed joints were subjected to static tensile testing, light microscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) analysis and hardness tests. By using appropriate parameters it was possible to reduce the phenomenon of diffusion of titanium atoms into the joint, which improved the properties of the obtained joints. The maximum tensile strength obtained was 244.2 MPa.

Introduction

The purpose of this research is to investigate the properties of dissimilar titanium and stainless steel electron beam brazed joints. Electron Beam Brazing (EBB) technology can be used to fabricate bimetallic elements intended for further use in other production processes. The ability to precisely position the focus of the beam, split it, and put it into oscillation allows control over the amount of heat introduced into the component. Therefore, EBB technology is suitable especially for components with complex geometries that cannot be heated entirely or are not cost effective to be brazed in a vacuum furnace. This technology also can be used to fabricate bimetallic elements intended for further use in other production processes [1, 2]. Previous tests performed at Łukasiewicz Welding Institute on electron beam brazing have shown that the application of this technology to brazing is feasible and yields good joint quality in stainless steel brazing [3]. Brazing tests on titanium [4] have shown a high tendency to form intermetallic phases and produce brittle joints. Therefore, further research on this technology is important as it may allow the production of high quality dissimilar joints of titanium and stainless steel.

There are a few examples of the use of electron beam in brazing process that have been described in the literature. The authors of the paper [5] performed tests of pure titanium TA2 brazing using electron beam in vacuum. Automatically fed 72Ag-28Cu wire was used as a filler material. Based on the study, the beam intensity and brazing speed were found to have a key effect on the amount of the surface quality, microstructure and tensile strength of the brazed joints. The microstructure consisted of Ag-based solid solution as well as Ti₂Cu and TiCu IMCs. The EDS results showed a high degree of Ti diffusion into the brazed joint. The highest tensile strength obtained was 366 MPa with a brittle fracture mode. In paper [6], the authors conducted electron beam brazing of dissimilar joints of AISI 304 steel and TA15 titanium with different beam current values. 72Ag-28Cu alloy was used as a filler material, and the joints were made in a lap configuration. The brazed joints, exhibited a reduced shear strength with increasing beam current. This was associated with an increased thickness of the Ti-Cu intermetallic phase layer. The maximum shear strength of the obtained brazed joints was 188.6 MPa.

In papers [7-11], the authors showed results of dissimilar brazing of joints made of titanium alloys with austenitic corrosion-resistant steels. The joints were brazed Ag-based filler materials. In article [7], samples were brazed in a vacuum furnace. The highest shear strength achieved was 85 MPa. As the temperature increased, the researchers observed a decrease in tensile strength, correlating with an increased amount of Cu-Ti and Fe-Ti IMCs in microstructure. In paper [8], samples were butt brazed in a vacuum furnace using 72Ag-28Cu filler material. The revealed microstructure consisted mainly of Cu-Ti IMCs and unreacted silver-based solution. The maximum tensile strength obtained was 112 MPa with a brittle fracture mode. Authors of [9, 10] heated the samples using infrared in a chamber filled with argon. To further reduce the diffusion of copper atoms into the titanium alloy, it was coated with a 45 μm thick silver layer. The use of an additional layer of pure silver helped to reduce the formation of brittle Ti-Cu IMCs. Only a thin layer of TiAg phase was present at the titanium alloy interface. A tensile strength of 442 ± 10 MPa was obtained, the fracture was ductile. The authors have conducted corrosion resistance tests of the achieved brazed joints and compared them with joints brazed without Ag coating. For the joints brazed without Ag interlayer, corrosion occurred mainly in silver-based solid solution, indicating the higher corrosion resistance of Cu-Ti and Cu-Fe IMCs. For the joint brazed with pure Ag interlayer, electrochemical corrosion occurred mainly in the TiAg phase with high material loss. In article [11], the joints were brazed in vacuum furnace using Ti-15Cu-15Ni, Ag-28Cu and pure Ag filler materials. The IMCs formed in the joint brazed using Ti-Cu-Ni alloy did not impair the good corrosion resistance of both brazed materials. In the case of Ag-Cu and pure Ag filler materials, the potentiodynamic polarization tests and the microstructure of the corroded brazed joints showed the occurrence of electrochemical corrosion, to which the Ag-rich phases were particularly susceptible.

Experimental Procedure

Materials Used. The materials used for this study were AISI 304 steel, grade 2 titanium alloy sheets with a thickness of 1.5 mm, and AWS BAg-21 brazing filler material foil with a thickness of 0.2mm with chemical composition of 62 - 64 % Ag, 27.5 - 29.5 % Cu, 5.0 - 7.0 % Sn and 2.0 - 3.0 % Ni. According to the AWS A5.8 specification [12] its solidus temperature is 690 °C with recommended brazing temperature range of 700 - 900 °C. In comparison, the most common eutectic AWS BAg-8 filler material (Ag72-Cu28) has solidus temperature of 780 °C with recommended brazing temperature range of 770 - 890 °C. The lower solidus temperature of the filler material used, as well as the recommended brazing temperatures range have a key impact on the process, due to the reduction of diffusion phenomena that contribute to the formation of brittle IMCs and segregation of elements.

Sample Preparation and Brazing. The components were prepared for brazing by milling to obtain parallel faces. The brazed surfaces were then sanded with 800-grit sandpaper and then washed with acetone. The components were put together in a special positioning fixture on the CNC table of an electron beam welding machine. Sheets measuring $100 \times 200 \times 1.5$ mm were butt brazed with an offset of the electron beam. The electron beam was defocused and oscillating with a frequency of 1000 Hz in a circular shape with diameter of 2 mm. The reduction in surface energy density caused by defocusing and oscillation allows more heat to be applied to the joint at the same time without melting the surface of the heated component. In case of the offset brazing, the heat needed to melt the filler material is supplied by heat conduction in the steel element. Brazing was performed using a CVE EB 756 electron beam welding machine Model XW150:30. The parameters that were changed are shown in Table 1. The brazing speed in this case is understood as the speed of the CNC table movement in the direction parallel to the joint axis (electron beam gun is stationary). During the brazing tests, the accelerating voltage was set to 60 kV, with the electron beam working distance of 420 mm, pressure of 10^{-5} mbar and the offset of 1 mm. The resulting brazed joints were subjected to static tensile testing, light microscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) analysis and hardness tests.

Table 1. Parameters changed during brazing tests.

Joint no.	Beam current [mA]	Brazing speed [mm/min]
1	4.00	150
2	4.25	150
3	4.50	150
4	6.00	300
5	6.50	300
6	7.00	300

Test Results and Discussion

Metallographic Examination. Specimens measuring $40 \times 10 \times 1.5$ mm were cut from each brazed joint, and then were embedded in resin for SEM examination. The specimens were ground on 2500-grit sandpaper and polished with $3 \mu\text{m}$ diamond suspension and $0.01 \mu\text{m}$ Al_2O_3 suspension. The samples thus prepared were digested in a reagent containing 6% HNO_3 and 3% HF and visually inspected on a light microscope. The light microscopy examination was conducted using a Nikon Eclipse MA200 microscope. Pictures of cross-sections of specimens number 2 and 4 are shown in Fig. 1. The microstructure of samples 2, 3, 5 and 6 was characterized by visible phase segregation both in top and bottom regions of the joints. Only sample no. 4 microstructure was without visible macrosegregation. None of the samples had cracks. EDS analysis was performed to identify the distribution of elements in the brazed joint.

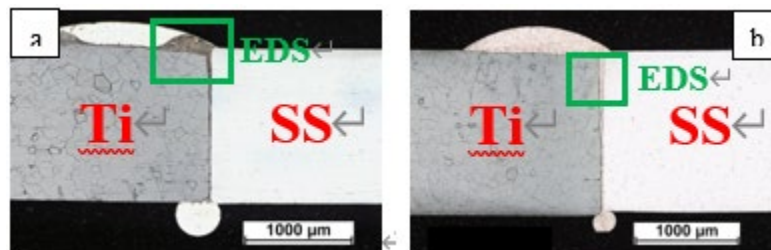


Fig. 1. Cross sections of electron-brazed samples with EDS scan locations marked a) sample no. 2, b) sample no. 4.

SEM Examination and EDS Analysis. Specimens used for light microscopy examination were ground again on 2500-grit sandpaper and polished with $3 \mu\text{m}$ diamond suspension and $0.01 \mu\text{m}$ Al_2O_3 suspension. The examination was conducted using SEM (FEI Inspect S 50). The microscope was equipped with the Octane Elect EDS System. Fig. 2 and 3 show SEM images of the microstructure of samples 2 and 4 in the upper region of the brazed joint and an EDS scan of these regions. EDS analysis of the brazed joints revealed segregation of Ag atoms in samples no. 2, 3, 5 and 6. The brighter areas seen in the light and scanning microscope images are Ag-rich areas with no Ti atoms. These areas have a dendritic structure and, according to the literature examples, are mostly composed of Ag-solid solution. In the interdendritic spaces there is a lamellar structure with higher content of Cu, Sn and Ni in chemical composition than in Ag-solid solution matrix (Fig. 4). The darker regions of these brazed joints are rich in Ti which diffuses into the molten region. There is also a high content of Cu, Ni, and Sn which show a high propensity to form IMCs with Ti due to the lower enthalpies of intermetallic phase formation of Ti-Cu, Ti-Sn, and Ti-Ni than Ti-Ag. In the case of sample number 4, almost no segregation of elements in the interface occurred. EDS analysis showed a higher concentration of Ni and Sn atoms at the Ti interface (Fig. 5). Due to the lowest enthalpies of Ti-Sn and Ti-Ni compound formation, these elements have the highest tendency to form IMCs with Ti. The phenomenon of Ag segregation in brazed joints with alloys containing high contents of Ag and Cu is

due to much lower diffusion coefficient of Ag than Cu and also due to lower values of enthalpies of formation of Ti-Cu, Ti-Sn, Ti-Ni compounds than Ti-Ag compounds. Atoms of filler material other than Ag can easily diffuse deep into Ti and form IMCs leaving unbound Ag in large clusters [5-17].

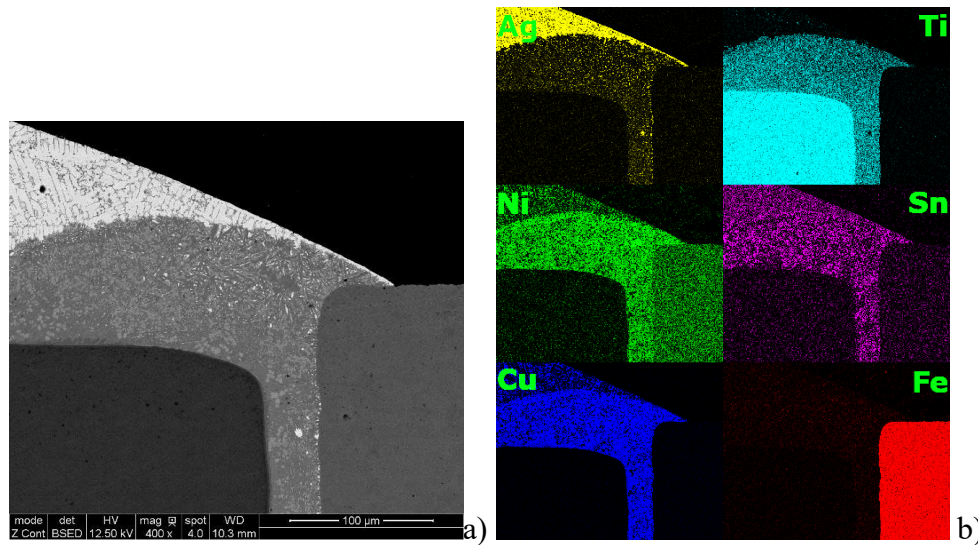


Fig. 2. SEM examination and EDS analysis results a) SEM image of upper region of sample no. 2, b) EDS analysis results of upper region of sample no.2

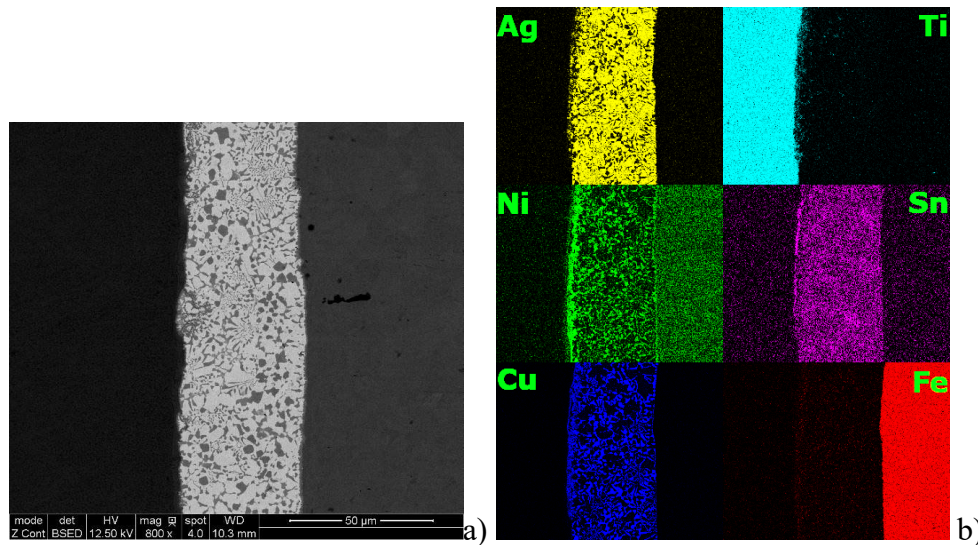


Fig. 3. SEM examination and EDS analysis results a) SEM image of upper region of sample no. 4, b) EDS analysis results of upper region of sample no. 4.

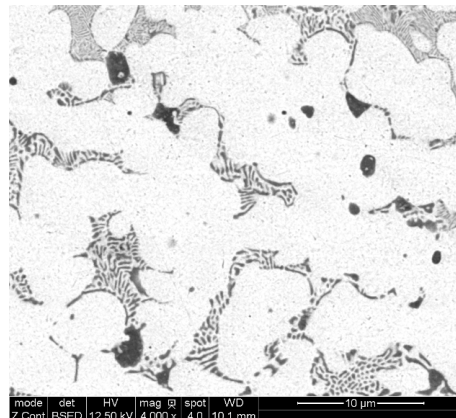


Fig. 4. SEM image of segregated Ag-solid solution with interdendritic lamellar structure.

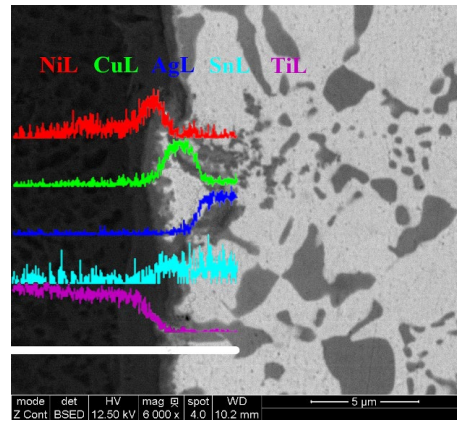


Fig. 5. EDS line scan of Ti brazed interface.

Hardness Testing. The Vickers Hardness tests were conducted using a KB Prüftechnik machine with a load of 0.1kg. Hardness was measured in the upper and middle part of the brazed joint. The average measured hardness values are shown in Table 2. The hardness distribution in joint number 4 is uniform. All measured hardness values were in the range of 115-132 HV0.1. For joints number 2, 3, 5 and 6, hardness was measured in the Ag segregation zone and in the Ti diffusion zone. The measurements showed an increase in hardness values with increasing beam current and also with decreasing brazing speed. The hardness of the Ag segregation zone in samples 2, 3, 5, 6 decreased with increasing beam current and with decreasing brazing speed, which is opposite to the measurements in the Ti diffusion zone. According to the cited literature examples [5-11], the high hardness far exceeding the hardness of both the parent material and the used filler material is due to the presence of titanium IMCs that have formed in the molten region. An increase in beam current as well as a decrease in brazing speed increases the amount of heat applied to the joint, thus increasing the maximum temperature and dwell time. This leads to an increase in the diffusion coefficient of the filler material atoms into the Ti parent material, causing an increase in formation of brittle IMCs, thus raising the hardness in the brazed joint. Titanium IMCs are generally very brittle and their presence in the brazed joint deteriorates its ductility reducing tensile and flexural strength. In addition, the large difference in the properties of the Ag solid solution and the hard IMCs results in the formation of a structural notch, which reduces the strength and especially the fatigue properties of the brazed joints.

Table 2. The average hardness values.

Joint no.	2	3	4	5	6
Upper region average hardness [HV0.1]	112	104	115	96	88
Middle region average hardness [HV0.1]	277	349	127	402	481

Static Tensile Testing. The tests were conducted using a MTS Criterion C45 machine with a maximum force of 100 kN. The dimensions of the specimens cut from the brazed joints were $200 \times 10 \times 1.5$ mm. Any excessive metal was ground off. Only for joint no. 1 no connection was obtained due to lack of Ti wetting with molten filler material. For each brazed joint, 5 tensile tests were carried out. The tensile strength testing results are shown in Table 3. For joint no. 4, the maximum tensile strength (UTS) obtained was 256 MPa, with an average result of 244.2 MPa. The fractures of all specimens from joint no. 4 were ductile. For joints no. 2 and 5, the UTS results varied widely. The fractures of these specimen were similarly varied, with mostly brittle fractures, however some had mixed or mostly ductile fractures. Specimens from joints no. 3 and 6 achieved the lowest tensile strength results. The fractures of all specimens from joints no. 3 and 6 were brittle. There is a visible tendency of decreasing UTS values with increasing beam current and with decreasing brazing speed which

clearly correlates with the measured hardnesses. The increase in hardness causes a decrease in tensile strength. The presence of hard phases in the areas with increased Ti content causes an increase in the brittleness of the brazed joint thus lowering its tensile strength. The maximum UTS of 244.2 MPa obtained for no. 4 sample is equal to 40% of the measured average tensile strength of 304 stainless steel, which was 608.1 MPa. This value is also equal to 58.5% of the measured grade 2 titanium tensile strength, which was 417.1 MPa. Obtaining the tensile strength at the level of 244.2 MPa with fully ductile fracture of the brazed joints can be considered as a satisfactory result.

Table 3. The average UTS values.

Joint no.	2	3	4	5	6
Ultimate tensile strength [MPa]	131.2	76.6	244.2	151.8	83.8

Conclusions

The following conclusions can be drawn from the study:

1) Electron beam can be successfully used for brazing dissimilar joints of titanium and austenitic stainless steel using AWS BAg-21 filler material. The application of optimal parameters, i.e. beam current of 6 mA and brazing speed of 300 mm/min, allowed to obtain a brazed joint with tensile strength of 244.2 MPa, with an average hardness of 127 HV0.1 and 115 HV0.1 in the middle and upper zones of the joint, respectively.

2) The use of AWS BAg-21 filler material makes it possible to carry out the electron beam brazing process at lower parameters than with the use of common 72Ag-28Cu filler material, thus obtaining a lower temperature and reducing the mutual diffusion of the parent and filler material atoms.

3) The use of AWS BAg-21 filler material which does not contain Zn allows to avoid the negative effect of evaporation of filler material components in vacuum. The applied filler material wettability was satisfactory on both brazed surfaces.

4) The use of a beam offset which results in heating the joint with heat conducted by the stainless steel, reduces the maximum temperature of the titanium element, thereby further reducing the mutual diffusion of the Ti parent material and filler material elements.

5) It has been shown that both increasing the beam current and decreasing brazing speed beyond the optimum values increases the diffusion of Ti into the joint contributing to the formation of brittle IMCs and segregation of filler material elements. It has also been shown that using too low beam current results in a lack of wetting thereby failing to achieve a bond.

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Tool Wear of Cubic Boron Nitride in Cutting Sintered Steel

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Keywords: cutting, polycrystalline cubic boron nitride compact, tool wear, sintered steel.

Abstract. In the powder metallurgy method, after sintering, it is often necessary for the sintered steel machine parts to be machined by the metal removal process for dimensional accuracy. In this case, it is imperative that the tool materials have good wear resistance. Polycrystalline cubic boron nitride compact (cBN) seems to be an effective tool material because it has good heat and wear resistance. In this study, in cutting sintered steel with cBN tools, various cBN tools have been used in cutting experiments to identify an effective combination of binding phase and cBN content. As a result of experimentally examining the wear progress of the CBN tools, a cBN tool having a binder phase of ($\text{Al}_2\text{O}_3\text{-Al}$) and a cBN content of 60% was effective for wear resistance.

Introduction

Although the powder metallurgy route of product fabrication is recognized for its near-net-shape abilities, economic constraints often demand involvement of minimal machining in the processes [1].

After sintering, it is often necessary for the sintered steel machine parts to be machined by the metal removal process for dimensional accuracy. As the sintered machine parts are often cut at high cutting speed for mass-production, it is imperative that the tool materials have good wear resistance. Polycrystalline cubic boron nitride compact (cBN) seems to be an effective tool material because it has good heat and wear resistance.

The properties of cBN depend on the binder phase, the content of cBN or the particle size of cBN [2]- [5]. Therefore, it is necessary to select an effective binder phase, content or grain size of cBN for cutting sintered steel. To clarify an effective tool material for the cutting of the sintered steels, this study experimentally investigated tool wear. The sintered steel was turned with four types of cBN tools.

Experimental Procedure

The work material used was the sintered steel from diffusion alloyed powder. This material had a density of 7.1Mg/m^3 . Microscopic observation of the microstructure revealed that this material had several pores. The chemical compositions and the mechanical properties of the hardened sintered steel are shown in Table 1. That is, the sintered steel had a hardness of 70 HRB.

Table 1 Chemical composition and properties of the sintered steel

Chemical composition [mass %]				
C	Cu	Ni	Mo	Fe
0.3 - 0.7	1 - 2	3 - 5	0.2 - 0.8	Bal.
Properties				
Hardness		Density		
70 HRB (129 HB)		7.1 Mg/m^3		

The cutting materials used are shown in Table 2. Al is often used as the binder in the sintering of PCBN products because of its low melting point. Under high temperature, Al melts into liquid phase to fill the gap between cBN crystals, and Al reacts with BN to produce ceramic phase AlN and AlB_2 , which will inhibit the transition of cBN to the hBN phase, beneficial to the preparation of PCBN [6]. Li et al. [7] reported that almost all Al reacted with cBN during sintering, resulting in AlN as well as

AlB₂ phases, while the remaining Al, Ni formed intermetallic compounds. Therefore, Al is often added to the binder in the production of CBN [8]- [12]. cBN tools combine different binding phases and different contents ratios and with a cBN particle size of 3.0 μm . cBN tool material containing the Al binder phase was used as shown in Table 2.

The configuration of the tool insert was ISO TNGA160408. The insert was attached to the tool holder MTG NR 2525M16. In this case, the tool geometry was (-6, -6, 6, 6, 30, 0, 0.8 mm). The insert had a chamfered and honed cutting edge, namely the width of the chamfered edge was 0.13 mm, the angle of the chamfered edge was 25° and the radius of the honed edge was 0.15 mm.

The turning tests were conducted on a precision lathe (Type ST5, SHOUN MACHINE TOOL Co., Ltd.) by adding a variable-speed drive. The driving power of this lathe is 7.5/11kW and the maximum rotational speed is 2500 min^{-1} . Sintered steel was turned under the cutting conditions shown in Table 3. The tool wear was investigated.

Table 2 Properties of sintered cubic boron nitride compact

Tool material	Binding phase *	Contents rate **	Grain size of cBN [μm]	Hardness [HV]	T. R. S. [GPa]
cBN B	TiN-Al	65/35	3.0	3200-3400	1.00-1.10
cBN D	WC-Co-Al	95/5	3.0	4100-4300	1.90-2.10
cBN E	Al ₂ O ₃ -Al	60/40	3.0	2900-3100	0.90-1.10
cBN F	TiC-Al	60/40	3.0	3000-3200	0.95-1.20

*: Main element, **: (cBN grain/ binding phase), T. R. S.: Transverse-rupture strength

Table 3 Cutting conditions

Cutting speed	5.0 [m/s]
Feed speed	0.00937 (about 0.01) [mm/rev]
Depth of cut	0.1 [mm]
Cutting method	Dry

Results and Discussion

In turning of the sintered steel with the various cBN tools, tool wear was observed. Figure 1 shows the tool wear tool at a cutting speed of 5.0 m/s. In the case of all the cBN tools, the wear is seen on both the flank face and the chamfered edge. As the width of the feed rate of 0.01 mm/rev was smaller than that of the 0.13mm chamfered edge, the sintered steel was cut by only the chamfered edge, and there was no significant formation of craters on the rake face. Furthermore, no significant characteristic wear, such as chipping or boundary wear, was observed.

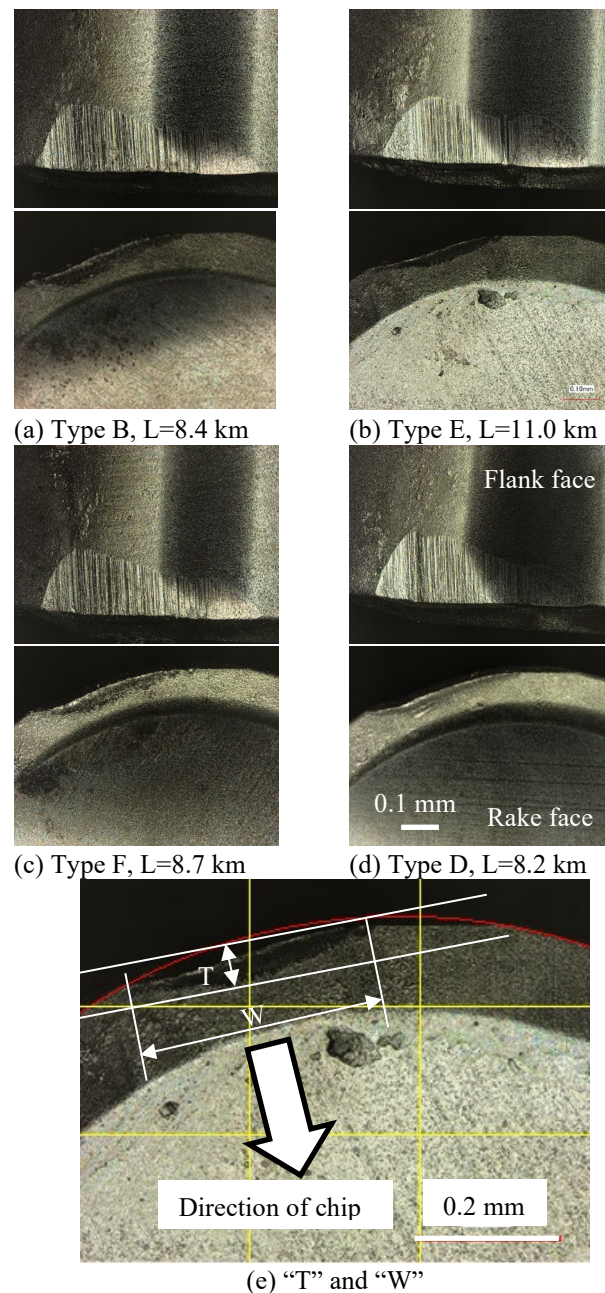
As described above, it is considered that the main tool failure of all the tools in this study was the flank wear within the maximum value of the flank wear width VBmax of about 0.2mm.

Figure 2 shows the wear progress of various cubic boron nitrides at a cutting speed of 5.0 m/s, feed rate of 0.01 mm/rev and depth of cut of 0.1 mm. The cutting experiment was repeated twice to improve reproducibility. The “circle mark” indicates the first time, and the “triangle mark” indicates the second time. The first and second wear progress shows almost the same value. The solid line in this figure shows the case where VBmax is 0.15 mm. "Lc" indicates the cutting distance at which VBmax=0.15 mm. Lc is an average value of two cutting experiments.

Comparing the wear progress of Type B, E, and F tools with the same content of 62.5 ± 2.5 %, the wear progress of the Type E tool with the (Al₂O₃-Al) bonding phase is smaller than that of the Type B or the Type F tool.

Finally, the influence of the wear progress on the cBN contained was investigated. The above results indicate that the (Al₂O₃-Al) is an effective bonding phase. The cBN tool with the (Al₂O₃-Al) bonding phase and the high cBN content is not commercially available. Therefore, the wear progression of the Type D tool with a cBN content of 95% and without the (Al₂O₃-Al) bonding phase was investigated. Figure (d) shows the wear progress of the Type F tool. Comparing the wear progress

of the Type E tool and the Type D tool shown in Fig. (b) and Fig. (d), respectively, the wear progress of the Type E tool is slower than that of the Type D tool. Comparing the properties of sintered cubic boron nitride compact as shown in Table 2, both the hardness and the transverse-rupture strength of the Type E tool are lower than that of the type D tool. Therefore, it is considered that the binding phase has a greater influence on the tool wear than the cBN content in the cutting of sintered steel by the cBN tool. On the other hand, it is also reported that in dry-cutting of the sintered steel (content of carbon: 0.5-0.9%) at a cutting speed of 5.0 m/s, feed rate of 0.05mm/rev, and cut depth of 0.1 mm, the wear progress of the higher cBN content is slower [13]. This may be due to the change in the binding phase of the cBN tool, feed rate, and sintered steel used in this study. In other words, in this study, Al was added to the binding phase, the feed rate was reduced to 1/5, and the carbon content of the sintered steel was reduced, respectively. Regarding the wear mechanism of the cBN tools used in this study, it is necessary to observe the worn surface of the cBN tools in detail, such as by a scanning electron microscope (SEM) and an energy dispersive X-ray spectroscopy (EDS) analysis.



W: Contact width between the rake face and the chip
 T: Contact length between the rake face and the chip
 L: cutting distance

Fig. 1 Tool wear of cBN tools at a cutting speed of 5.0 m/s.

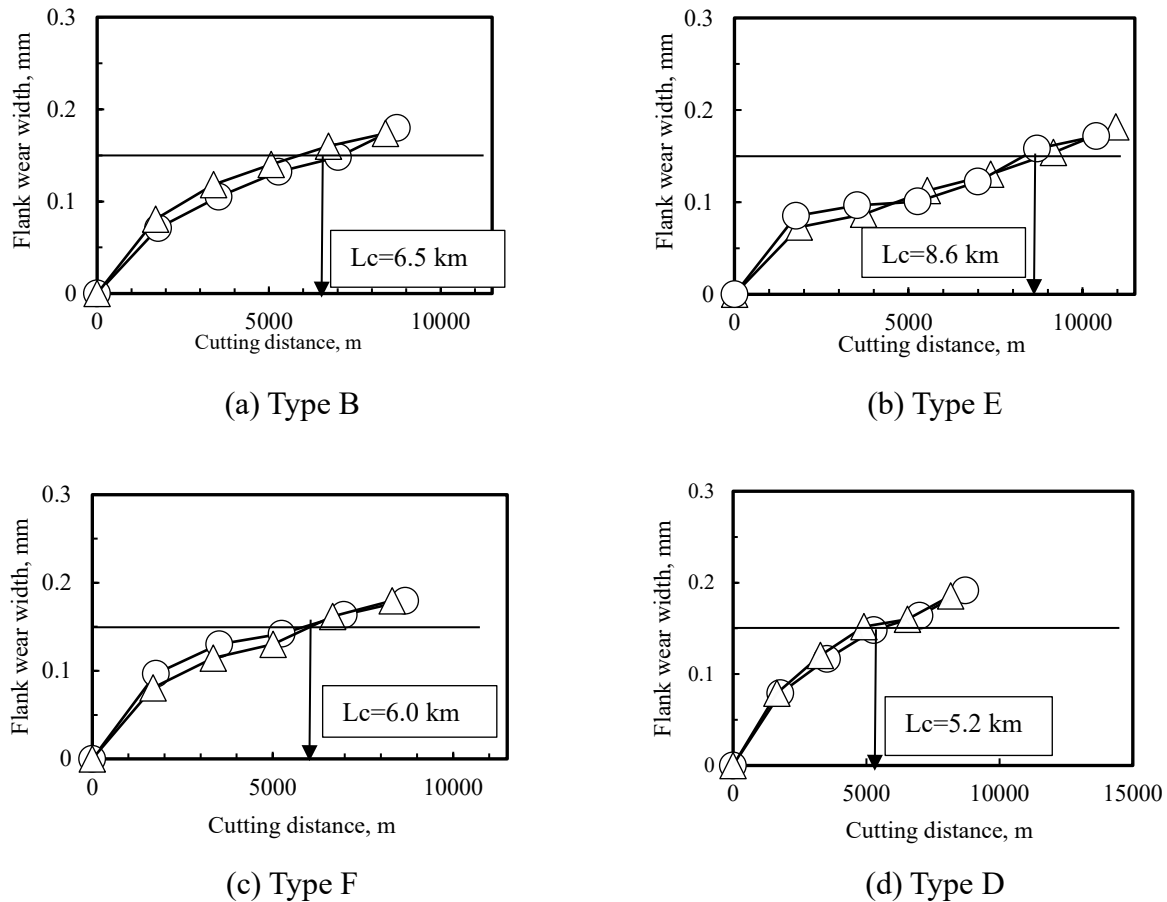


Fig. 2 Wear progress of various cubic boron nitrides at a cutting speed of 5.0 m/s, feed rate of 0.01 mm/rev, and depth of cut of 0.1 mm

In this study, it is considered that in cutting sintered steel, the Type E tool is effective tool material. During cutting, the chips flow out while in contact with the tool at both high pressure and high temperature. As a result, wear marks remain on the tool due to the contact of chips after cutting. So, in order to clarify why the Type E tool is effective, the contact state of the tool and the chip on the rake face were investigated.

Table 4 shows the “W” and the “T”. In Table 4, as shown in Fig. 1(e), the “W” is the contact width between the rake face and the chip and the “T” is the contact length between the rake face and the chip. Comparing the four type tools, both the “W” and the “T” of the Type E tool are smaller than that of the Type D tool. The contact area between the rake face and the chip of the Type E cBN tool is smaller than that of the Type D cBN tool. Therefore, it is considered that in the case of the cutting of sintered steel by the Type E tool, due to the friction force between the rake face and the chip being small, the cutting temperature is lower and the wear progress is slower.

Table 4 “W” and “T”

Tool type	W [mm]	T [mm]
Type B	0.425	0.050
Type D	0.420	0.065
Type E	0.355	0.045
Type F	0.400	0.055

W: Contact width between the rake face and the chip.

T: Contact length between the rake face and the chip.

Conclusion

In cutting sintered steel with cBN tools, various cBN tools have been used in cutting experiments to obtain an effective combination of binding phase and cBN content. As a result of experimentally examining the wear progress of the CBN tools, the following results were obtained.

- (1) As the binder phase, (Al_2O_3 -Al) was effective for wear resistance.
- (2) The wear progress was slower when the cBN content was 60% rather than 95%.

Acknowledgment

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Experimental Research on the Effect of the Rotary Friction Welding Process on Carbon Steel AISI 1030

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Keywords: Rotary Friction Welding, AISI 1030, Microstructure, Hardness

Abstract. The aim of this study is to investigate the rotary friction welding (RFW) technological parameters when welding two parts with medium carbon steel AISI 1030. Rotary friction welding has several parameters that can influence the quality of the weld joint. In this study, the adjustable and observable parameters are selected, i.e. friction pressure and friction time. The samples welded are observed in microstructure and their Rockwell hardness is measured to consider the effect of the parameters. The results reveal that friction pressure and friction time are the main factors of this welding process. Besides, the microstructures and hardness change in the welding zone because of the difference in the welding temperature.

Introduction

Nowadays, rotary friction welding technology has been considered to be the useful development in metal joining. It also has many amazing advantages like energy efficiency, environmental friendliness and the capability to weld different materials. Rotary friction welding is considered as a solid state of bonding materials and structures below their melting temperatures. In comparison with the traditional welding methods, its products have higher strength, longer fatigue span, as well as lower distortion [1-3].

The ability to fuse various parts together has made this method come to shine in the development of modern technology for the aerospace industry, since it enables the components manufactured in different metals to become fused and chemically united. Moreover, the heat-affected zone caused by the fusion in welding processes generates less heat, which minimizes the low-quality junctions and weld and the weld zone even has higher hardness than the base metals [1-3].

In the welding process, the materials are welded in three steps in Figure 1. The first step is rotating the specimen and applying the friction pressure P_1 in the friction time T_1 . The next one is the formation of the flash. Finally, stopping the rotation, applying forging pressure P_2 forging time T_2 and finishing the process are the last step.

When two materials come into contact with relative movement to each other, heat is generated and deformation takes place in the region of the contact surface area with the action of friction force. The temperature keeps rising until they are about to reach their melting points. At this point, an upset pressure will be applied, which will cause the diffusion between the elements at the intercept face, then welding is finished [4-6]. There are many parameters like: rotation per minutes, rotation speed, moment of rotation, brake moment, heating pressure and forge pressure, the post-processing length changes of the specimens, friction time, forge pressure time, volume of inertia, temperature and heating time, the relative translation speed of the materials during the process [5-9]. However, to make it less sophisticated, unnecessary elements are reasonably eliminated. In order to secure feasibility and effectiveness of the experiment, in this research, friction pressure and friction time were chosen as the two concerned factors; these are the parameters that can be checked and controlled. Although the rotary friction process has been used for many years, the data on microstructure and

mechanical aspects of welded components under different welding conditions are not readily available. Among steels, AISI 1030 is classified as high grade carbon steel, its strength is quite considering high and also its hardness even though the fact that the material has not been heat-treated. This steel grade has a decent ability to be machined, an ability to sustain a large load before reaching its permanent deformation point, and can easily be fit to any kind of welding.

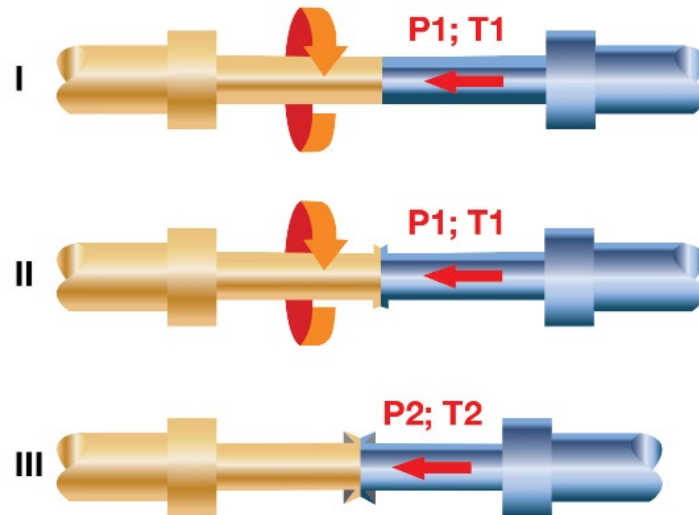


Figure 1. Steps of rotary friction welding process.

In this study, SAE 1030 carbon steel was selected as a material for investigation. The rotary friction welding process was performed under various conditions. The properties and mechanical properties of welded samples were investigated to consider the effect of the condition process.

Experimental Methods

The specimens used in this study were AISI 1030 medium carbon steel and were welded by the rotary machine RFW Machine 1. The original workpieces are cylindrical steel rods with a diameter of 11 mm and length of 70 mm. The nominal chemical composition of the SAE 1030 steel (weight %) is composed of C (~0.30), Mn (~0.60), Si (~0.17), S (≤ 0.050), and P (≤ 0.050). The rotation speed of the welding machine is 3000 RPM. The parameters for the RFW procedure is presented in table 1.

Results and Discussion

Figure 2 illustrates the results of welded parts with different technological parameters. Figures 2a and 2d show that the friction pressure and friction time is small, the weld and flash have just formed, so the weld does not meet the connection requirements. Figure 2c illustrates that with high friction pressure, the part is compressed too much, thus creating too much flash. Figures 2b and 2e show a satisfactory weld in terms of appearance when the welding parameters are guaranteed. To see the macro view of the part, all the parts were cut along the axis, polished and etched with 4% HNO₃ Acid solution, then viewed under the microscope. The rotary friction welded specimens No.2 (Figure 3a) and No.4 (Figure 3b) have diffused completely. However, the weld of No.2 is not uniform on both sides and the welding area is small, the connection level is weak, so the weld will be easily destroyed when there is an external force.

Table 1. Table of parameters for the RFW procedure.

No	P1 (Mpa)	T1 (s)	P2 (Mpa)	T2 (s)	Notice
1	0	0	0	0	As-received
2	19	150	30	120	
3	21	150	30	120	
4	23	150	30	120	
5	25	150	30	120	
6	27	150	30	120	
7	29	150	30	120	
8	23	100	30	120	
9	23	130	30	120	
10	23	170	30	120	
11	23	190	30	120	
12	23	210	30	120	

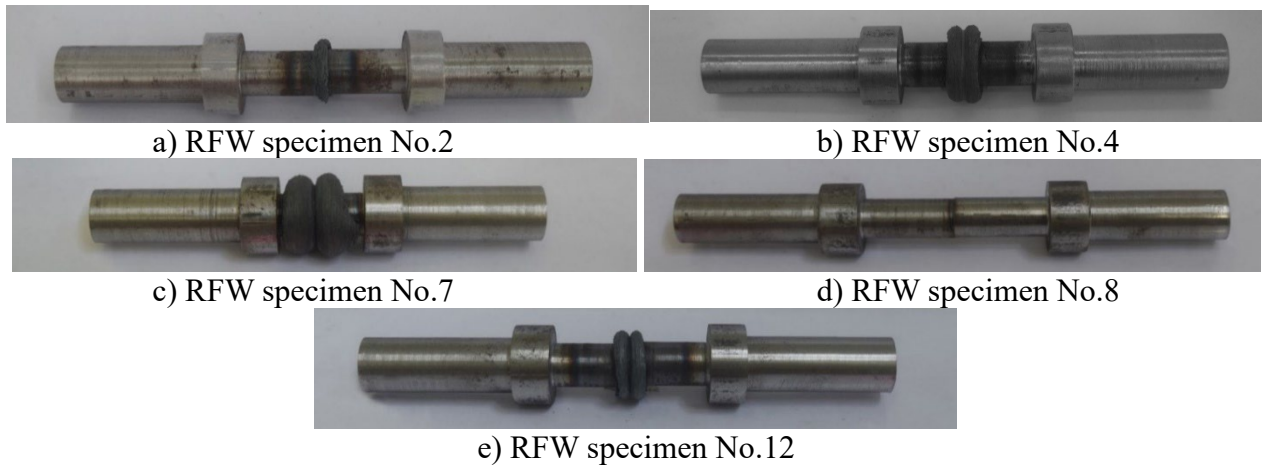


Figure 2. Rotary friction welded specimens.

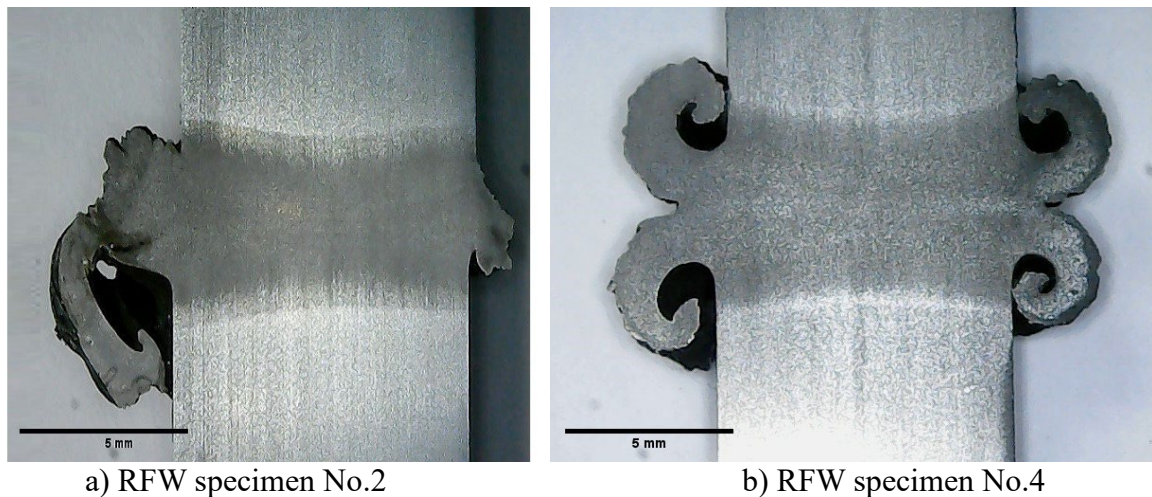


Figure 3. Macrostructure of the rotary friction welded specimens.

Microstructure analysis samples were obtained from welded samples. The samples were cut axially, ground with grit sandpapers, and then polished using aluminum oxide solution. Samples were etched with Nital solution (100 ml ethanol and 5 ml nitric acid) with an etching time of 15 seconds. Optika microscopes with magnifications from 50x to 500x were used to observe the microstructure. The cross-section of welded joint can be divided into four different zones, which are fusion zone,

weld interface, heat-affected zone (HAZ), and the base metal (Figure 4) [5, 7]. Due to the thermal influence of the welding process, the microstructure and mechanical properties of these regions are completely different.

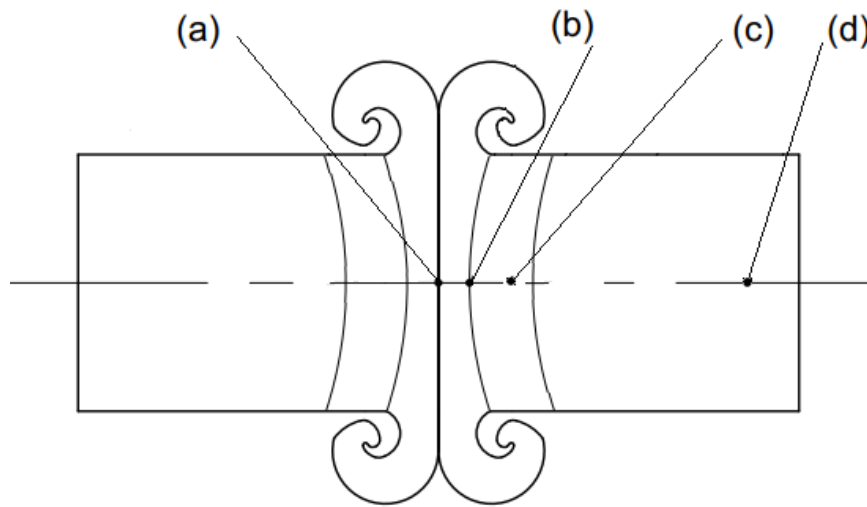


Figure 4. The cross-section of welded joint.

Figure 5 demonstrates the microstructure of the rotary friction welded specimen No.4. Figure 5a illustrates the microstructure of the fusion zone of the welded samples. It shows that the microstructure of the fusion zone is a needle-shaped structure. This is the crystalline structure of the weld metal in the semi-liquid state. However, RFW's weld zone structure is not the same as the one of other fusion welding methods. The dendritic structure is not observed in this structure. Because of the absence of the dendritic structure, this welding method produces better mechanical properties than other fusion welding methods.

Figure 5b presents the microstructure of weld interface of the welded samples. This region has smaller grains than the HAZ region and the grain tends to be elongated in the direction of part rotation. The average grain size in this region is $15.4\ \mu\text{m}$. Figure 5c shows HAZ of the welded part. Although it retains the chemical composition of the base metal, under the effect of heat during welding, this area is affected by residual thermal stresses and recrystallization when heated above the crystallization temperature. Recrystallization is similar to the crystallization in liquid metal, which also involves germination and germ development. This is the area that causes poor mechanical properties. The average grain size of the HAZ is $25.5\ \mu\text{m}$. The unaffected base metal zone is presented in Figure 5d. This zone is neither melted, nor does it undergo any changes in microstructure. The average grain size of this zone is $18.3\ \mu\text{m}$.

The Rockwell hardness of welded samples are measured at different positions that are separated by 2 mm. It can be clearly seen in Figure 6 that the hardness of the specimens reached the greatest in the weld center (about 64 HRA) and started to decrease when it strayed further to the side away from the weld center [1, 5]. The based zone has the hardness of about 56 HRA.

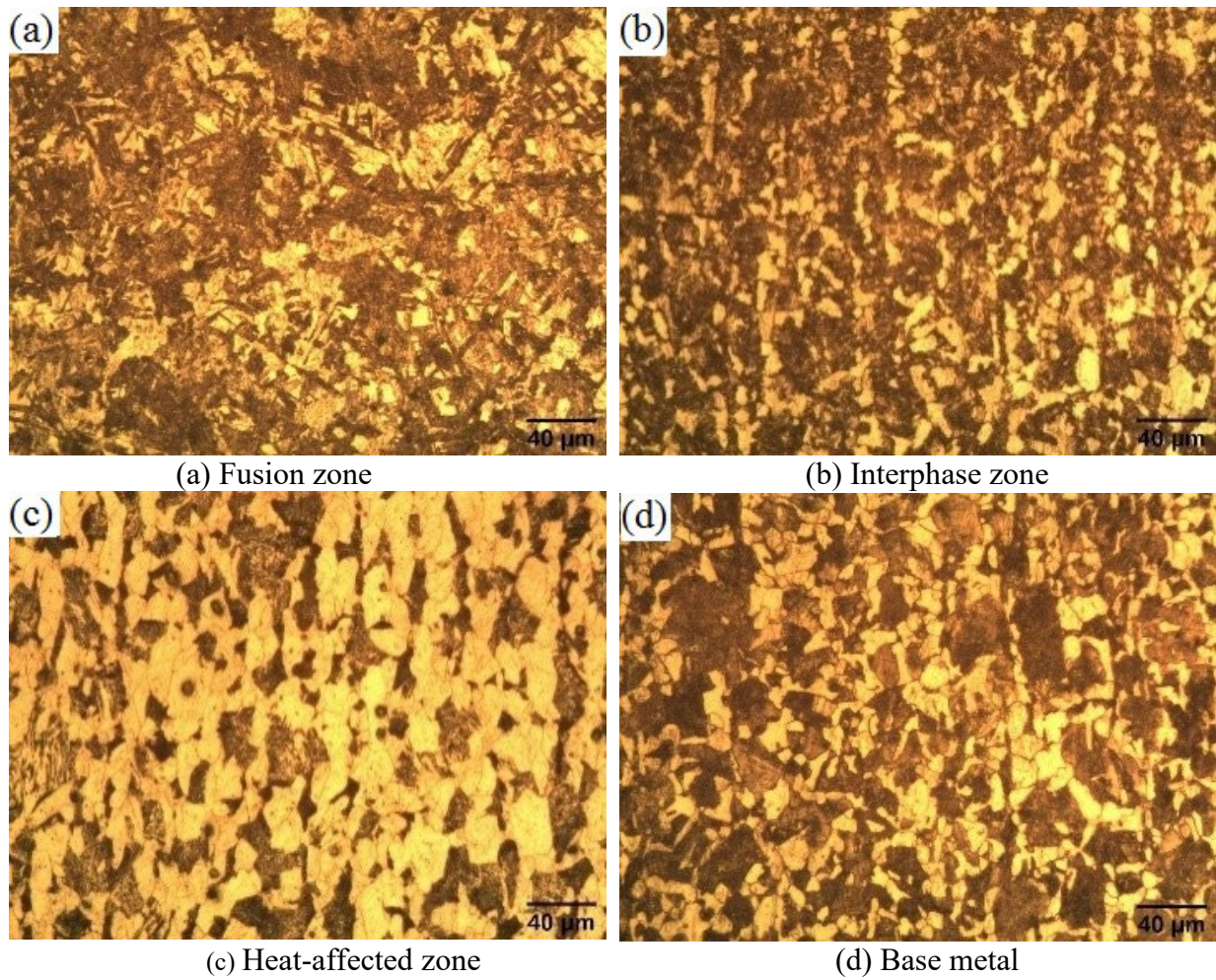


Figure 5. Microstructure of rotary friction welded specimen No.4 of (a) Fusion zone, (b) Interphase zone, (c) Heat-affected zone, (d) Base metal.

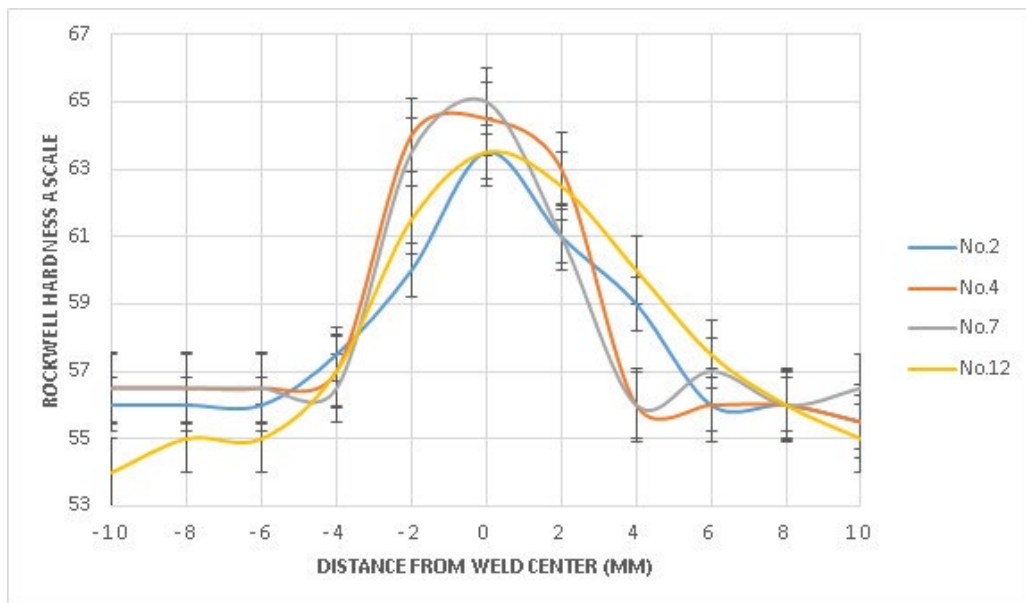


Figure 6. Rockwell hardness A scale of the rotary friction welded specimens.

Conclusion

The microstructure and mechanical properties of the welded AISI 1030, a carbon steel, under different rotary friction welding process conditions were investigated. The following conclusions are derived from this study:

- The friction pressure and the friction time are the main factors that determine the quality of the weld.
- Microstructures change in the welding zone because of the difference in the welding temperature.
- The hardness of the specimens reaches the greatest in the weld center (about 64 HRA) and started to decrease when it strayed further to the side away from the weld center.

Acknowledgments

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Sheet-Metal Formability Study on a Circular Tube with a Folding Bottom Feature

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Keywords: Deep drawing; Sheet metal forming; Finite element analysis; Taguchi method.

Abstract. The formability of sheet-metal with a folding-bottom circular hollow tube has been studied both by numerical simulation and experiment. A mesh-convergence analysis has been carried out to determine an optimum element size for purposes of numerical simulation. The geometry and dimension of the dies and of the punch are designed to simulate the multi-stage deep drawing operation to take place. During the deep drawing operation, the strains of the sheet blank are always located in the second quadrant of the forming limit diagrams, and it continuously moves in a linear state to the left side of the diagram. At the final stage, the tube is drawn to a certain height without evidence of fracture. In order to obtain a quality product, an optimization of input parameters for the deep drawing operation is conducted using Taguchi method. Finally, a validation test is also employed to demonstrate the accuracy of forming processes. The result reveals sufficient agreement in both geometry and dimension between simulated and actual tubes to meet a good quality standard.

Introduction

With the rapid development of modern industry, the metal tube is widely used in many different industrial fields as automobile, aerospace, electrical, and so on. In general, the tubular parts are often made by the different forming process. Jin et al. [1] studied the incremental die forging operation for manufacture the helical tube. Becker et al. [2] reported the tube forming process based on the combination of the continuous bending with the spinning operation. Generally, the sheet metal forming process includes many deformation modes such as bending, drawing, stretching, ironing, etc. However, the deep drawing is the most representative and typical deformation mode among the given modes in the sheet metal forming process. Faraji et al. [3] used the finite element method (FEM) to investigate the formability of cylindrical components. Husain et al. [4] also employed the numerical and experimental research of formability for cylindrical parts by using LS-Dyna solver.

Furthermore, in the deep drawing process, selection of proper input parameters for sheet metal forming is an important work that need to be conducted. Reddy et al. [5] reported the experimental research on influence of input variables such as punch nose radius, die shoulder radius and blank holder force (BHF) on the thickness of the cup wall in deep drawing based on Taguchi method. Their results indicated that the most influential factor among the given factors on the thickness of cup wall was BHF followed by the punch nose radius and, finally, by die edge radius. Volk et al. [6] presented numerical study of effect of BHF on quality of product in the deep drawing process.

Most of the above researches only performed for forming of the simple tubular parts. With complex shaped tubes, a single forming operation becomes more difficulties. Therefore, a combination of the different sheet metal forming operations (i.e., deep drawing, pressing, trimming, folding bottom forming, and reverse extrusion and bottom pressing) need to be carried out to produce the complex shaped parts as a hollow circular tube with folding-bottom feature. In addition, many of the above studies also did not mention to the analysis of mesh convergence in the metal tube forming.

This can lead to an increase in solution, processing time and lack of accuracy of the result when analysis of the metal forming process.

In order to fill these gaps, the present study focuses on the analyze the multi-stage sheet metal formability for a folding-bottom circular hollow tube using FEM based on Dynaform and Deform-3D software. The tube forming process is based on the combination of the different sheet metal forming operations such as deep drawing, pressing, trimming, folding-bottom forming, and reverse extrusion and bottom pressing.

Research Methods

Tube-forming Operation based on Dynaform. The required specification of the desired final part is shown in Fig. 1. In order to avoid waste of material for the drawn part, the geometry and size of the blank must be calculated precisely in deep drawing operation. The specifications for the blank are achieved through the assumption that the volume of the blank is equal to the volume of the desired final part to be drawn. The diameter of the blank is determined as 31.87 mm. In this research, the finite element simulation of the deep drawing operation was carried out using Dynaform software. The geometrical model for punch, die, blank holder and blank were illustrated in Fig. 2. The blank was considered as a deformable body while the other tools such as the punch, die, and blank holder were considered to be rigid bodies. Input process parameters for the simulation were as follows: Blank thickness: 1 mm, Workpiece: JIS-S15C, Mesh size: 0.4 mm, BHF: 5 kN, Process information: Single action, Contact method: Forming surface-to-surface, Friction type: Coulomb. In finite element analysis, the mesh convergence analysis is an important work aspect that needs to be made to obtain precise results derived from numerical simulation. An optimal element size for the discretization of the blank in simulation process will provide an accurate result, whereas the finer mesh will lead to an increase in solution and processing time. Therefore, in order to enhance the credibility of the study, analysis of mesh convergence is absolutely essential to the research methods.

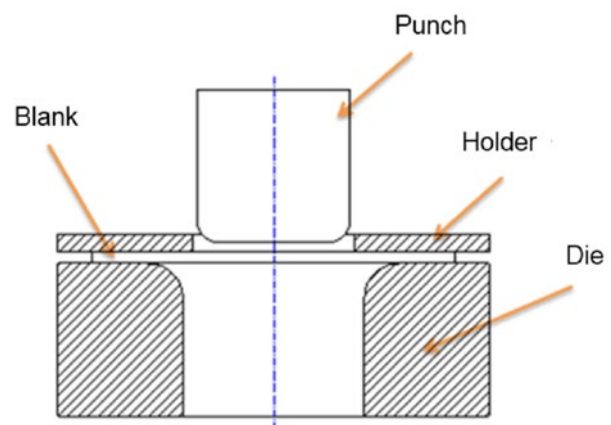
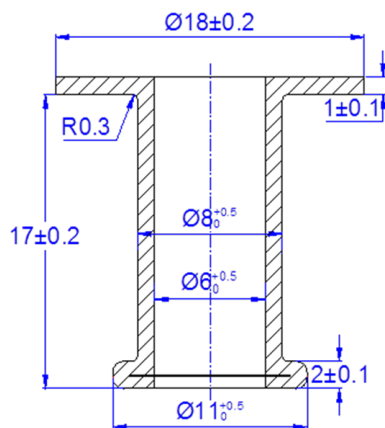


Fig. 1. The specification of the desired part (in mm) **Fig. 2** Schematic of deep drawing process

In deep drawing operation, limiting drawing ratio (LDR) is among the most important parameters that is used to determine the required number of drawing steps (stages). LDR is defined as the maximum drawing ratio that may be achieved while drawing a part without fracture [7]. In order to make a desired drawn part, a multi-stage drawing process is necessary. In the present work, there are three stages according to three drawing ratios that were considered for deep drawing operations. Thus, the limiting draw ratio of each stage was calculated and shown in Table 1. The geometrical and FE models for the dies and the punch for three steps were designed and given in Figs. 3. After simulation, the raw data need to be transformed into a signal-to-noise ratio (S/N) to analyze given process characteristics. In this study, output response characteristic is the minimum thickness of the tube wall after deep drawing occurs. In order to achieve the best quality of drawn tube, the larger values are preferred among the minimum thickness of the tube wall. Thus, the type of

“the-larger-the-better” characteristic is selected and the design should be able to maximize the S/N ratio based on Taguchi method.

Table 1 LDR for each stage in deep drawing operation

Stage	Blank diameter	Tube diameter	LDR
First step	31.87	13.5	2.36
Second step	13.5	8.8	1.53
Final step	8.8	6.5	1.35

Table 2 Levels of input variables

Factors		Code of levels		
		1	2	3
Punch velocity (mm/s)	A	90	120	150
Die edge radius (mm)	B	3	5	7
Punch edge radius (mm)	C	3	5	7
Friction coefficient	D	0.01	0.05	0.125

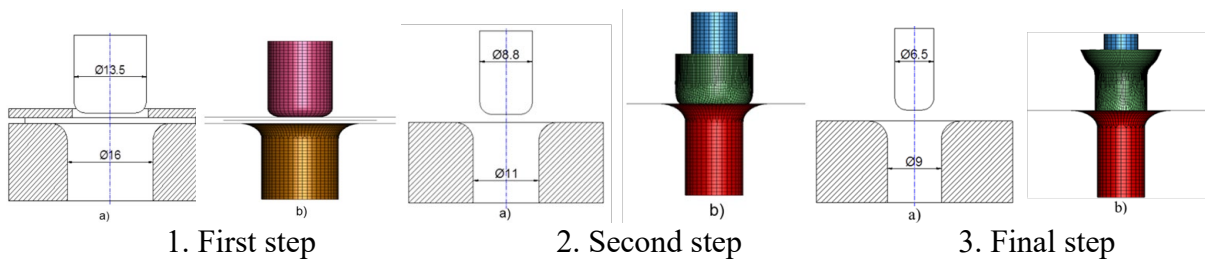


Fig. 3 Deep drawing process design for three steps

The Tube’s Bottom-forming Operations based on Deform. After the first part is conducted, the forming operations of the second part will be simulated by using Deform-3D. The workpiece is considered to be a deformable body, whereas the punch and die are considered to be rigid bodies. The input process parameters for the simulation are given as follows: Die material: Rigid body, Workpiece: JIS-S15C, Number of element: 80000, Die temperature: 20°C, Friction type: Shear, Friction coefficient between die and workpiece; 0.7, Friction coefficient between workpiece and workpiece: 1, Punch movement per step: 0.5 mm/step, and Punch velocity: 1 mm/s.

Results and Discussion

Analysis of Mesh Convergence. The difference of maximum and minimum metal flow values as the representative parameter for analyzing the mesh convergence was used. To determine this parameter, with the mesh sizes within a range from 3 mm to 0.1mm, eleven different tests have been conducted. During deep drawing, material in the surrounding zones is forced continuously into the die cavity. The minimum error of metal flow during deep drawing should be considered for purposes of mesh convergence analysis. The simulation results of convergence of the blank’s mesh sizes are represented in Fig. 4. This diagram indicates the difference between maximum and minimum metal flow values versus the mesh sizes in the deep drawing process. From this graph, it can be seen that the difference of metal flow fluctuated widely for the mesh sizes from 3 mm to 0.6 mm. If the value of mesh size of this interval is selected, the simulation result cannot become accurate due to the unstable situation presented.

Fig. 5 indicates the relationship of the forming force with the punch stroke for the different blank meshes. It can be seen that the forming force is similar for all meshes. The forming load increases rapidly from the onset of contact until it reaches approximately 16 kN at a punch stroke of 13 mm, then falls dramatically to close to 5 kN at 23 mm of punch travel. The punch travel from 23 mm to the end of operation caused the punch force to change insignificantly. In addition, Fig. 5 also shows a fluctuated forming load for mesh sizes from 3 mm to 0.6 mm. With mesh size of 0.5 mm ~ 0.2 mm, the forming forces reach a relatively stable state. In this range of mesh size, the most stable forming load is observed at an element size of 0.4 mm. Based on both the plot of forming load and the metal flow, the convergence value of the mesh size is found to be 0.4 mm. Consequently, this finding will be used for purposes of simulation during the deep drawing operation.

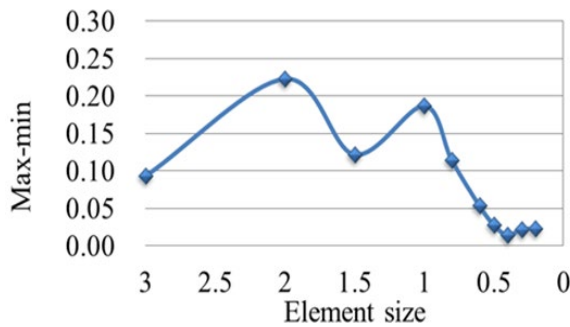


Fig. 4 Metal flow versus mesh

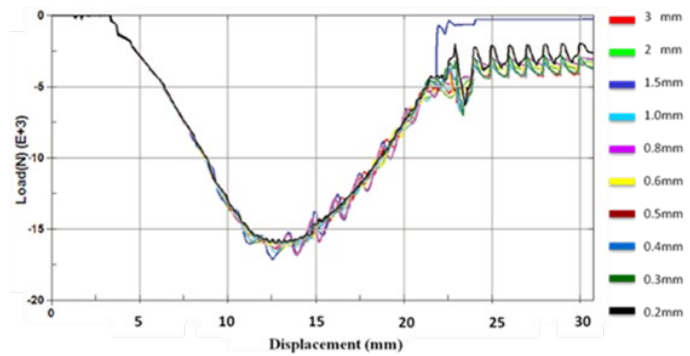


Fig. 5 Punch force versus displacement in deep drawing

Three steps in Deep Drawing Operation. Figure 6 a-c indicate the shapes of drawn part and forming limit diagram (FLD) from the S15C sheet metal blank with a thickness of 1 mm. From analysis of these graphs, it can be seen that a fracture normally occurs at around the corner of the punch where the radius of the punch is in contact with the tube wall. During the first stage, the tube is drawn as shown in Fig. 6a, in which the deformation zone of the blank (zone A1) still belongs to the safe area of the FLD. Subsequent forming stage (see Fig. 6b) zone A1 is stretched to zone A2. The height of the tube is increased due to in large part to the increased strains. At this time, the strains enter the critical region of the FLD; however, it is not beyond the forming limit curve (FLC) which is depicted in the FLD. At the final forming stage (see Fig. 6c), zone A2 is pulled into zone A3 and the deformation of the blank still falls within the safe region of the FLD.

In addition, Fig. 6a-c reveal that the wrinkle tendency occurs in the deformation areas of the metal blank, namely with zone B1, zone B2 and zone B3. In these zones, the metal blank is simultaneously subjected to radial tensile stress due to a pulling of the blank into the die cavity by the punch and compressive stress due to a decrease in the periphery of the blank during the deep drawing operation. Generally, during the deep drawing operation, the strains in zone A and zone B of the sheet blank are always located in the second quadrant of the FLD, and it continuously moves in a linear state to the left side of the diagram. At the final stage, the tube is drawn to the height of 25.68 mm without evidence of fracture. Finally, an upper flange pressing operation was conducted to flatten the top geometry.

Optimization of Die Design and Process Parameters. Based on S/N ratio and ANOVA from Table 2, the highest S/N ratio value of each factor is called the optimal value. The optimal parameter setting obtained from Taguchi analysis is A1, B3, C1 and D3 (i.e., a punch velocity of 90 mm/s, a die edge radius of 7 mm, a punch edge radius of 3 mm and a friction coefficient of 0.125) and the most influential factor among investigated factors on the thickness of the tube wall is the punch edge radius (contribution of 89.534%) followed by the die edge radius (contribution of 4.492%), the friction coefficient (contribution of 3.026%) and, finally, by the punch velocity (contribution of 2.948%).

Manufacturing Process of the Folding-bottom Circular Hollow Tube. The next operation in the manufacturing process is the tube-bottom forging based on Deform-3D. In this operation, the blank undergoes two stages with two types of different cone punches. The simulation results are depicted in Fig. 7.

Comparison with Experiment. Once the forming process of the folding-bottom circular hollow tube is completed, the validation experiment needs to be performed to verify accuracy of the geometry and dimension of the product. Figure 8a-b indicate that the difference of dimension between the simulated and the experimental parts which is found to be insignificant and it falls within the limit of tolerance interval. Correspondingly, it can be concluded that the forming process of a hollow circular tube with folding bottom feature based on a combination of the different sheet metal forming operations is reasonably acceptable.

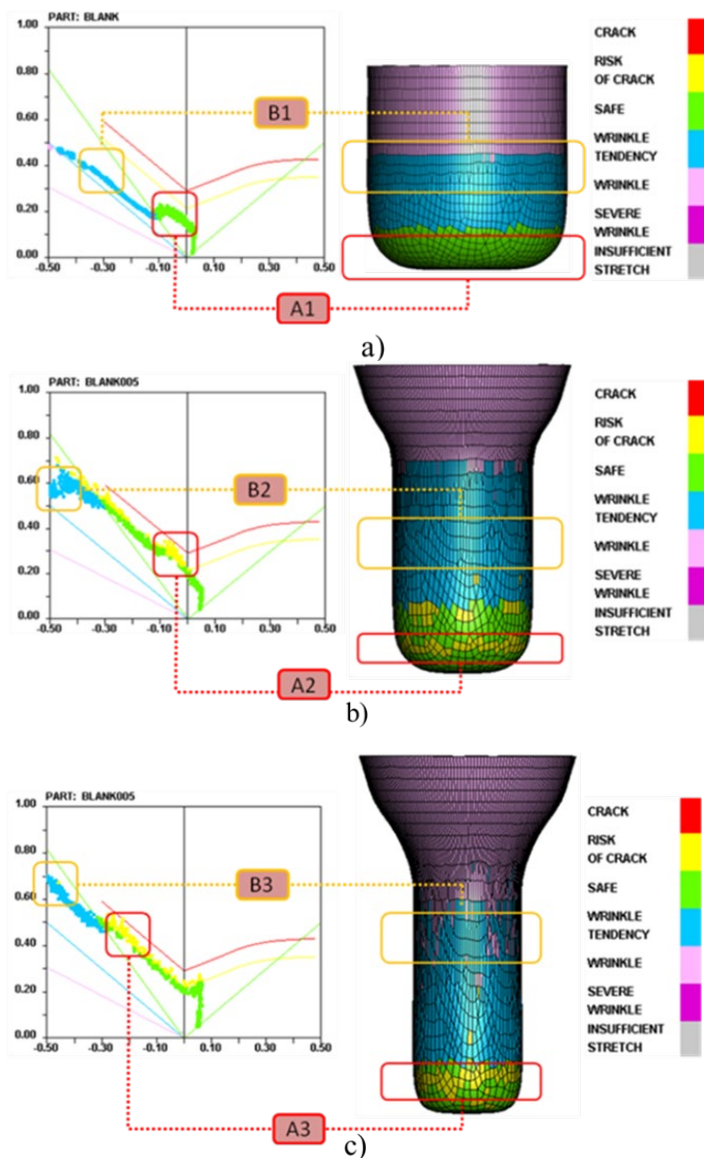


Fig. 6 Forming limit diagram of S15C steel blank. a) The first stage; b) The second stage and c) The third stage

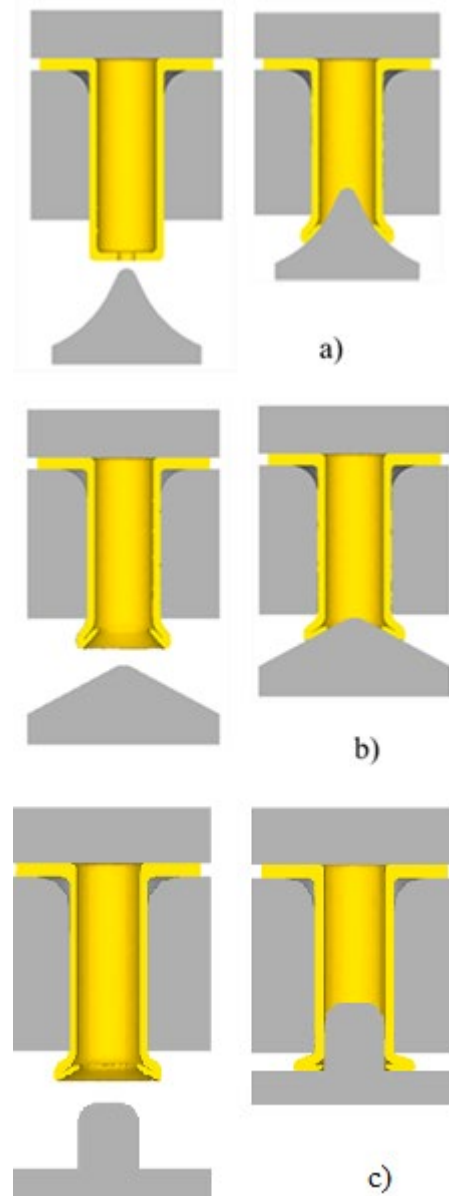


Fig. 7 The geometrical model of the folding bottom forming operation. a) First step, b) Second step and (c) Final step - reverse extrusion

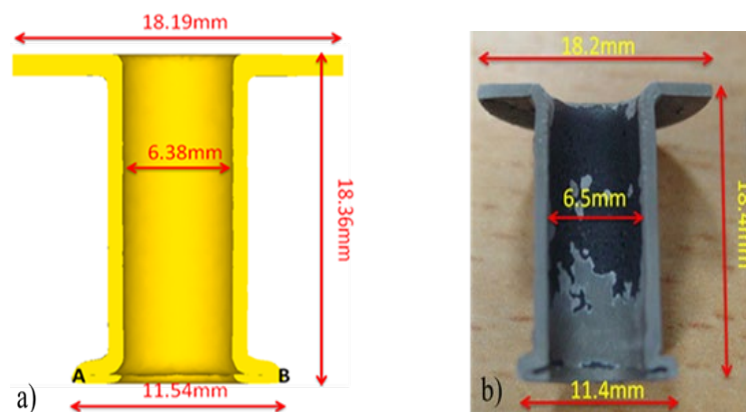


Fig. 8 Dimensional comparison of simulated and experimental results. a) Simulated part and b) Experimental part

Summary

The main aim of this paper is to study the forming process of a folding-bottom circular hollow tube, in which the finite element analysis based on Dynaform and Deform-3D software is used. This forming process involves various operations, namely deep drawing, flange pressing, trimming, folding-bottom forging, bottom pressing operation. Based on this work, conclusions are drawn as follows:

- The mesh convergence analysis has been conducted and the result reveals that the optimum element size for numerical simulation is 0.4 mm.
- During the deep drawing operation, the strains on the sheet blank are always located in the second quadrant of the FLD. At the final stage, the tube is drawn to the height of 25.68 mm without evidence of fracture.
- Through ANOVA, the most influential factor among investigated factors on the thickness of the tube wall is the punch edge radius (contribution of 89.534%) followed by the die edge radius (contribution of 4.492%), the friction coefficient (contribution of 3.026%) and, finally, the punch velocity (contribution of 2.948%).
- The optimized input parameters for the deep drawing process are the punch velocity of 90 mm/s, the die edge radius of 7 mm, the punch edge radius of 3 mm, and the friction coefficient of 0.125.
- The validation experiment is produced to verify accuracy of the geometry and dimension of the product. The result depicts that the difference of dimension between the simulated and the actual part is found to be insignificant and it falls within the limit of tolerance interval.

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CHAPTER 3:

Materials for Electronics and Energy Storage

In₂O₃/MoS₂/Reduced Graphene Oxide Nanostructure as Composite Electrodes for Supercapacitors

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Keywords: supercapacitor; reduced graphene oxide; indium (III) oxide; molybdenum disulfide; ternary composite; hydrothermal.

Abstract. In this study, a novel reduced graphene oxide, indium (III) oxide, and molybdenum disulfide (rGO/In₂O₃/MoS₂) ternary composite for supercapacitor electrode application was developed via green hydrothermal synthesis. The topography, morphology, crystalline structure, phase identification and molecular structure of the composites were examined by applying Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDX), Transmission Electron Microscopy (TEM), X-ray Diffraction Spectroscopy (XRD), and Raman Spectroscopy. SEM and TEM reveal the uniform dispersion of In₂O₃ nanoparticles on the rGO/MoS₂ nanosheets. EDX and XRD analysis confirmed the coexistences of rGO, In₂O₃, and MoS₂, and hence the composite formation. Electrochemical performance of the rGO/In₂O₃/MoS₂ electrode was investigated via cyclic voltammetry (CV) in 1 M sodium sulfite (Na₂SO₃) aqueous electrolyte. The electrochemical results reveal that the rGO/In₂O₃/MoS₂ composite electrodes exhibit enhanced specific capacitance of 77 F/g at 25 mV/s scan rate, a modest 29% enhancement over pure In₂O₃ and In₂O₃/MoS₂ binary composite electrodes.

1. Introduction

Energy is vital for human development. With the rapid advancement of technology and the increasing global economic growth, energy has become one of the most crucial problems in the world. Conventional energy generation by combustion of fossil fuel has severely affect the world ecology in the form of global warming with all its associated environmental problems. Accordingly, there has been an increasing demand and expansion of renewable energy such as solar power and wind energy. In this regard, the development of energy storage technology is crucial in conjunction to the widespread application of renewable energy sources [1]. Among the predominant energy storage devices, supercapacitors have been explored for their remarkable capability to meet short-term and temporary energy demands. As such, supercapacitors find applications in regenerative braking systems, portable consumer electronics, memory backup, and seaport cranes because of their unique properties, namely high specific capacitance, rapid charge-discharge property, exceptional cycle performance, and safe to handle [2].

The components in a supercapacitor are similar to those of rechargeable batteries, comprising current collectors, two electrodes, electrolyte, and a separator. However, supercapacitors do not store charge via chemical reactions, but depend on the electric field to affect the ions to move towards or against the electrode surface. Moreover, supercapacitors are characterised by more superior energy density in comparison to conventional capacitors while outperforming lithium-ion batteries in terms of power density and cyclability, and hence lie between these two technologies. Consequently, supercapacitors excel in short burst discharge where high power is required over a short time span, for example in overcoming fluctuations in renewable energy sources.

Among the carbonaceous electrode materials for EDLCs, graphene shows a tremendous potential due to its high specific surface area, high charge carrier mobility, and high electrical conductivity [6]. Research revealed that a single layer of graphene can achieve a theoretical specific capacitance of about 550 F/g along with high power density, high cycle stability, and high energy density [7]. However, single layer graphene without defects is difficult to obtain. It takes a longer duration and more costly to synthesise single layer graphene. Therefore, the synthesis of single layer and few layers graphene has remained as one of the major challenges for mass production in order to meet the industrial needs [9]. As a result, reduced graphene oxide (rGO), a derivative of graphene, was introduced as one of the ways to solve the demands of graphene at a lower price.

Graphite powder has been widely used in the synthesis of rGO. Briefly, graphite powder is oxidised to obtain graphene oxide (GO), typically through modified Hummer's method. Then, the GO will be further reduced into rGO. This transformation can be accomplished via thermal, chemical, physical, or electrochemical reduction, resulting in different morphology and electrical properties of the final rGO product [9]. Sodium borohydride (NaBH_4) and diazene (N_2H_2) are the commonly used reducing agents for the chemical reduction of GO. However, the fast reduction kinetics caused by reducing agents give rise to defects and subsequent compromises on the properties of rGO, particularly electrical conductivity. Therefore, electrical transport in rGO can be ascribed to hopping and lead to lower conductivity, which differs from pristine graphene. All in all, rGO can serve as an effective alternative for pristine graphene in mass production.

Pseudocapacitive materials are the basis of the emerging pseudocapacitors. These materials include transition metal oxides (TMOs) such as RuO_2 and In_2O_3 , as well as conducting polymers (CPs) such as polypyrrole and polyaniline. TMOs offer higher specific energy and superior specific capacitance while CPs have good intrinsic conductivity, making them the unique candidates for supercapacitor application [10]. Nevertheless, TMOs and CPs have their own weaknesses. TMOs have low electrical conductivity, resulting in lower specific capacitance when compared to theoretical expectation. Meanwhile, the poor cycling-stability of CPs arises from the natural behaviour of polymer in which the polymer chains tend to swell and shrink during charge-discharge cycles. In recent studies, mixed transition metal oxides (MTMOs) were proposed as affordable and compelling alternatives for supercapacitor electrodes. This is because MTMOs are able to advocate diverse redox reaction with the complementarity of two different metal species [11]. Furthermore, synergetic effects of TMOs in MTMOs could increase the voltage window and maximise accessible electroactive sites which in turn bring about enhance specific capacitance [12]. However, poor cycle performance, inferior conductivity, and possible particle aggregation during charging and discharging remain the drawbacks of MTMOs [13].

Since both carbonaceous and pseudocapacitive electrode materials have their own limitations, many approaches have been made to address these shortcomings. One such approach is the creation of hybrid capacitors by combining the merits and behaviours of both EDLCs and pseudocapacitors. The hybridising of MTMOs with carbon-based materials (e.g. graphene) can generate synergetic effects such as increased electrical conductivity, and enhanced ionic diffusion at the electrode-electrolyte interface as well as the subsurface of electrode. Also, graphene provides a larger electrode surface area to promote sufficient Faradaic redox reaction during continuous charge-discharge process.

Recently, there have been much research on the applications of MTMOs and graphene-based materials as the supercapacitor electrodes. However, the study that focus on the combination of both materials, especially ternary composite is rare. In this study, a novel reduced graphene oxide, indium (III) oxide, and molybdenum disulfide (rGO/In₂O₃/MoS₂) ternary composites was synthesised through a green hydrothermal method. The morphology and electrochemical performance of the rGO/In₂O₃/MoS₂ ternary composites were investigated and analysed through various characterisation techniques and cyclic voltammetry (CV).

2. Experimental Procedure

2.1. Chemicals and methods

Indium trichloride (InCl₃), polyvinylpyrrolidone (PVP), and sodium hydroxide (NaOH) were purchased from Sigma Aldrich. GO solution (50% GO content, average thickness: ~1 nm, lateral size: 100 nm to 0.1 μ m, layers: < 5) was purchased from Ugent Tech Sdn. Bhd. Molybdenum disulfide (MoS₂) and N-methyl-2-pyrrolidinone (NMP) were acquired from R&M Chemicals.

Indium (III) oxide (In₂O₃) was synthesised via wet chemical synthesis using InCl₃, PVP and NaOH. In brief, 0.6004 g of PVP was added into 25 mL distilled water. Next, 1.1059 g of InCl₃ was dissolved in the solution under stirring, and was labelled as solution A. In another beaker, 0.72 g of NaOH was added into 20 mL distilled water under stirring and was labelled as solution B. After both solutions were fully dissolved, solution B was dropwise into solution A under constant stirring. The mixture was then sonicated for 10 mins. The resultant precipitate was centrifuged and washed three times with distilled water at 9000 rpm and 4 °C for 10 mins each. The white precipitate was dried at 60 °C overnight. Finally, yellowish precipitate of In₂O₃ was obtained.

The rGO/In₂O₃/MoS₂ ternary composites was synthesised via hydrothermal process with NaOH as the reducing agent for GO and stabiliser for In₂O₃. In depth, 0.2 g of GO solution (0.1 g of GO since 50% GO content) was dispersed in 45 mL of NaOH solution (adjusted to pH 9 by adding NaOH) followed by 30 mins of sonication. After that, 0.1 g of In₂O₃ and 0.017 g of MoS₂ were added into the homogenous GO-dispersed solution and continue stirring for 30 mins. The weight ratio of the precursors rGO:In₂O₃:MoS₂ is 6:6:1. The final homogenous solution was transferred to an autoclave, heated to 180 °C and hold for 8 h in an oven. After natural cooling, the solution was centrifuged at 6000 rpm for 15 mins and the precipitate was washed with ethanol followed by distilled water twice, each for 10 mins. Finally, powder of rGO/In₂O₃/MoS₂ was obtained after drying at 80 °C overnight.

2.2. Characterisation and electrochemical testing

Scanning Electron Microscopy (SEM) was carried out using 'FEI-Quanta 400 FESEM' system. Energy Dispersive X-ray Spectroscopy (EDX) was conducted using an X-Max 20 mm² silicon drift detector (Oxford Instruments, UK) with AZtecEnergy EDS Software. Transmission Electron Microscopy (TEM) was performed through 'Hitachi HT-7700' series. Raman spectrum was recorded with 'Horiba Labram HR Evolution'. 'PANalytical X'Pert Pro' system was employed for X-ray Powder Diffraction (XRD).

Electrochemical assessment was performed using a two-electrode cell in 1 M sodium sulfite (Na₂SO₃) aqueous solution. CV was conducted using ADVANTECH 510 potentiostat and a computer with Gamry Instrument Framework software. The electrodes were fabricated by mixing the active material, carbon black and polyvinylidene fluoride with the weight ratio of 7:2:1. Then, a few drops of NMP were added. The slurry was coated onto 1×1cm² current collector and dried at 60 °C for 4 h.

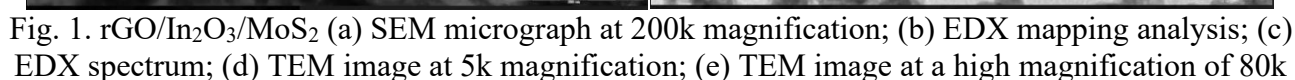
3. Results and Discussion

3.1. Structural characterization

Fig. 1a shows the SEM image of the as-synthesised rGO/In₂O₃/MoS₂ ternary composite. The distribution of In₂O₃ particles on the rGO (sheet-like morphology) is relatively uniform with some agglomeration at the bottom right corner. The dimensions of the In₂O₃ nanoparticles are ranging between 25 nm to 40 nm. Besides, the rGO sheets are mixed with MoS₂ sheets that prevent the MoS₂ sheets from stacking together. The interaction between rGO and MoS₂ sheets and how it affects the electrochemical performance will be described in section 3.2.

Fig. 1b depicts the EDX layer image obtained from rGO/In₂O₃/MoS₂. The In₂O₃ nanoparticles (yellow) are evenly distributed across the rGO (purple) with MoS₂ (green) scattering across the area. The EDX spectrum in Fig. 1c shows the percentage of each element in the mapping area. The carbon (C), indium (In), molybdenum (Mo), and sulphur (S) content are about 39, 38, 2.3, and 1.1 wt% respectively. This reflects the weight ratio of 6:6:1 of the precursors applied during the synthesis of the ternary composite, indicating that the elements are reacting properly during the hydrothermal reaction. In the EDX spectrum, the presence of two characteristics peaks of 'In' and 'MoS₂' shows that both constituents are successfully deposited onto the rGO sheets.

TEM was employed to reveal the internal structure and morphologies of rGO/In₂O₃/MoS₂. The TEM image at 5k magnification (Fig. 1d) shows a high degree of distributions of sand-like In₂O₃ nanoparticles. However, the bottom half of the image is unclear. This may be due to the deposition of In₂O₃ nanoparticles on the other side of the rGO/MoS₂ nanosheets. Fig. 1e shows the TEM image of rGO/In₂O₃/MoS₂ at a high magnification of 80k and captured the dimensions of In₂O₃ nanoparticles (7 nm to 13 nm) that were attached on a single rGO sheet. The principle of both TEM and SEM techniques should be highlighted to explain the differences in the dimensions of In₂O₃ nanoparticles obtained by both techniques. The image provided via TEM technique is only in 2-dimensional, i.e. a distribution of electron density on a thin flat sample whereas SEM produces a quasi-3-dimensional micrograph. Despite that, TEM has higher resolution (~ 0.5 Å) as compared to SEM (~ 0.5 nm), and hence the larger dimension in the latter. Therefore, the dimensions of In₂O₃ nanoparticles obtained by SEM will be slightly larger than those of TEM.



XRD analysis was performed to study the structure and to identify the phase of rGO/ In₂O₃/MoS₂. Fig. 2 depicts the acquired XRD spectrum. The diffraction peaks appear at 2θ : 30.610°, 35.398°, 51.036°, and 60.820° can be associated to the crystal planes (222), (400), (440) and (622) of body centred cubic In₂O₃ (PDF 00-006-0416), respectively. The low angle peak of graphite at 26.555° is attributed to the (002) crystallographic plane. The diffraction peaks at 2θ = 32.680°, 39.559°, 51.036° correspond to the planes (100), (103), and (105) of Mo (PDF 00-037-1492) with hexagonal crystallographic structure. However, the diffraction peaks of graphite and Mo have shifted. This

shifting may be due to the reactions that occurred during the formation of the rGO/In₂O₃/MoS₂ ternary composite. Furthermore, the relationship between 2θ positions and the size of particles intercalation is not directly proportional, leading to a shift of diffraction peaks to a lower 2θ position for bigger particle. Accordingly, the XRD analysis the formation of the ternary composite.

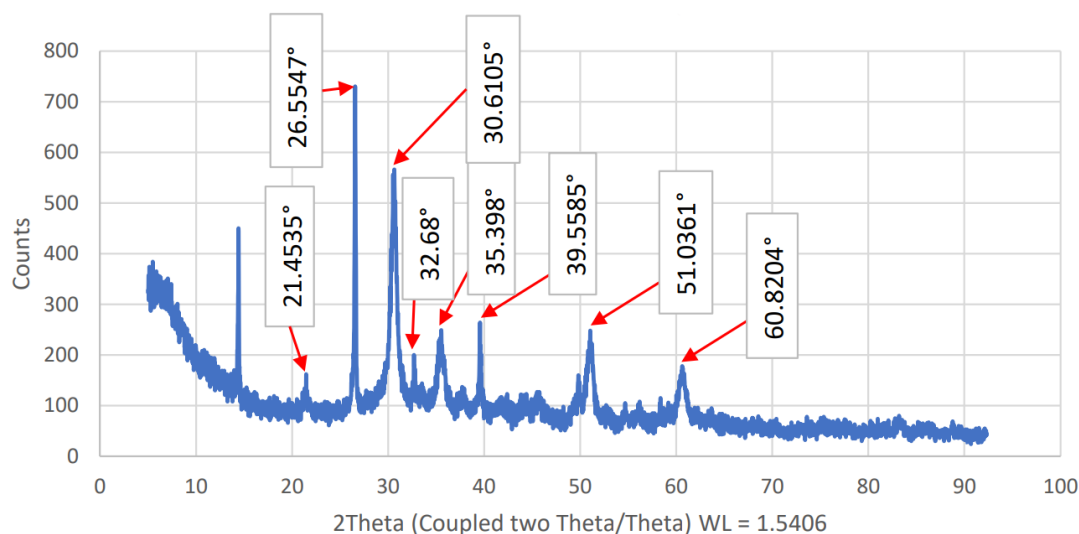


Fig. 2. XRD spectrum of rGO/In₂O₃/MoS₂.

Raman spectroscopy was performed to investigate the molecular structure of the ternary composite. Fig. 3 shows the Raman spectrum of rGO/In₂O₃/MoS₂. The Raman peaks presented at 1328, 1572, and 2680 cm⁻¹ are attributed to the D, G, and 2D bands of rGO, respectively. The D band or defect band relates to the out of plane vibrations of structural defects whereas the G band signifies the in-plane vibration of hybridised sp² carbon atoms [14]. Besides, the 2D band or secondary D peak is the second-order two-phonon vibration [15]. The ratio of intensity of the D and G bands (I_D/I_G) is used in the estimation of the defects in graphene-based samples. Typically, high I_D/I_G ratio indicates that the graphene layer has more defects [14]. With an I_D/I_G ratio of 0.213, the rGO has minor structural disorder caused by the functional groups that was still attached to the rGO. Furthermore, I_G/I_{2D} is a ratio that is used to determine the number of graphene layers. For a single layer, I_G/I_{2D} ratio is approximately 0.24. The calculated I_G/I_{2D} from the Raman spectrum is 0.587, indicating that the as-synthesised rGO is multilayer [15]. On the other hand, the Raman peaks at 132, 379, and 630 cm⁻¹ are associated with the In-O vibration of InO₆ crystal structure, stretching vibrations of In-O-In, and stretching vibrations of the v-(InO₆) octahedrons in In₂O₃, respectively [16]. Meanwhile, the peak at 406 cm⁻¹ is assigned to the out-of-plane vibration of sulphur atoms. The next peak at 451 cm⁻¹ is due to the overtone of longitudinal optical M-phonons in bulk MoS₂, which is a combination of longitudinal acoustic mode and an optical mode. The characteristic peaks of rGO, In₂O₃, and MoS₂ appears in the Raman spectrum, confirming the formation of the ternary composite.

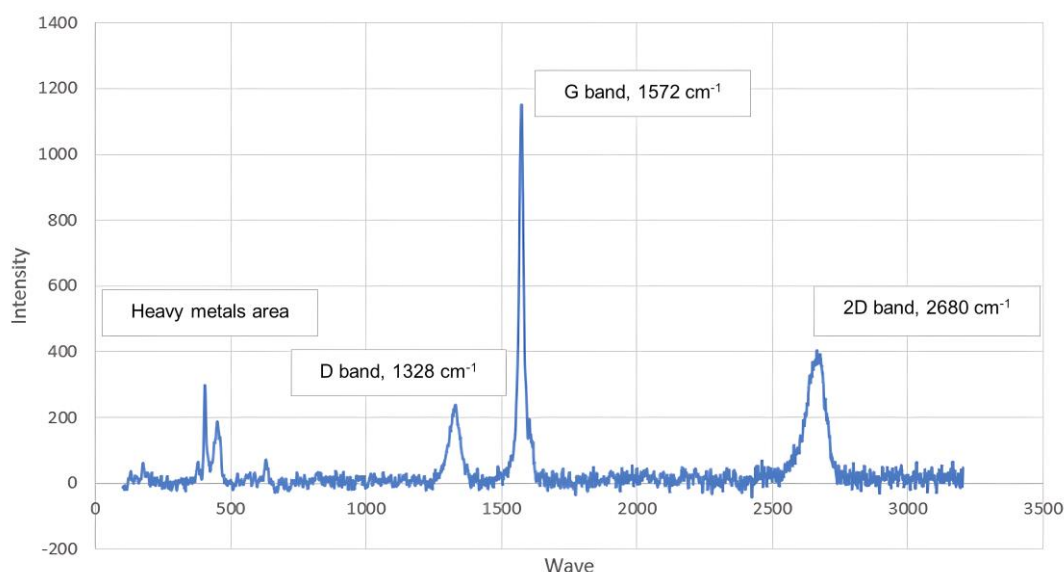


Fig. 3. Raman spectrum of rGO/In₂O₃/MoS₂.

3.2. Cyclic voltammetry

The electrochemical performance of rGO/In₂O₃/MoS₂ electrodes was evaluated by CV in 1 M Na₂SO₃ from -1 V to 1 V at scan rates of 25, 50, and 100 mV/s. The specific capacitance (F/g) is computed by applying the following equation (Eq. 1), where q = charge (C); computed by Gamry software, V = voltage window (V), and m = mass of electrode materials (g).

$$\text{Specific capacitance} = q / Vm \quad (1)$$

The recorded CV curves of pure In₂O₃, binary In₂O₃/MoS₂, and ternary rGO/In₂O₃/MoS₂ at the scan rate of 50 mV/s are presented in Fig. 4. Accordingly, the CV curve of rGO/In₂O₃/MoS₂ shows a slightly larger integrated area as compared to In₂O₃ and In₂O₃/MoS₂, indicating that the ternary composite can store more charge. Moreover, Fig. 5 shows the specific capacitance of In₂O₃, In₂O₃/MoS₂, and rGO/In₂O₃/MoS₂ at 25, 50, and 100 mV/s. From the figure, In₂O₃ and In₂O₃/MoS₂ have nearly the same specific capacitance at all scan rates with no enhancement effect towards the pure In₂O₃. The highest achievable specific capacitance for both samples is approximately 60 F/g at 25 mV/s. Although both In₂O₃ and MoS₂ are known to have good specific capacitance, their low inherent electrical conductivity for the diffusion process of ions and transfer of electrons which limits the maximum attainable specific capacitance.

In contrast, rGO/In₂O₃/MoS₂ exhibits the highest specific capacitance of 77 F/g at 25 mV/s, a 29% increment over the In₂O₃ and In₂O₃/MoS₂. This is due to the presence of rGO that provides a better conductivity pathway for the electron/ion transfer since rGO has good electrical conductivity and high charge mobility. The large specific surface area of the rGO also promotes better distribution of In₂O₃ nanoparticles as well as providing sufficient Faradaic redox reaction during continuous charging and discharging. Further, due to the similar morphology and structure of rGO and MoS₂ (in nanosheets form), heterostructures with improved mechanical robustness are formed, preventing both types of nanosheets from restacking [17]. Moreover, the incorporation of In₂O₃ nanoparticles also prevent the rGO/MoS₂ nanosheets from restacking. Therefore, the overall internal resistance of the ternary composite is reduced, resulting in higher specific capacitance.

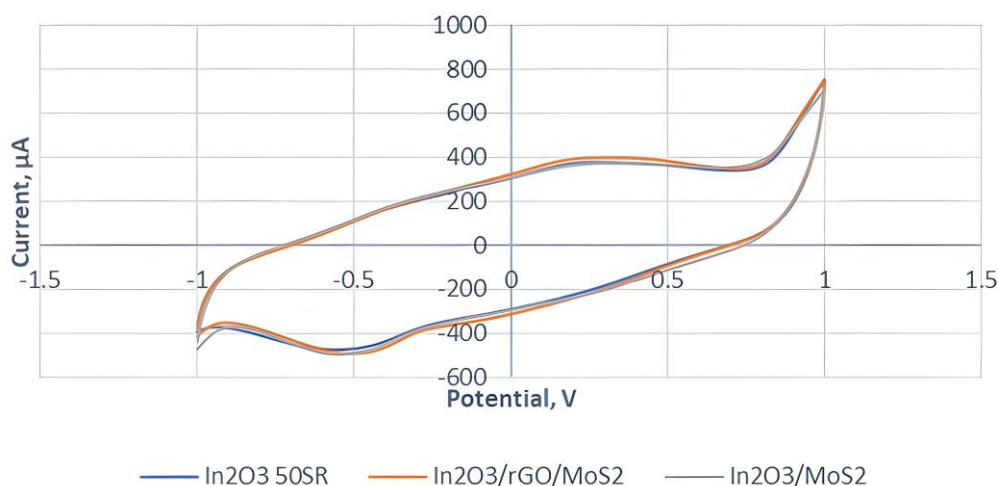


Fig. 4. Cyclic voltammograms of In_2O_3 , $\text{In}_2\text{O}_3/\text{MoS}_2$, and $\text{rGO}/\text{In}_2\text{O}_3/\text{MoS}_2$ at a scan rate 50 mV/s.

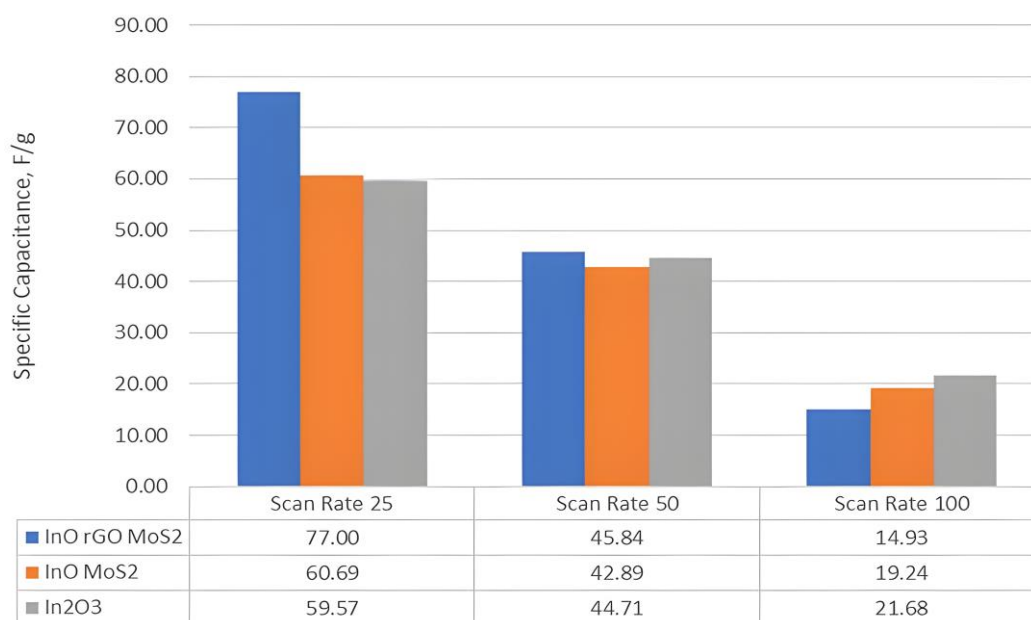


Fig. 5. Specific capacitance of In_2O_3 , $\text{In}_2\text{O}_3/\text{MoS}_2$, and $\text{rGO}/\text{In}_2\text{O}_3/\text{MoS}_2$ at scan rates of 25, 50, and 100 mV/s.

4. Conclusion

In conclusion, a novel $\text{rGO}/\text{In}_2\text{O}_3/\text{MoS}_2$ ternary composite for supercapacitor electrode was successfully synthesised using facile, green hydrothermal method. SEM and TEM reveal the uniform dispersion of sand like- In_2O_3 nanoparticles on the rGO/MoS_2 heterostructure. The EDX analysis confirmed the uniform distribution of In_2O_3 nanoparticles and the 6:6:1 ratio of the ternary composite. EDX, XRD, Raman and XPS analysis confirm the presence of rGO , In_2O_3 , and MoS_2 , and hence the composite formation. The electrochemical study was assessed via CV in two-electrode configuration in 1 M Na_2SO_3 electrolyte. In_2O_3 and $\text{In}_2\text{O}_3/\text{MoS}_2$ have virtually same specific capacitance at all scan rates. The highest achievable specific capacitance for both samples is about 60 F/g at the scan rate of 25 mV/s. In contrast, $\text{rGO}/\text{In}_2\text{O}_3/\text{MoS}_2$ shows the greatest specific capacitance of 77 F/g at 25 mV/s, an enhancement of 29% as compared to pure In_2O_3 and $\text{In}_2\text{O}_3/\text{MoS}_2$ binary composite. As such, the synergistic effect of rGO in the ternary composite provides an enhancement to the specific capacitance.

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Structural Morphological and Optical investigations of Nano Silver Oxides Nanostructures

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Keywords: Pulsed Laser Deposition; Optical properties; Silver oxide; Nano thin films; laser wavelength

Abstract. High purity, micro, and nano size Ag₂O nanostructure films were deposited by pulsed laser deposition on the quartz substrates at different pulsed laser Energies. The Ag₂O cubic structure is supported by structural and optical features, with the primary diffraction occurring from the (002) plane. The obtained band gap energy was around 2.25eV, and optical features indicate the temporal dependency of the energy gap.

Introduction

A significant p-type semiconductor with excellent conductivity, silver oxide may be found in a variety of phases, including Ag₃O₄, Ag₂O, Ag₂O₃, and AgO [1-3]. The forms of Ag₂O and AgO are the most appealing among all phases. It attracted the attention of researchers because to its significant uses in photo detectors, sensors, optical storage high density systems, solar cells, and antireflection coatings [4–6].

Numerous preparation techniques, including the sol-gel procedure, FRM sputtering, (PLD) pulsed laser deposition, Pulsed laser ablation, etc., were applied in the manufacture and research of the nano films of silver oxide [7–10]. The preparation process has a significant impact on the physical characteristics of Ag₂O, including the energy band gap value [11–13]. A. C. Nwanya et al. employed chemical bath deposition to generate Ag₂O thin films on glass substrates, where the AgNO₃ precursor and tri-ethanolamine were used as a complex agent at various deposition parameters. This is one of several efforts on the fabrication of Ag₂O nanomaterial [14-17]. With the passing of time, the values of optical constants like the energy gap and index of refraction rise [18, 19]. IA Ezenwa and colleagues used chemical bath deposition to create Ag₂O films at various (TEA) concentrations, and their findings revealed a clear correlation between the two parameters the thickness of the nano films and the concentration. Das et al. [20] studied the influence of

deposition temperature and used CBD to demonstrate the impact of the heat temperature on the Nano-structure of the silver oxides Nano films [21, 22]. They discovered that size of the grains was inversely effects to with the heating temperature while the porosity values of the Nano-film are increased [23]. The Effect of Pulsed laser energies for depositing Ag₂O Nano-films on different substrates using a Pulsed laser deposition technique has received much attention in the literature on the impact of pulsed laser energies. This study focused to prepare a high quality Ag₂O Nano films deposited by PLD method at various pulsed laser energies, and studying the physical properties for the deposited films to find the optimum condition for sensing applications.

Experimental Work

The quartz substrates were prepared to deposited the Ag₂O Nano-films by PLD technique. The quartz slides with dimensions of (1.5x1.5) cm were polished and cleaned with distilled water and ethanol before being dried in the air. A target made of Ag₂O (RY 280, Chin) has been ablated with a Nd: YAG laser from 300 °C temperature is used to create the silver oxide Nano films. To deposition of the Nano-films on the quartz substrate, three different pulsed laser energies were used (1600, 1800, and 2000) mJ were utilized.

After the films were deposited, the structural characteristics of the films were examined using an X-ray diffraction experiment with a Cu-ka x-ray source from Shimadzu 6000. The optical properties were studied using a Shimadzu spectrophotometer double beam.

Results and Discussions

The effects of pulsed laser energy (1600, 1800, and 2000 mJ) could be seen on the XRD patterns in the first Figure. The two peaks of diffraction, which are initially shown at planes (200) and (201), respectively, belong to the 2 θ (38.28, 45.1) diffraction angle and are related to the Ag₂O crystals. They also match the conventional standard-carts (00-001-1041). However, at the (200) diffraction plane, (Ag₂O) silver oxide predominates. It is possible to identify an improvement significant in the composition of the crystalline for the Nano-film at an interaction period of (1800) mJ, and comparable results have been reported in previous publications [24-26]. The following mathematical formulas [27-29] were used to estimate the structural of the crystal parameters that specified the values of the structure for the deposited Nano-films using the X-ray diffraction results:

$$D = \frac{K\lambda}{\beta(\cos\theta)} \quad (1)$$

$$\delta = \frac{1}{D^2} \quad (2)$$

$$\varepsilon = \frac{\beta}{4 \tan \theta} \quad (3)$$

β are (FWHM) in a radius, D are a crystalite size in the (nm), K are the constant (shape factor), θ are the Bragg angle, δ are the dislocation density, and ε are the strain are all given in the formula.

The average grain sizes were discovered to be constant, and table (1) could be used to display the acquired value of the structural constant. As a result, there is relatively little change in the structural strain values or the density of structural dislocations over time.

The following formulae [30-33] were used to analyze the X-ray diffraction results and characterize the characteristics that define the deposited film structure:

$$D = \frac{K\lambda}{\beta(\cos\theta)} \quad (4)$$

$$\delta = \frac{1}{D^2} \quad (5)$$

$$\varepsilon = \frac{\beta}{4 \tan \theta} \quad (6)$$

where the λ are refers to the X-ray radiation wavelength.

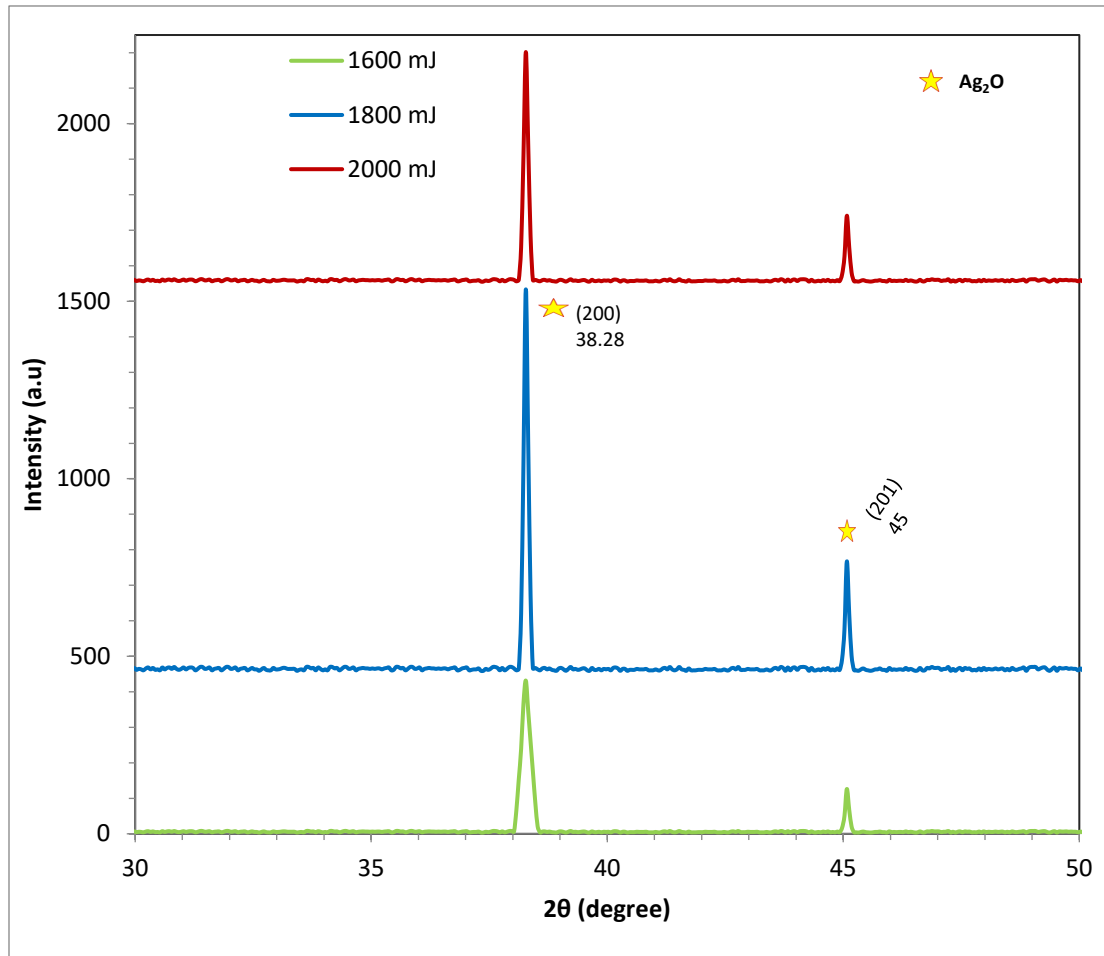


Fig. 1. XRD results of Ag_2O film as a function of pulsed laser energies

Table 1. Structural parameters of samples prepared at different pulsed laser energies.

Pulsed laser energy (mJ)	2 θ (deg)	Inter planer spacing (Å)	hkl	FWHM β Deg.	D (nm)	(δ) * 10^{-3} lines/ m^2	ε * 10^{-3}
1600	38.28	2.431	200	0.689	15.46	5.68	3.1
1800	38.28	2.442	200	0.895	14.53	5.41	3.3
2000	38.28	2.437	200	0.764	15.29	5.53	3.2

Figure (2a-c) may display the AFM pictures for the deposited Ag_2O Nano-films at various pulsed laser energy. The Nano-films depict a surface of uniform made up of large spaces on the substrate; this surface uniform may be due to an increase in film thickness by increasing the rate of ablation, and increased in the grain sized for the deposited nanofilms which results in the adsorption of the atoms on the substrate surface. The increased in the pulsed laser energy has been discovered to significantly enhance in the surface morphology and show an increased in the grains for the deposited nanofilms. The latter trend could be a result of both a high chance of grains aggregation and lengthening crystal growth times. The Nano size effect is confirmed to be prominent on the films surface by the average particle size being in the range of Nano grains. The table in which the results were obtained (2). There were other places to find similar works [34, 35].

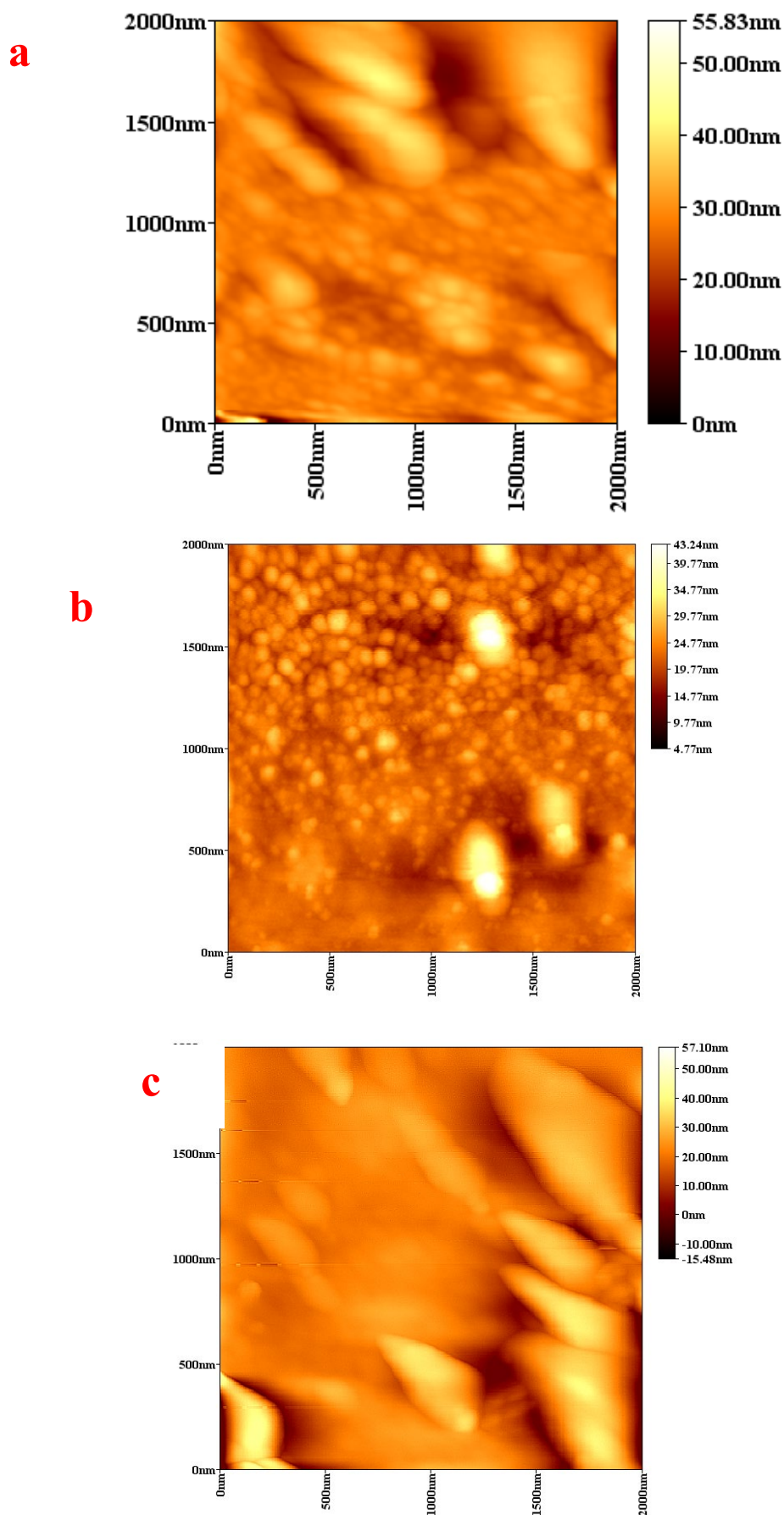


Fig. 2. 2D AFM pictures of Ag₂O Nano-films deposited at various pulsed laser wavelengths

Table 2. The tasted and calculated morphological data of Ag₂O Nano-films deposited at various pulsed laser wavelengths.

Pulsed laser energy (mJ)	Roughness Average (nm)	Root mean square(nm)
1600	0.774	13.37
1800	1.24	11.68
2000	0.942	12.77

Figure shows the optical transmittance of the produced Nano-films at various pulsed laser energy (3). The figure shows that the thin film formed at (1600) mJ pulsed energy has a greater transmittance than the others. According to other investigations, the low thickness and full production of the Ag₂O as a suitable TCOs material can be linked to the film's excellent transmittance. [37, 38].

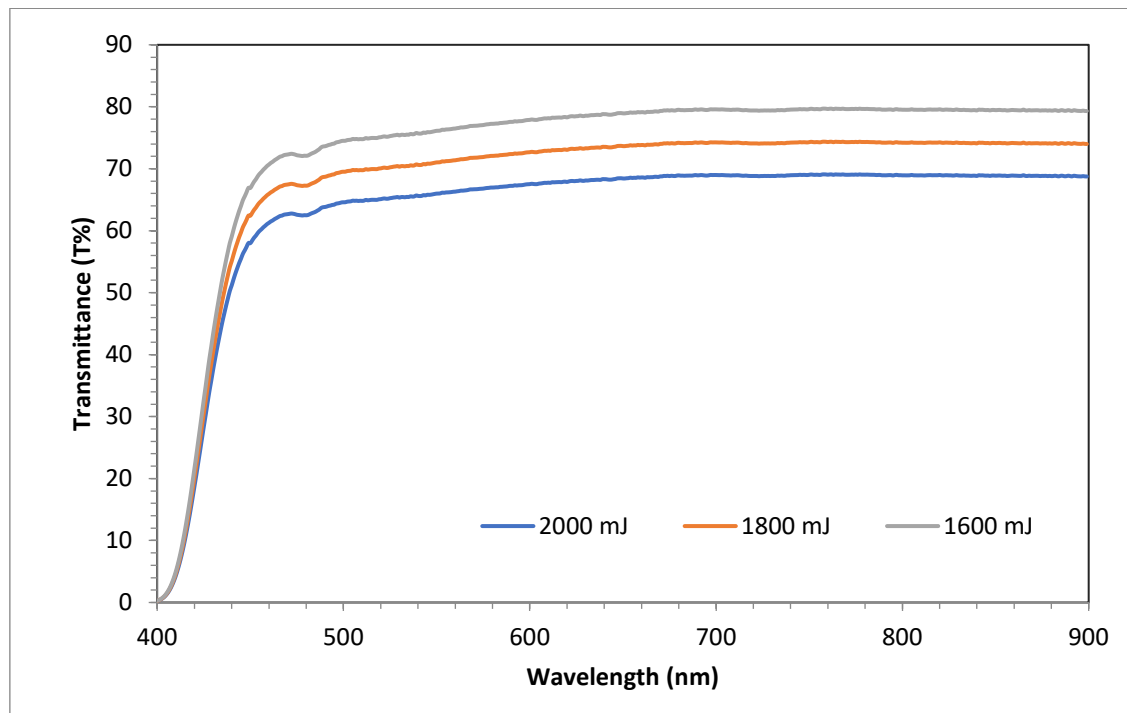


Fig. 3. Optical transmittance of Ag₂O films at different pulsed energies.

The change in the absorbance coefficient (α) of Ag₂O Nano-films at wavelengths between 400 and 900 nm is shown in Figure 4 at different pulsed laser energy (1600, 1800, and 2000 mJ). The optical energy band gap of the deposited layer might be calculated based on the transmittance values using Tauc equation [39-41].

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (7)$$

where E_g is the optical band gap, μ is the frequency of the photon, n depends on the kind of transition, and the h is the constant of Planck's. For either $n=1/2$ direct or $n=2$ indirect [42].

The presented results in this figure (4) demonstrate that the values of the coefficient absorption starts to grow after the pulsed energy condition of 2000 mJ, which is caused by an increase in peaking density. The transmittance at this condition for 1600 mJ pulsed energy exhibits the lowest absorption coefficient, which is perhaps connected to an improved crystallite structure [43, 44].

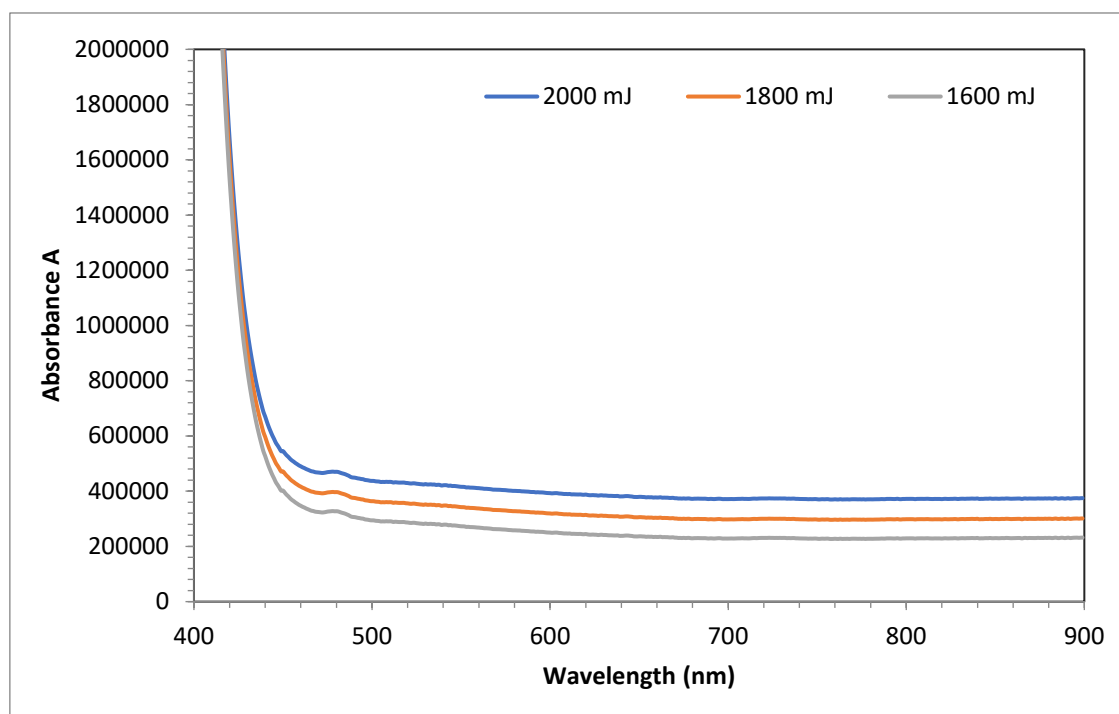


Fig. 4. Ag₂O coefficient of Absorbion at different pulsed laser energies.

Figure (5) depicts the optical energy gap of silver oxide thin films at various pulsed laser intensities. The calculating values of the optical energy gap are range from 2.42 to 2.58 mJ for pulsed laser intensities. According to prior x-ray diffraction studies [40, 45], the increase in the quality of the structure crystalline for the deposited Nano-films is what caused the optical energy gap fluctuation [46, 47].

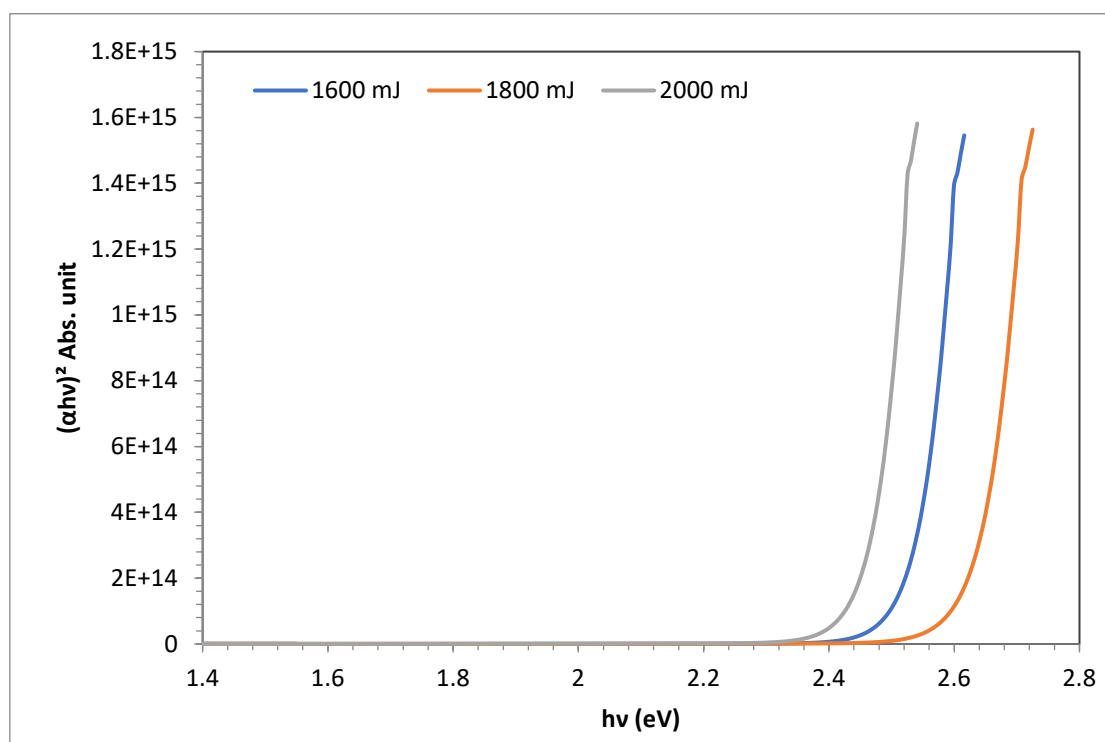


Fig. 5. Optical Energy gaps with different pulsed laser energies

Table 3. Activation Energies E_a and optical band gap E_g for silver oxide thin films

Pulsed laser energy (mJ)	Energy band gap E_g (eV)	Activation energies E_a (eV)
1600	2.42	0.435
1800	2.51	0.382
2000	2.58	0.418

Conclusion

Pulsed laser energy of 1800 mJ demonstrated the development of a consistent and smooth Ag_2O nanostructure thin layer. As pulsed laser energy, it was possible to get a blue shift in the energy gap along with reductions in the particle size of the manufactured material.

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Dielectric, AC Conductivity, and Optical Characterizations of (PVA-PEG) Doped SrO Hybrid Nanocomposites

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Abstract. Strontium Oxide (SrO) nanoparticles have a specific structure, and excellent optical, mechanical, and thermal properties, within direct bandgap semiconductors applications. SrO impact on the optical and electrical properties of newly (PVA-PEG/ SrO) nanocomposite were investigated. The electrical properties were measured at 100 Hz – 6 MHz frequencies. An increase in frequency caused a reduction in the dielectric loss (δ) and dielectric constant (ϵ). ϵ value revealed an improvement with an increased loading ratio of SrO. The optical properties of the (PVA-PEG/SrO) nanocomposite showed a reduction in the energy gap values. In contrast, the absorption, extinction coefficient, absorption coefficient, optical conductivity, refractive index, and dielectric constant (imaginary, real) increased with the increased concentration of SrO NPs.

Introduction

Polymers are a crucial material class in people's lives because they have deficient concentrations regarding the free charge carriers and are therefore non-conductive [1]. In addition, polymers as electric materials have the disadvantage of being transparent to electromagnetic radiation and providing protection against electrostatic discharge when dealing with sensitive electronic devices [2]. To overcome such limitations. The polymers' electrical properties represent through the response to the applied electric field (the subject of polymers' electrical characteristics encompasses a wide variety of molecular phenomena) [3]. When exposed to an electric field, polymers behave differently than metals. Polarisation is a phenomenon presenting the polymers' molecules rotating in the applied electric field direction [4].

One of the effective ways of probing important information about the polymers' electrical response in nature is molecular dynamics [5]. The electrical properties related to the final product might improve by combining at least two polymers (as blends) [6]. On the other hand, the appearance of additional properties depends on the blend's miscibility [7]. Blending may have significant and often unexpected impacts on thermal stability that cannot predict solely based on relative proportions and component behavior [8]. Televisions, displays, cellular phones, LEDs, batteries, solar cells, sensors, electromagnetic shielding, actuators, and microelectronic devices use conductive polymers [9].

Polymer-based composites are another type of material [10]. Electronic ones emphasize low dielectric constant, low thermal expansions, high thermal conductivity, and electromagnetic interference protection effectiveness could come from involving the nanomaterials with blended polymer to form environment conductive materials [11,12]. Conductive nanocomposites utilized as fillers could be ambitious for different applications [13]. In addition, a composite material is used as a structural material. The structural composites emphasize high modulus and strength based on the electronic application [14,15].

SrO is one of the direct bandgap semiconductor nanofillers belongs the II-VI semiconductor compounds group that is widely studied [16–19]. It has interesting properties, for instance, electrochemical stability, considerable exciting binding energy up to (60 meV), nontoxic, low-temperature growth, high transparency, and radiation resistance [16]. Because of the unique

hierarchical morphology of SrO NPs, it is used to design various electro-optical devices such as doped semiconductors, gas sensors, dye-sensitized solar cells, transistors, batteries electrodes, and supercapacitors [16,20]. This investigation aims to impact SrO nanofillers on the optical and electrical properties of (PVA-PEG/SrO) nanocomposites.

Experimental and Theoretical Part

Materials

Polyvinyl alcohol (PVA) made in Merck, Germany, with (14000) molecular weight, polyethylene glycol (PEG), and strontium oxide (SrO) nanoparticles, materials were used in this investigation.

Sample preparations

SrO nanoparticles were utilized as an additive and added to a blended polymer matrix (PVA-PEG) with various loading weight percentage values (0, 1, 2, and 3) wt%. The samples for (PVA-PEG) and the (PVA-PEG/SrO) nanocomposites were made with the casting approach to create a sample with 1.5 μm thickness.

Characterizations

UV/1800/Shimadzu spectrophotometer was used to photometrical measure the spectra. The dielectric constant of (PVA-PEG-SrO) composites was assessed with the use of an LCR meter with a frequency (f) between (100 Hz - 6 MHz) at room temperature.

Calculations

The capacitance (C) was evaluated using the equation below [21].

$$C = \epsilon' - \epsilon_0 At \quad (1)$$

here, represents dielectric constant; t represents sample thickness, and ϵ_0 represents the value of the vacuum permittivity. Loss factor (D) was evaluated from equation (2).

$$D = \epsilon'' / \epsilon' \quad (2)$$

This represents electrical energy' loss that was dissipated as heat in the insulator. In addition, specifying power factors is vital in electrical applications. Also, the dielectric constant might be evaluated based on the following equation.

$$\epsilon = C_p / C_0 \quad (3)$$

here: C_0 represents vacuum capacitor, and C_p represents parallel capacitance. Also, dissipated power in an insulator has been specified via the presence of alternating potential as an alternating conductivity function.

$$\sigma_{A.C} = w \epsilon'' \epsilon_0 \quad (4)$$

here, ϵ'' denotes the dielectric loss, and w represents the angular frequency.

Results and Discussion

Figure (1) shows the dielectric constant variations with frequency. The constant dielectric results exhibited a decrease in the dielectric constant with the increasing applied frequency. In contrast, the increase in frequency leads to a reduction in the space polarised. The dielectric constant's value is impacted via the mechanism of polarization. The dielectric constant value increases at low-frequency values because material molecules will be partially polarized [22]. The dielectric constant value increased with the contribution of an increase in the loading ratio of SrO in PVA-PEG/SrO nanocomposites, as shown in Figure 2. The increase in the dielectric constant's value is because the particles of SrO are connected to create a network inside the polymer mixture. The increase in the

dielectric constant value is related to the increasing the SrO contained in the nanocomposites. The results matched the ones in the literature [23].

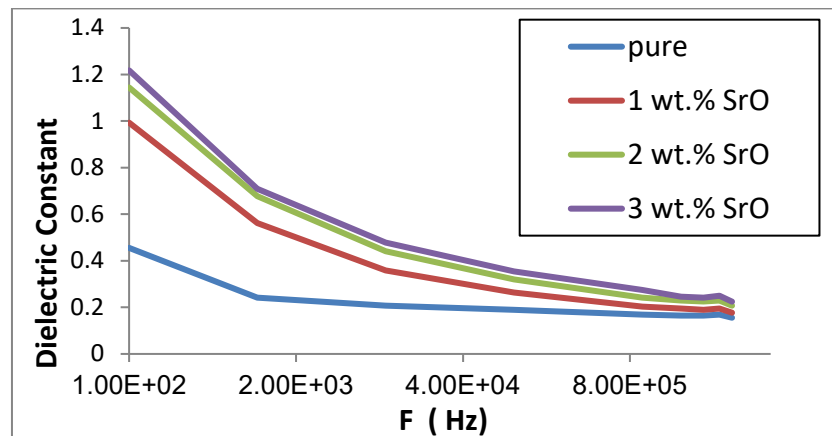


Figure 1: Effect of frequency on the dielectric constant of samples.

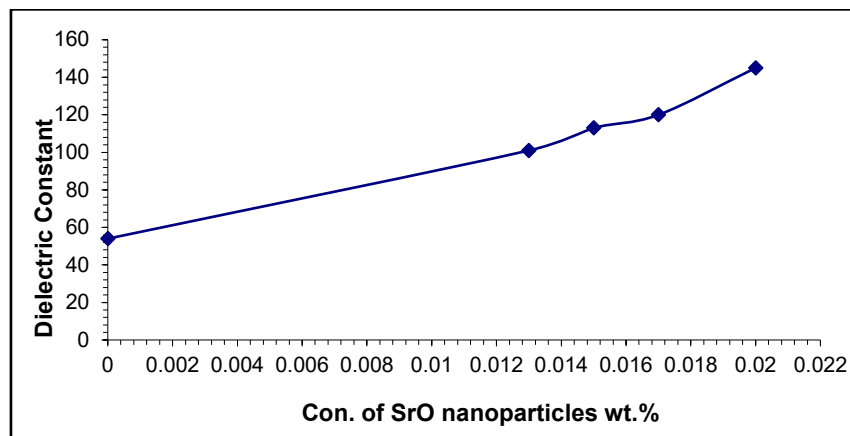


Figure 2: Effect of SrO concentrations on the dielectric constant of samples.

Figure 3 displays the relation between dielectric loss (δ) with frequency. The results indicate a reduction in the dielectric loss with increases in frequency. The results showed a high dielectric loss value at low frequency, decreasing with the frequency increase. This could be related to reducing the impact of the galaxy charge polarisation when the frequency was increased [24]. In addition, results showed improvement in the value of the dielectric loss with an increasing the SrO ratio in PVA-PEG/SrO nanocomposites; as shown in Figure 4, that trend might be related to an increase in dipole charge' alignments [25].

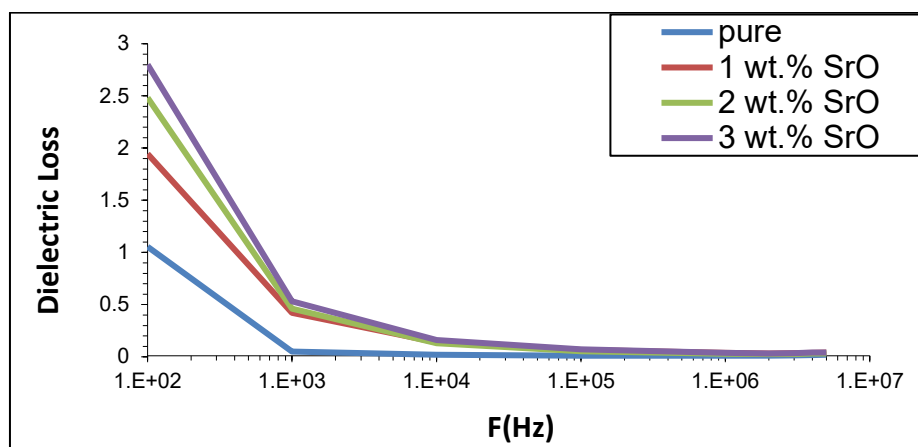


Figure 3: Effect of frequency on the level of the dielectric loss of samples.

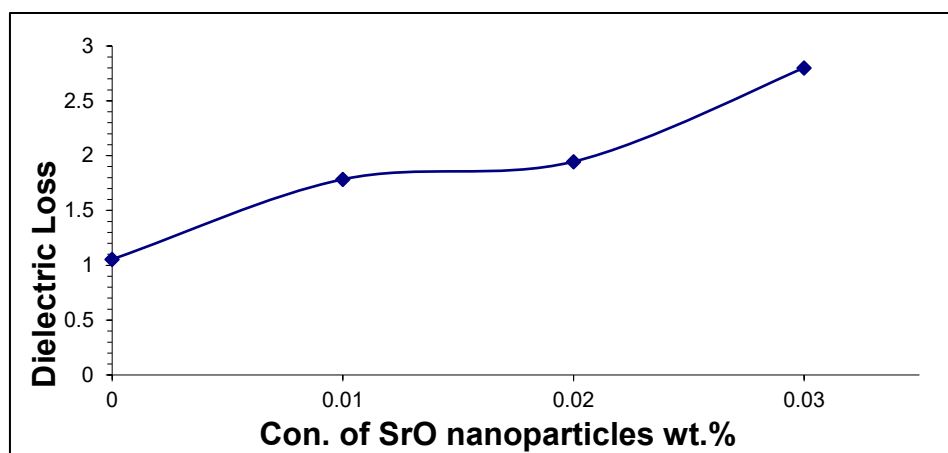


Figure 4: The effect of the Sb₂O₃ concentration on the dielectric loss of samples.

Figure 5 displays variations in electric conductivity results with frequency. This figure demonstrates enhancing the nanocomposites' conductivity with an increase in frequency, which might be due to space charge polarisation occurring at low-frequency values, along with charge carriers' motions, which move as in the hopping process. In conductivity, the increase was insignificant at high-frequency values, which might belong to electronic polarization and carriers of charge traveling via the hopping [15].

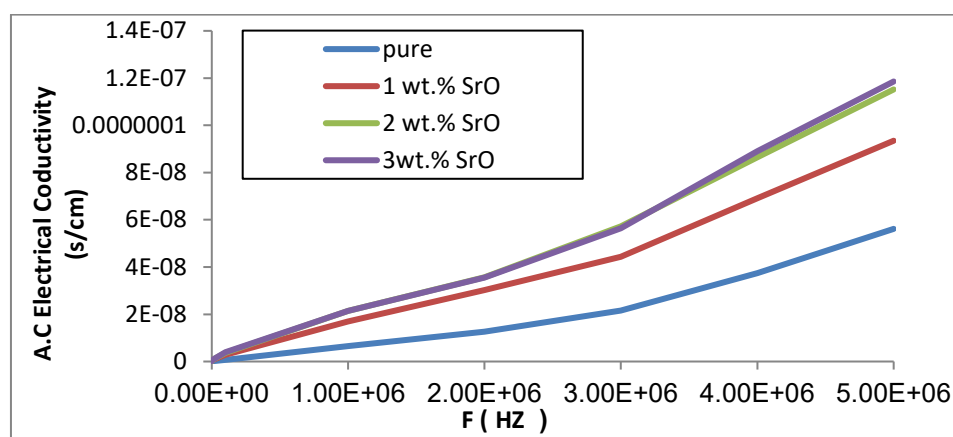


Figure 5; Effect of frequency on the electrical conductivity of samples.

The optical absorbance (A) behavior of blended polymers and nanocomposites was characterized by variable wavelengths in the range of (200-1100) nm at room temperature, as shown in Figure (6). Absorption spectra revealed a higher absorbance level in the UV range at 200 nm related to π - π^* . Additional small peak features were presented at 280 nm that could be related to the nanofillers [26,27]. At high wavelengths, the incident photons do not have adequate energy for interacting with atoms and causing transmitting photons. However, all nanocomposites displayed low absorbance in the visible range; such behavior might be indicated in the following way, where the interactions between incident photon and material will occur. Thus, the increase in SrO NPs concentrations is associated with an increase in absorbance. Those results are comparable to the effects of researchers [28].

Figure (7) illustrates the transmittance spectra with a wavelength function of the samples. The transmittance decreased with increasing SrO nanoparticles concentrations that increased the adsorbed and attention the other light, as well as nanoparticles molecules, filled the most vacancies between (PVA-PEG) blends polymer [29].

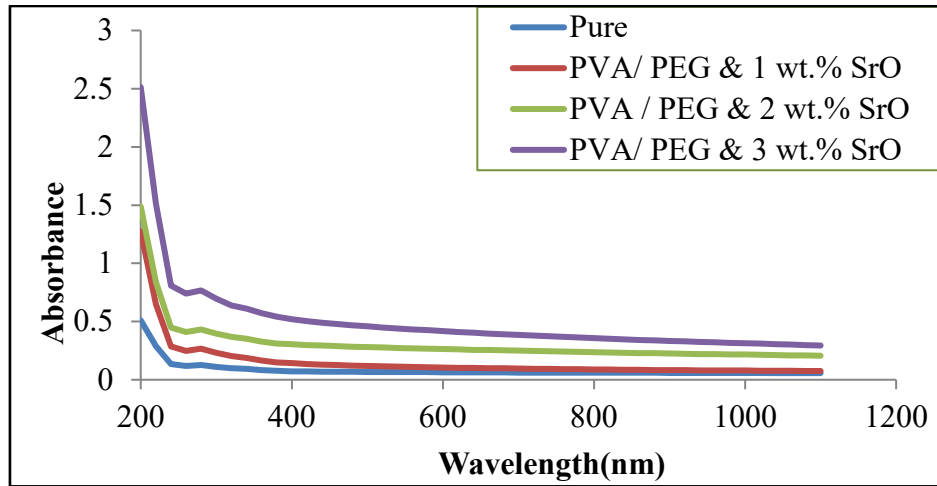


Figure 6: The absorbance as a wave-length function for the samples.

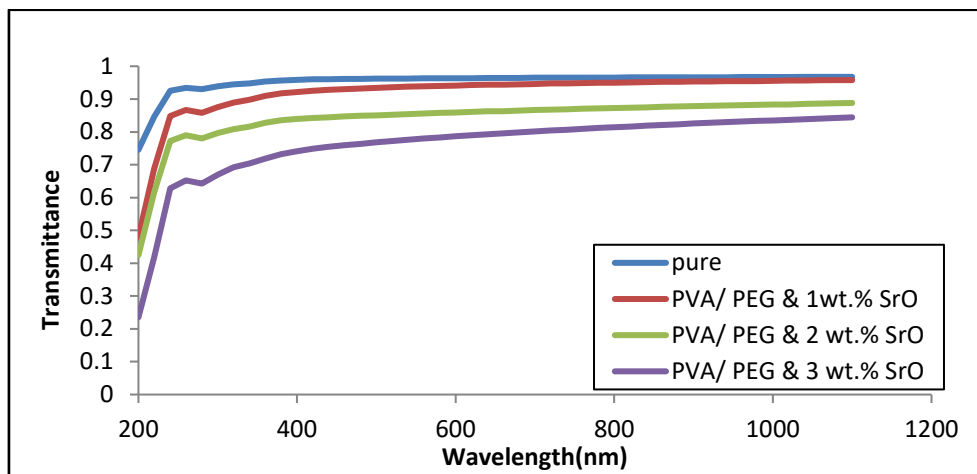


Figure 7: Transmittance with the wavelength for samples.

The absorption coefficient of the absorption α is computed using Eq. (5) [30].

$$\alpha = 2.3030 \frac{A}{t} \quad (5)$$

Here, A represents absorbance, and (t) represents the sample thickness.

Figure (8) illustrates the absorption coefficient (α) as a function of the samples' wavelength. The results showed small changes at the high wavelength (low energies), indicating the potential of low electronic transitions. At the low wavelength (high-energies), the absorption coefficient increased sharply, specifically at the photon's higher energy, indicating the significant probability that electronic transitions are the region's absorption edge [31]. Also, the absorption coefficient allows concluding the nature of the electronic transitions, where when the high absorption coefficient values (α is more than 10^4 cm^{-1}) at high energies, direct electronic transitions are presented, and the energy and moment are maintained via photons and electrons [32].

The absorption coefficient values are low (α is less than 10^4 cm^{-1}) at low energies where indirect electron transitions occur, while electronic momentum is maintained using a phonon [17]. The absorption coefficient values are low energies in the presented study, and indirect electronic transitions were deduced.

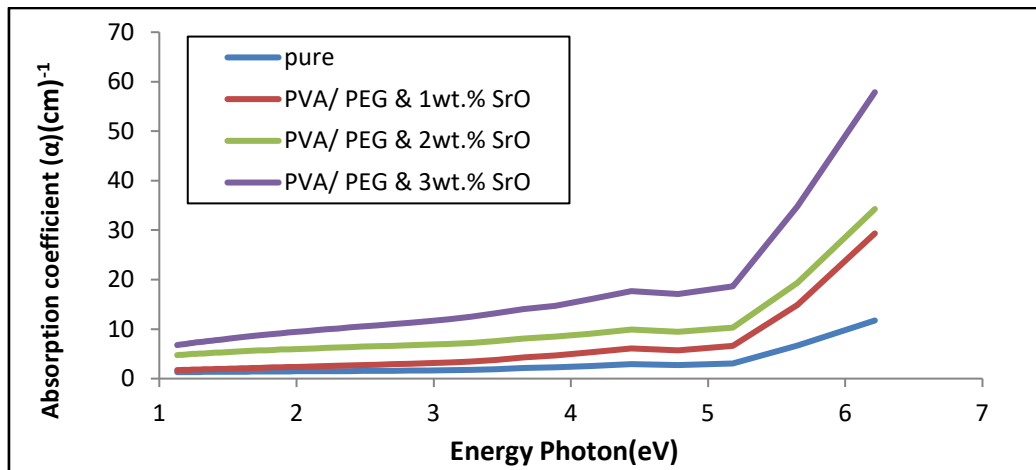


Figure 8: The absorption coefficient with energy photon of samples.

Figure (9) shows the relationship between $(\alpha h\nu)^{1/2}$ for samples with a photon energy function. On drawing a straight line from a curve's upper part towards the (x) axis, at a value of $(\alpha h\nu)^{1/2} = 0$, the result is an energy gap for allowed indirect transitions. The values are listed in Table 1 using the Tauc relation [29].

$$(\alpha h\nu) = B (\nu - E_g^{\text{opt}} \pm E_{\text{ph}})^r \quad (6)$$

It can be seen that the energy gap values were decreased by increasing the ratio of SrO NPs in the samples. This resulted in the on-site levels in the energy gap [33]. In this case, the transition is carried out in 2 stages, involving the electron transition from the band of valence to local conduction band levels due to the increase of SrO NPs. Such behavior results from electronic conduction's dependence upon the impurities that have been added [34]. The rise in SrO NP concentration levels provides electronic paths in blended polymer, facilitating the electron crossing from the valence to conduction bands. This explains the reduction in the energy gap with increasing the SrO NP concentrations [16]. The forbidden transitions of the indirect energy gap were computed similarly. Table (1) and Figures (9) note the energy gap for allowed and forbidden indirect transitions for samples.

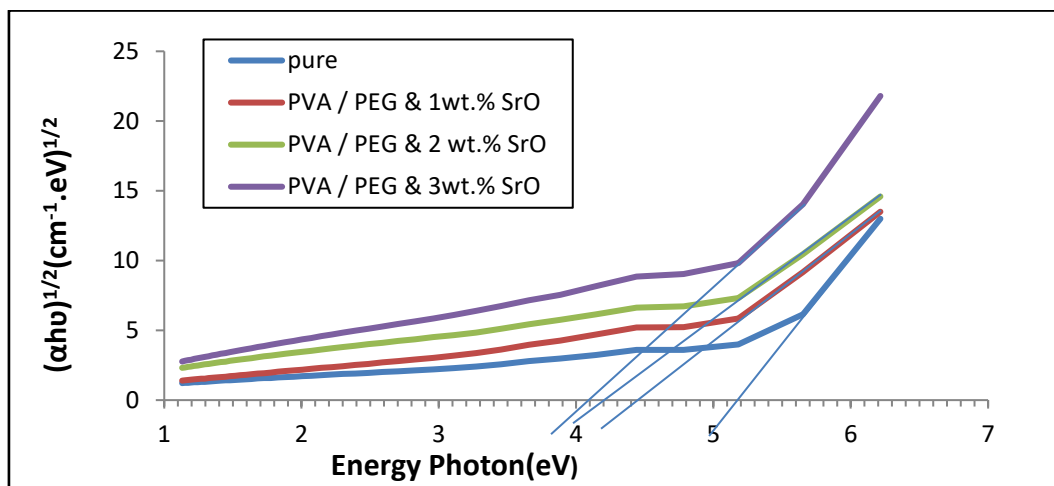


Figure 9: Energy gap for allowed indirect transition $(\alpha h\nu)^{1/2}$ of samples.

Table 1: Energy bandgap for allowed and forbidden indirect transitions for samples.

SrO Nanoparticles concentrations	E _g (eV)	
	Allowed	Forbidden
0.00	5.15	4.9
0.01	4.45	3.95
0.02	4.2	3.6
0.03	4.1	3.4

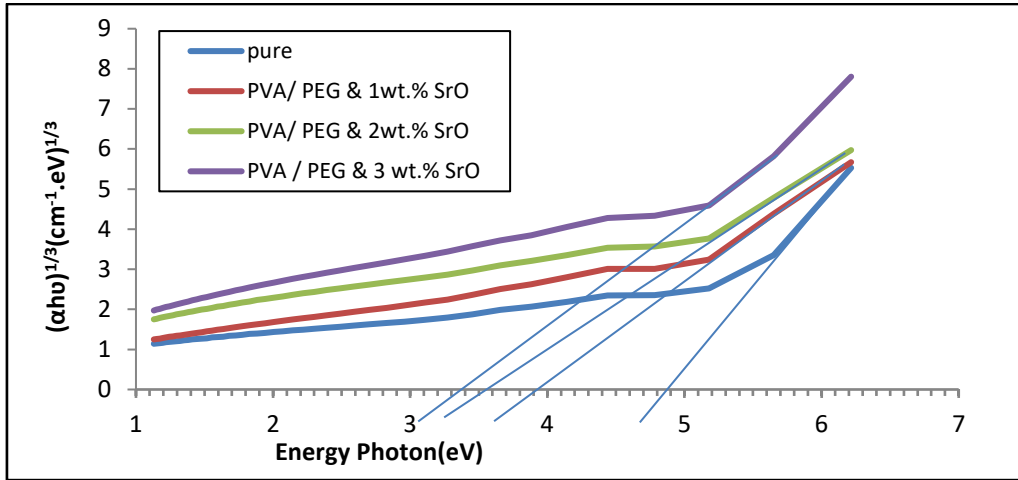


Figure 10: Energy gap for forbidden indirect transition $(\alpha h\nu)^{1/3}$ of samples.

Extinction coefficient (K) can be calculated according to eq (7) [25].

$$k = \alpha \lambda / 4\pi \quad (7)$$

The behavior of extinction coefficient (K) as a wavelength of samples is illustrated in Figure (11). (K) value was decreased with increasing the wavenumber slightly increased at the visible and the near IR region [35], which is why the extinction coefficient increased with the increase of the wavelength according to equation (6). The result of the absorption coefficient increased with the increasing the SrO nanoparticles concentrations [16,36], where it can conclude from equation (6) that the absorption coefficient is directly correlated to (K).

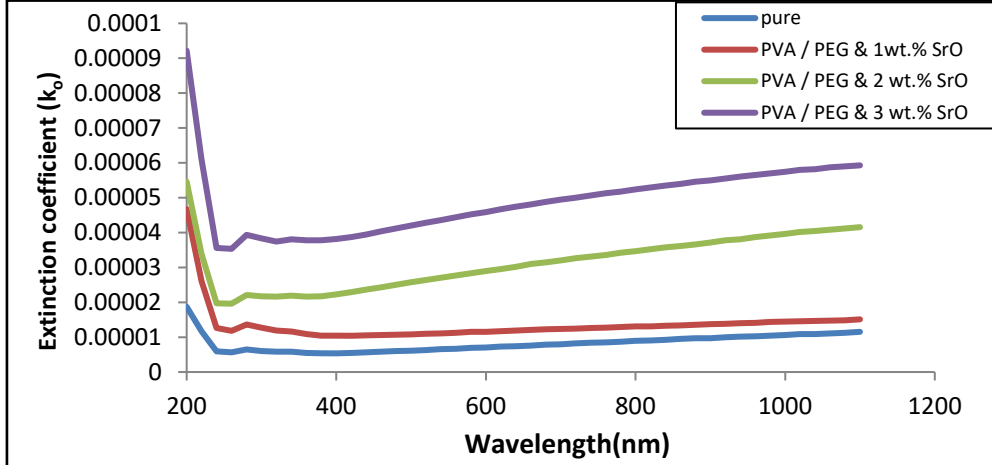


Figure 11: Coefficient of Extinction with the wavelengths for the samples.

The film's refractive index was estimated using equation (8) [37].

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R)^2} - K_0^2 \right]^{1/2} \quad (8)$$

The dispersion curves related to refractive index n , (λ) in the typical dispersion region ($\lambda = 200$ - 1100 nm) are indicated in Figure (12) samples. Results illustrated a reduction in the values of (n) with the increase in wavelength and reached an almost constant value at the very long wavelength value [38]. Also, it was found that (n) was increased with the increased concentration ratio of SrO nanoparticles. The refractive index of (PVA-PVP) blends increased after embedding increasing SrO nanoparticles could result from the structural modifications in the polymeric matrix [17,39].

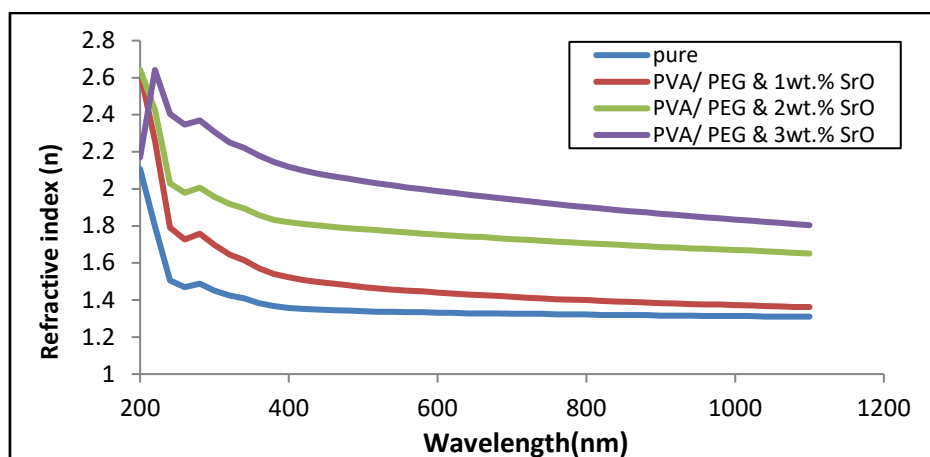


Figure 12: Refractive index with wavelength for samples

Conclusions

The applied method successfully prepared PVA-PEG/SrO nanocomposite with different content of SrO. The contribution of SrO significantly improved the dielectric loss, dielectric constant, and electrical conductivity. Increasing the loading ratio of SrO and the applied electrical field' frequency enhances the electrical conductivity. The Absorbance at 200 nm increased from 0.51 to 2.51, and the energy gap improved from 5.15 to 4.1 eV for allowed from 4.9 to 3.4 eV of forbidden transactions after increasing the loading ratio of SrO NP. The absorption coefficient allows concluding the electronic transitions' nature when high absorption coefficient values ($\alpha > 10^4$) cm^{-1} at high energies direct electronic transitions. The extinction coefficient also increased with the increase in wavelength. It is identified that there is an increase in (n) with the rise in SrO NPs concentrations. These results exhibited exiting nanocomposites promising for applications such as senses, solar cells, and elector-optical devices.

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Characterization of Zinc Oxide Semiconductor Thin Film Treated with Cold Plasma

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Abstract. In this study, the photovoltaic properties of zinc oxides are investigated. Different stoichiometries of zinc oxide can be made using vacuum deposition. Thermally evaporated zinc produces thin films of ZnO composed of orthorhombic and tetragonal phases that define the material's characteristics and performance. A plasma has removed a very thin layer from the surface of the thin film, known as non-thermal plasma, and made a surface cleanup. Measurements of the Atomic Force Microscope (AFM) show that the value of the granular volume rate increases when the duration of exposure to non-heat plasma increases. Measurements of the Atomic Force Microscope (AFM) show that there is an increase in thin film surface roughness values (Roughness, Sq), as well as the square root of the average roughness of the thin film surface (RMS), and this increase in roughness appears as the duration of exposure to non-thermal plasma increases.

Introduction

The survival and advancement of rich and modern societies require a reliable and long-term energy supply. However, suppose fossil fuels are used indefinitely. In that case, they will deplete existing fossil fuel supplies, causing environmental problems like global warming and political and military conflict, and significant fuel price increases [1]. Several analyses have shown that oil production has already passed its peak year [1]. All that's left is solar energy in all its forms, including photovoltaics, wind turbines, hydroelectric dams, and biomass. A fusion reactor known as the sun has been functioning for four and a half billion years and will continue for another three and a half billion years. It provides more energy than humans use in a year's worth of fossil fuel consumption. It is possible to fulfil the rising need for energy, which will only get worse as the world's population grows and modernization progresses. Nearly two-thirds of the rise in global energy consumption is attributed to emerging economies like China and India, which are predicted to more than double their energy consumption by 2025 compared to 2002 [1]. There is a 25% yearly growth rate in renewable energy in China, including wind, solar, wave, tidal, and biomass.

While India has made great strides in solar, biogas, and wind energy development, only a small percentage of this potential has been tapped. In contrast, the market for renewable energy has grown rapidly, and costs have dropped significantly [2]. Renewables might account for up to half of the world's energy needs by the mid-21st century, according to long-term projections. De Vries et al. believe that the technical potential of photovoltaic (PV) energy is far larger than that of wind and biomass energy [3]. 1.2×10^{17} Wh was reported by Asif et al. in 2004 [1], 1.3×10^{16} Wh was suggested by de Vries et al. in 2001 [2], and 4×10^{18} Wh was estimated for 2050 by de Vries et al. in their study on photovoltaics (PV) [3]. By 2050, the cost of a kWh of electricity is expected to be between 0.06-0.25 dollars [3]. According to other organizations, the potential for long-term cost reduction in PV through market growth and innovation is substantial. The right regulations and advances were needed in research to get a large market share and lower costs [4]. Good policies have been enacted in many countries, pioneered by Germany and Japan, where market development is developing swiftly [1, 2, 5].

The present state of photovoltaic technology, particularly thin film systems, will be examined in this literature study. Novel materials systems for large-scale photovoltaics deployment will be a

significant focus of this research effort to identify new materials systems that meet the economic and sustainability requirements for large-scale photovoltaics deployment.

Compared to the first generation of thin film technology, second-generation devices use less material while keeping the same efficiency level as the first generation of cells. CdTe, CIGS (CuIn(Ga)Se_2), and amorphous-Si are the leading technology, with a combined market share of roughly 17% [8]. Due to their greater absorption coefficients than crystalline Si (c-Si), these materials can be employed in thin film solar cells since they use significantly less material to produce films with thicknesses in the range of μm for efficient absorption. Understanding interfaces and innovative multijunction designs, along with developing low-cost, high-performance TCO materials and new module concepts [7], are major research priorities for thin film PV materials and ideas. Weighing only a few grams and requiring fewer processing steps and less material, thin film solar cells have several advantages over other solar cells [5, 6, 9]. Thin-film systems' benefits For the deposition of thin films, a variety of processes are available. These include thermal evaporation alone, multi-source evaporation, physical-chemical vapour deposition, and electrochemical approaches. The microstructure of the films can range from amorphous or nanocrystalline to highly orientated or even epitaxial growth or massive grains, depending on the production procedures, factors, and substrate materials used [7, 11]. Even though many interfaces and grain boundaries generally decrease the efficiency of a solar cell, the interfaces can be controlled and passivated or modified to provide, for example, diffusion barriers and the design of thin film solar cells allows for different types of junctions. It is possible to grade the qualities of multicomponent materials in terms of lattice constants, composition, band gap, and other optical parameters. Six Three-thousandths of a percent Photovoltaic (PV) technology has grown to be a multibillion-dollar industry in several countries. There's little surprise that photovoltaic technology has piqued the interest of investors, and it looks like economic justifications rather than environmental arguments will help propel PV energy into widespread usage [6]. As the cost/W ratio decreases, so does the PV industry's primary goal of reducing costs [5, 6, 15]. Si single crystals are expensive to grow, whereas thin film materials may be created on vast areas and quickly throughput, often using physical or chemical deposition processes, such that second-generation thin film solar cells have the possibility for substantially reduced cost manufacturing [5, 6, 15]. Due to their usage of rare materials, the zincing second-generation PV cells (CIGS and CdTe) may soon be limited in production due to material shortage [16, 17]. Zinc resources, for example, contain sufficient indium reserves to meet global demand just for the next two decades. Additional indium reserves in copper, zinc, and tin ores and the usage of recycled secondary indium will have to be added to the reserve base to meet the growing demand [18,19].

Experimental

In this section, the Thermal Chemical Spray System (Atomizer), as well as the method of preparing and cleaning the glass bases used for deposition, and the steps used in the preparation of thin film of ZnO, with a temperature of 450°C , The most important factors influencing the high quality of the prepared thin film, also the measurement for thin film, a description of the non-thermal plasma system used in the research, and the identification of the devices used to perform synthetic and visual measurements of the thin film prepared before and after exposure to non-thermal plasma.

Pneumatic spray pyrolysis

To prepare ZnO thin films, the substrates were ultrasonically cleaned for five minutes in acetone followed by deionized water for that time, at room temperature, and finally dried. The precursor solution was investigated using $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ in the presence of acetic acid. The ZnO thin films were prepared at 350°C for a deposition time of 10 minutes. Pneumatic spray pyrolysis moves the nozzle x-y at 30 mm.s^{-1} and 5 mm.s^{-1} during deposition. Gas pressure is adjusted and stabilized at 5bar by the regulator, and the timer for spraying time and downtime is adjusted (5Sec) and (55Sec), respectively.

The deposition process begins with the operation of the automatic control system controlling the flow of gas to the spray machine. The spray flows at the smallest on the glass bases and for a period

(55Sec), and the mug is removed in the meantime, followed by a pause of (55Sec), and in the meantime, the mug is returned to its original position to avoid drop drops on the glass bases and break them, and then removed in the second spraying process; thus the process is repeated, and at the same time make sure that the base temperature and heat returns to the required temperature after each spraying, by placing a dual thermal sensor with gravity until the spraying process is completed and reach the required fish

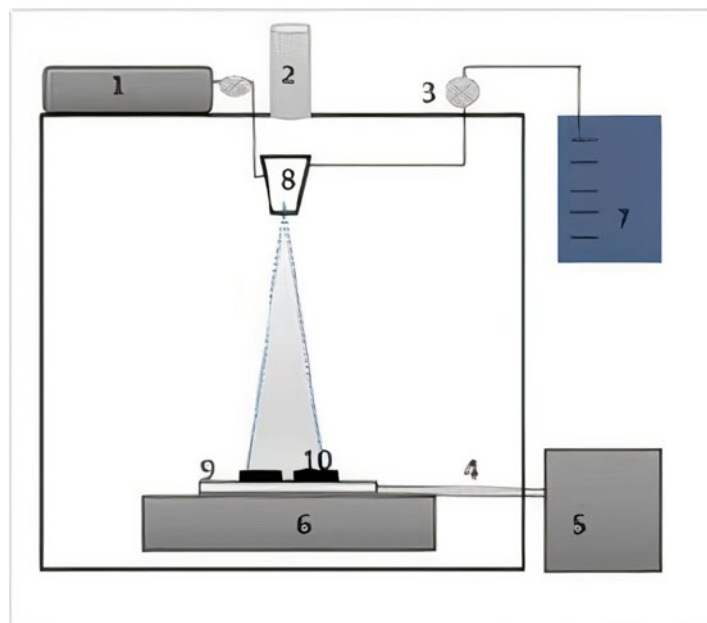


Figure 1: The spray system used for thin film coating

1.compressor,2.exhaust system,3.flow control,4.therocouple,5. Temperature controller,6.heater,7. Spray solution,8. Nozzle ,9.heater ,10.substrate

Non-thermal plasma

Zinc oxide (ZnO) prepared in the manner of the thermal chemical spray of non-thermal plasma was exposed .volt 3000-volt processor was connected to an electric converter.

The electrical converter was connected to a non-thermal plasma device, which consists of two poles:

1. Anode (positive pole), which represents the upper part.
2. Cathode (negative pole) that represents the lower part.

The circuit current is measured

Using a voltage fragmentary, which has connected resistance (10k Φ in the way of anode and measures. A Digital multimeter calculates the current passing through it. It separates the poles at a controllable distance by controlling the ascent and descent of the cathode, and a glass disc with a thickness (of 2mm) is placed on the cathode pole, after which the glass base deposited with a thin film (ZnO) is placed on it. Above the glass disc, the distance between the anode and *thin film (ZnO)* was determined by (2mm). A digital timer (DIGITAL TIMER) was used to calculate the exposure time of a *thin film (ZnO)* to non-thermal plasma at times (5,10,15) minutes, showing the figure 2 *plasma device non-thermal* The thermal used in the search.

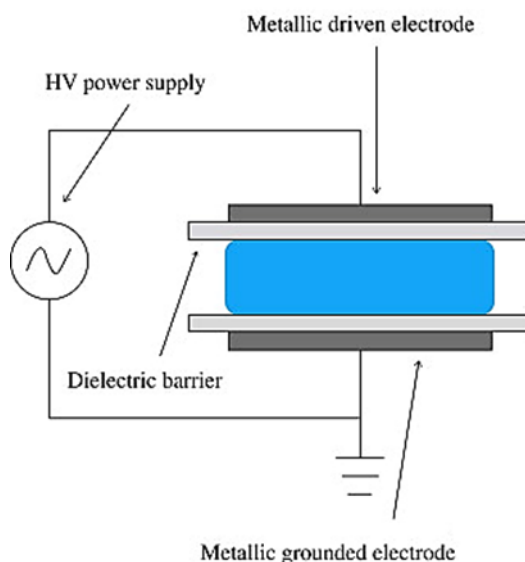


Figure 2: Non-thermal plasma for surface treatment

Results

In this section, review the findings reached through the study of the synthetic, optical, and electrical properties of zinc oxide thin film (ZnO) deposited on glass bases at a temperature of 450°C, prepared in the manner of thermal chemical spray, and the study of the effect of exposure (ZnO) exposed to non-thermal plasma at different times(5,10,15)

Structural Measurements

The synthetic properties of zinc oxide thin film (ZnO) were studied before and after exposure to non-thermal plasma from the presentation and analysis of the results of tests of synthetic properties techniques through:

X-ray results of X-rays Diffraction:

The X-ray diffraction (XRD) examination of all ZnO thin film, comparing their results with zinc oxide (ZnO) and using match! The model was found to be identical to what was present in the source and by suspicion of 1.4, as the thin film are of a polycrystalline nature that has a crystalline tetragonal composition, and the trend was For these thin films it is (002), as well as the appearance of six other less severe peaks [(001), (200), (110), (112), (101), (130)],

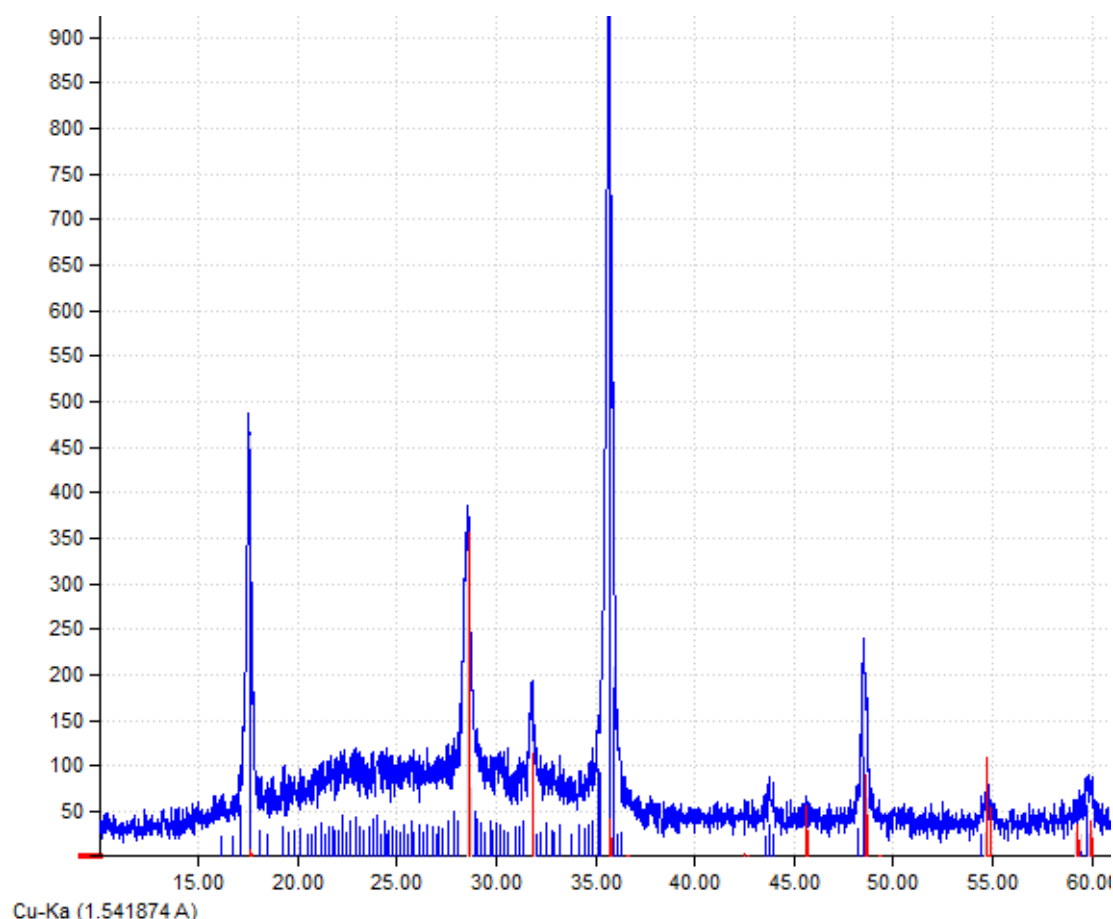


Figure 3:XRD for zinc oxide thin film coating

Figure 3 shows the extent to which the zinc oxide thin film prepared matches the source, explaining that the match occurs 100% with the same source mentioned from the database of the program, as well as the network constants of the thin film prepared for The cell unit where the constant values were $a=3.8748\text{\AA}$, $c=5.0227\text{\AA}$) as well as the calculated density $=9.5\text{ g/cm}^3$

X-ray form after exposure to thermal plasma at different times (5,10,15)min

The G.S. *granular volume rate* was calculated from the breadth of the line of life using the FWHM equivalent of samples exposed to cold plasma at times (5,10,15 min), where the equation was calculated directly by match! For trend peaks (101,200 (110,002,002, after taking FWHM values for the first exposure period (5 minutes) to know the decrease in FWHM values after increased exposure, The table shows the granular size of zinc thin film from exposure to non-thermal plasma, where at 5 minutes the granular size rate A 1906.4 and at 10 minutes the granular volume rate decreases to 670.3 A But in the period of exposure of 15 minutes the granular volume rate increases significantly to 3368.4 and continues to increase when the period of exposure to non-thermal plasma increases where at 20 minutes the average size is 4045.6 and at 25 minutes the average size is 4275.4

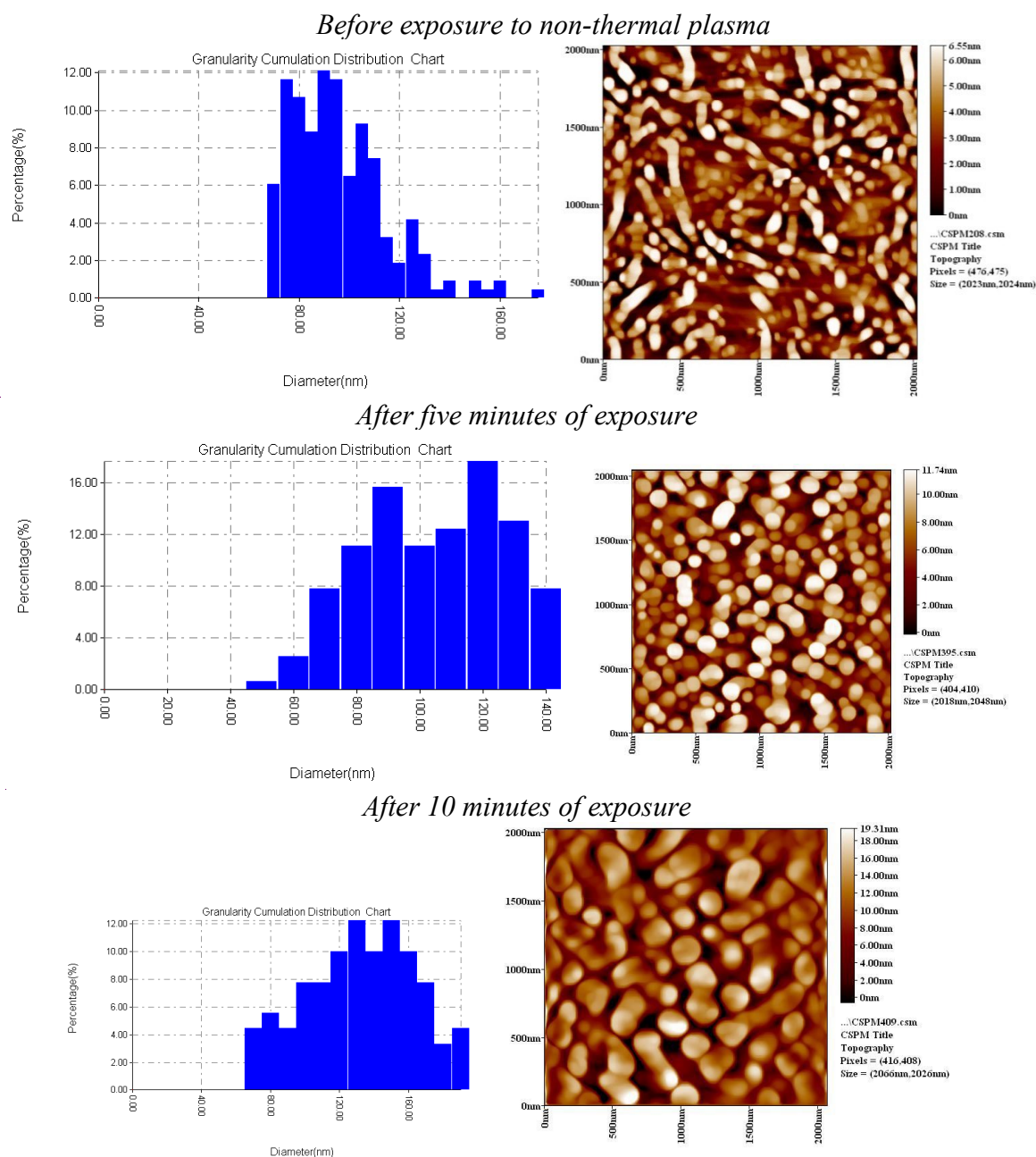
Atomic Force Microscope (AFM)

For a topographical study, some thin zinc oxide thin film surfaces were prepared and exposed to non-thermal plasma at different times (5,10,15min). The Atomic Force Microscope (AFM), with the ability to photograph and analyze these images of zinc oxide thin film (ZnO) before and after exposure to non-thermal plasma, was used at different times (5,10,15min), min Giving exact statistical values on the rate of granulated size and distribution per thin film, as well as surface roughness values (Roughness, Sq), as well as the square root of the average thin film surface roughness (RMS), observed through AFM images and results, that the non-thermal plasma process affects the

topography of the prepared thin film surfaces (ZnO). similar work with the same behaviour were seen in [19]

Point out from the drawing that the value of roughness, Sq) is low before the thin film is treated with non-thermal plasma and rises significantly when treated with cold plasma for more than 5 minutes. Still, the increased roughness is clear from the increase in the treatment time of the thermal plasma for more than 15 minutes, and the same analysis applies to the square root values of the average roughness square (RMS), as shown in the drawing.

The fig 4 shows the occasional AFM images, as well as the three-dimensional nature of zinc oxide thin film, surfaces before and after exposure to non-thermal plasma as well as the distribution of molecules that appear more consistently with increased exposure to non-thermal plasma as well as an increase in the granular diameter rate as the distribution of granules, approaches the natural distribution model the greater the duration of exposure to plasma



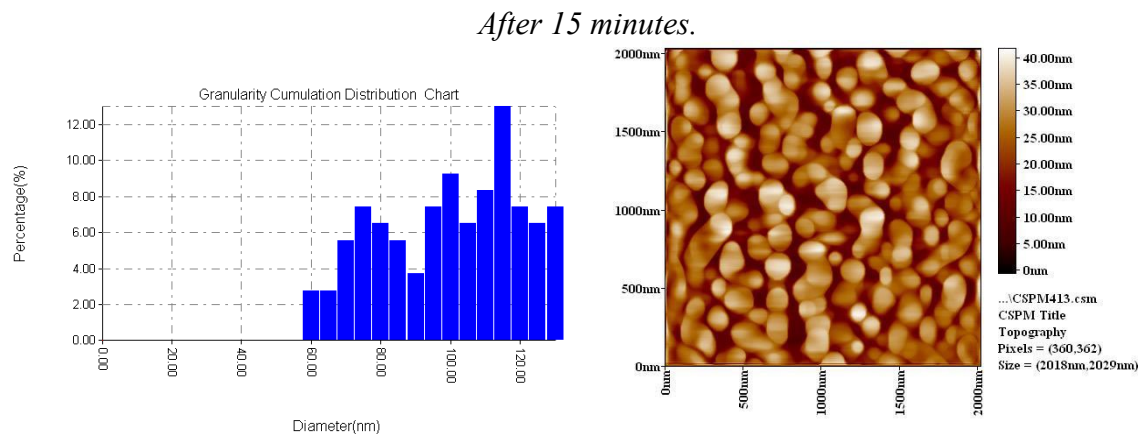


Figure 4: Shows the results of the AFM 3D atomic force microscope examination

Optical measurements:

Visual properties are of great importance in the study of the behaviour of semiconducting optical materials, through their study can be defined for appropriate practical application, as visual behaviour has been closely associated with the crystalline composition of the material and for the identification of the ZnO thin film prepared

Exposed to plasma at different times (5,10,15 min), it is necessary to study and calculate both spectral (absorption, permeability) as a state of wavelength within wavelengths. (nm), the optical energy gap for electronic transmissions, the damping plants, and the fixed insulation has also been calculated in its real and imaginary parts and visualization as a function of photon energy. The change in wavelength of the result was noticed with similar behaviour in [19]

Absorption spectrum (A):

Absorption measurements were performed within wavelengths of 300.1100(nm) of temperature-prepared thin film (ZnO) (450°C)

Before and after exposure to non-thermal plasma at different times (5,10,15,20,25 min) min has shown the results of UV spectrometer measurements. First, there is an increase in absorption values as a function of wavelength when the duration of exposure to non-temperature plasma increases, especially at the time of exposure (15,20,25 min).

Secondly, as for the exposure (5,10) min and before exposure, there is a convergence of absorption values with wavelength, as shown in fig 5.

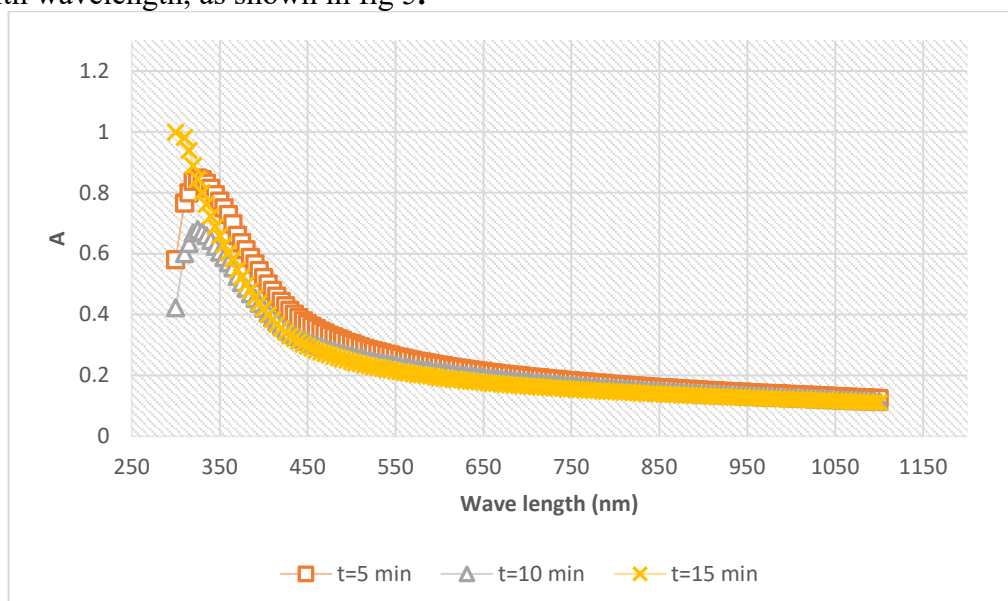


Figure 5 Comparison of absorption fee for thin film (ZnO) before and after exposure to plasma

Transition Permeability

Permeability has been studied as a wavelength function within the range (300.1100) nm, as shown in fig 6, where the permeability curve of all samples shows similar visual behaviour as permeability begins to increase at a wavelength of 300nm and then tends to saturate after wavelength (600nm). It was noted that permeability is adversely affected with increased exposure time to non-thermal plasma and unevenly where the permeability curve is very low.

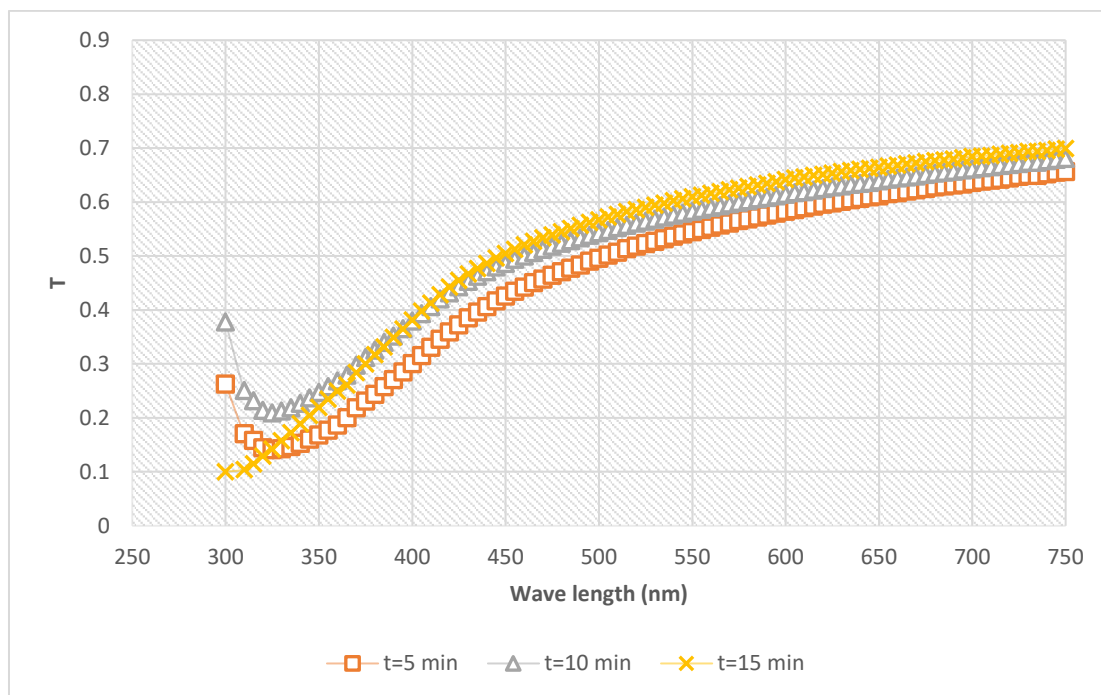


Figure 6: Shows the permeability values of zinc oxide thin film before and after exposure to non-thermal plasma and depending on the duration of exposure

Table 1: Optical properties of ZnO without treatment

Lambda(nm)	Value (ABS)	A	T	R
300.00	0.871	0.58066667	0.26256008	0.15677325
310.00	1.150	0.76666667	0.1710784	0.06225493
315.00	1.200	0.8	0.15843672	0.04156328
320.00	1.258	0.83866667	0.14493798	0.01639535
325.00	1.274	0.84933333	0.14142091	0.00924576
330.00	1.266	0.844	0.14316865	0.01283135
335.00	1.248	0.832	0.14718043	0.02081957
340.00	1.223	0.81533333	0.15293953	0.03172714
345.00	1.191	0.794	0.1606412	0.0453588
350.00	1.159	0.77266667	0.1687307	0.05860263
355.00	1.126	0.75066667	0.17749988	0.07183345
360.00	1.093	0.72866667	0.18672481	0.08460852
365.00	1.047	0.698	0.20038916	0.10161084
370.00	0.990	0.66	0.21871626	0.12128374
375.00	0.954	0.636	0.23114548	0.13285452
380.00	0.919	0.61266667	0.24390625	0.14342708
385.00	0.882	0.588	0.25816303	0.15383697
390.00	0.850	0.56666667	0.2711635	0.16216984
395.00	0.817	0.54466667	0.28525626	0.17007707

400.00	0.783	0.522	0.30054253	0.17745747
405.00	0.751	0.50066667	0.31567713	0.1836562
410.00	0.720	0.48	0.33106518	0.18893482
415.00	0.691	0.46066667	0.34613883	0.1931945
420.00	0.666	0.444	0.35968307	0.19631693
425.00	0.643	0.42866667	0.37261136	0.19872197
430.00	0.621	0.414	0.38541215	0.20058785
435.00	0.603	0.402	0.39621194	0.20178806
440.00	0.586	0.39066667	0.40668948	0.20264385
445.00	0.570	0.38	0.41680366	0.20319634
450.00	0.556	0.37066667	0.4258597	0.20347363
455.00	0.542	0.36133333	0.4351125	0.20355417
460.00	0.531	0.354	0.44252337	0.20347663
465.00	0.519	0.346	0.45075199	0.20324801
470.00	0.509	0.33933333	0.45772594	0.20294073
475.00	0.499	0.33266667	0.46480778	0.20252555
480.00	0.490	0.32666667	0.47127507	0.20205826
485.00	0.481	0.32066667	0.47783235	0.20150098
490.00	0.473	0.31533333	0.4837376	0.20092907
495.00	0.464	0.30933333	0.49046828	0.20019838
500.00	0.457	0.30466667	0.49576794	0.1995654

Reflectance

Reflectivity is defined as the ratio between the intensity of the reflected beam to the intensity of the falling beam, and the reflexivity is calculated based on the permeability spectrum (T) and the absorption spectrum (A) under the Energy Conservation Act,

In the case of exposure to non-thermal plasma, note that the reflective curved shape, in general, has not changed before exposure to plasma

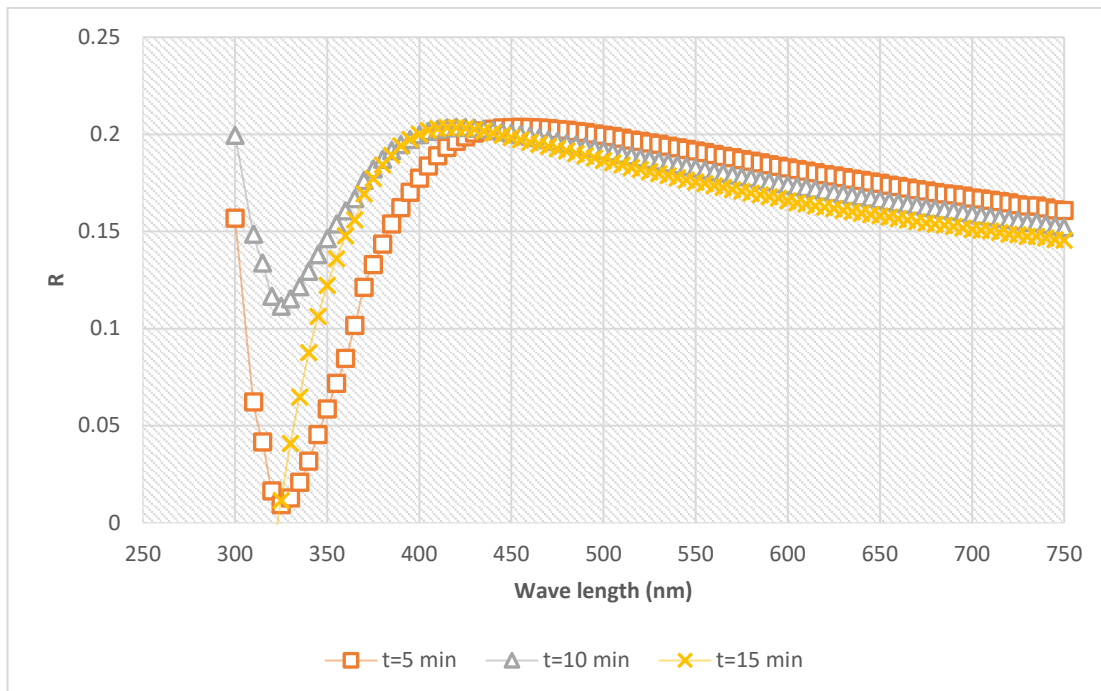


Figure 7: Reflective change as a function of the wavelength of ZnO thin film

Conclusion

Synthetic tests of the thin film prepared in the manner of thermal chemical spray at a temperature (450) °C before and after exposure to non-heat plasma proved to be of a multi-spiced and hexagonal structure, which is tight according to the elected preparation conditions. On-thermal plasma has removed a very thin layer from the surface of the thin film, known as non-thermal plasma, and made a surface cleanup. Measurements of the Atomic Force Microscope (AFM) show that the value of the granular volume rate increases when the duration of exposure to non-heat plasma increases. Measurements of the Atomic Force Microscope (AFM) show that there is an increase in thin film surface roughness values (Roughness, Sq), as well as the square root of the average roughness of the thin film surface (RMS), and this increase in roughness appears as the duration of exposure to non-thermal plasma increases.

Abbreviation

Symbol	Meaning
AFM	Atomic force microscopy
XRD	X-ray diffraction
RMS	the roughness of the thin film surface
Sq	General surface roughness
FWHM	the full width at half maximum

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Conductivity Modification of ZnO NRs Films via Gold Coating for Temperature Sensor Application

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Keywords: ZnO nanorods; Energy band gap; Gas sensor; Drop cast: seed layer; Temperature sensor.

Abstract. Zinc oxide nanorods (NRs) have been deposited on quartz employing a hydrothermal method. The ZnO NRs as a seed layer were prepared for the growth process using the drop-casting method. The zinc oxide nanomaterials produced were characterized by UV-Visible spectrophotometers, X-ray diffraction (XRD), and Scanning electron microscope (SEM). The crystal structure parameters were calculated from the XRD data and it was confirmed the growth of wurtzite crystalline crystal structures of ZnO NRs. The SEM images revealed that high-density nanowires were grown via drop cast coated seed layer. The bandgap in the ZnO NRs film was found to be 3.28 eV. This result confirmed the formation of ZnO nanostructure. The thermal and electrical properties of ZnO NRs were measured also and analyzed. The conductivity of the ZnO NRs film was modified with the addition of gold nanoparticles using the sputtering technique. The sensitivity of ZnO NRs film in the temperature range of 20-200°C was found to be exponential relation with thermal coefficient of ($\alpha/^{\circ}\text{C} - 8 \times 10^{-3}$) while the sensitivity of Au/ZnO NRs film at low and high-temperature ranges (20-160°C –and 40-250°C) was found $\alpha/^{\circ}\text{C} - 1.20 \times 10^{-3}$ and 4.7×10^{-3} , respectively. These modified films were promising and give an optimized temperature sensor performance.

Introduction

Band gap, and high binding energy at room temperature, are significant elements in realizing the potential of Nanomaterials[1-4]. High yield, Low cost, and controlled manufacturing are the main aspects of achieving their potential. Because of their unique characteristics, large surface area and aspect ratio [4], and ability to make many crystal morphologies, nanostructures such as nanorods and nanowires are perfect building blocks for various applications.

In recent years, vapor, liquid, solid growth [5, 6], solvothermal, metal-organic chemical vapor deposition (MOCVD) microemulsion synthesis [7-9], and many others [10] have been employed to produce ZnO nanostructure [11].

The hydrothermal growth method has generated much interest among these approaches due to its wide advantages, including low temperature, low cost, high yield [3, 12, and 13], simplicity, and scalability handling. The hydrothermal method has been used to fabricate a variety of nano ZnO forms, including nanorods, nanobelts, nanowires, nanoflowers, and nanoparticles [14, 15]. Hydrothermally produced ZnO NWs have been produced in the colloidal form [16, 17] or from a seed layer on various surfaces [18-20].

The particle size, aspect ratio [3, 21], and nanowire density [22, 23] are influenced widely by growth parameters such as growth temperature, duration time, and precursor concentration according to various studies [24-27]. The ZnO NRs investigated in this study are grown to utilize a simple and low-cost method. This new modified film Au/ZnO NRs structure was fabricated as a temperature

sensor. The main contribution of this study was to investigate the effect of the Au/ZnO NRs film on the sensor sensitivity in comparison with ZnO NRs pure film.

Material and Methods

The first step is to deposit of ZnO nanocrystals seed layer on substrates (quartz), followed by the drop-casting method. The ZnO solution was prepared using 5mM of $[(\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O})]$ (zinc acetate) in 10 ml of ethanol. The solution was then sonicated for 30 minutes. The quartz substrates were cleaned before the seed layer deposition. The substrate has been cleaned in DI water and finally dried with nitrogen gas.

The cleaned substrates were then coated by a ZnO seed layer by drop-casting. The ZnO seed layer substrates were annealed at 350°C for 60min. The second step is to grow ZnO nanostructures on the previously coated quartz substrates with a seeding layer. The deposited solution was prepared using 25mM of zinc nitrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and 25mM of hexamethylenetetramine (HMT/ $\text{C}_6\text{H}_{12}\text{N}_4$) in 100ml of deionized water (DI). The solution was sonicated for 45 min.

The substrates were vertically fixed on a Teflon block and immersed in the chemical solution. This autoclaved was placed in an oven at 90° for 4 hours to begin the growing process. The substrates were rinsed with DI multiple times and dried naturally at the end of the process.

Results and Discussion

The ZnO NWs structure has been characterized by using The Cu $K\alpha$ x-ray radiation ($\lambda = 1.5406\text{\AA}$) (XRD – 6000/ Shimadzu-Japan) was used to analyze the crystal structures of ZnO. Fig.1 presents the XRD diffractions of the prepared ZnO nanocrystal. The XRD peaks at $2\theta = 32.2^\circ$, 34.8° , 36.6° , 48.0° , and 63.2° , were observed. These peaks were related to ZnO (002), (100), (1 01), (1 0 2), and (103) respectively [28].

These peaks ensure the successful formation of ZnO nanorods. In addition, it has been found that the strongest peak has been observed for the ZnO at (002). The preferred crystal orientation along the (002) direction was found. The result shows that all the diffraction peaks are indexed to ZnO with the standard structure (JCPDS Card No. 36-1451). It confirms that the ZnO NRs possess the hexagonal wurtzite phase with the lattice parameters: $a=3.2469\text{\AA}$ and $c=5.2067\text{\AA}$. These XRD data are confirmed by other authors' data as shown in table (1) [29].

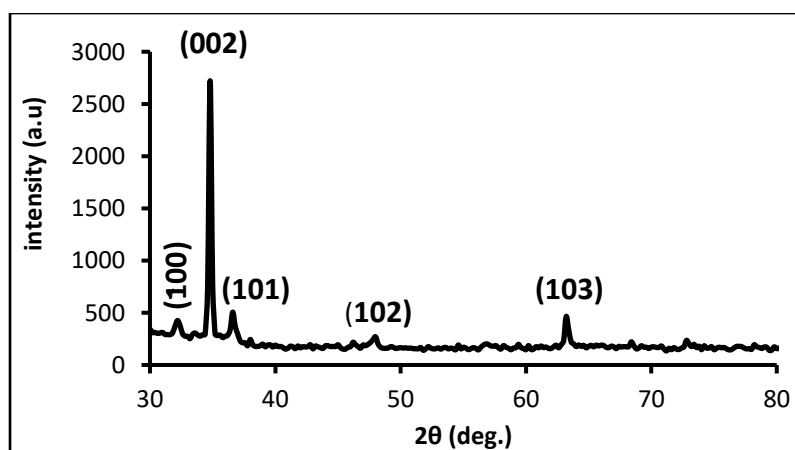


Fig. 1 X-Ray diffraction results of ZnO nanorods on a quartz substrate.

The crystallite size of the gold nanostructures was calculated via Scherrer's formula [30, 31]

$$D = 0.9\lambda / \beta \cos\theta \quad (1)$$

Using the two formulas, the lattice constants (a) and (c) for the (100) and (002) reflection planes were obtained. [32, 33] :

$$a = \lambda / (3)^{1/2} \quad (2)$$

$$c = \lambda / \sin\theta \quad (3)$$

The estimated crystal structure parameters are summarized in Table 1. The resulting lattice constants were found to be agreed with those reported in the literature [34-36]. Where the lattice constants for Wurtzite ZnO at 300K are $a = 0.32495 \text{ nm}$ and $c = 0.52069 \text{ nm}$ [37, 38]

Table 1 The estimated crystal constant for the zinc oxide nanomaterial.

Present work				
ZnO NRs	a=b nm	c	c/a	D (Scherer's) (nm)
	320.0	0.51486	1.6089	16.1
Reference work				
Wurtzite ZnO at R.T	0.32495	0.52069	1.6024	[35, 36]
	0.32535	0.52151	1.6029	[36]
	0.3218	0.5158	1.6028	[33]
	0.32498	0.52066	1.6022	JCPDS card # 36-1451

The morphology of ZnO nanostructures was studied using a scanning electron microscope. Figure 2 displays low and high magnification SEM pictures of ZnO NRs on quartz substrates. This image shows a typical as-synthesized ZnO nanostructure formed on a quartz substrate by the hydrothermal method. The high-density nanorods can be seen in large areas of the sample. This can be attributed to the homogeneity of the ZnO drop-cast seed layer [39].

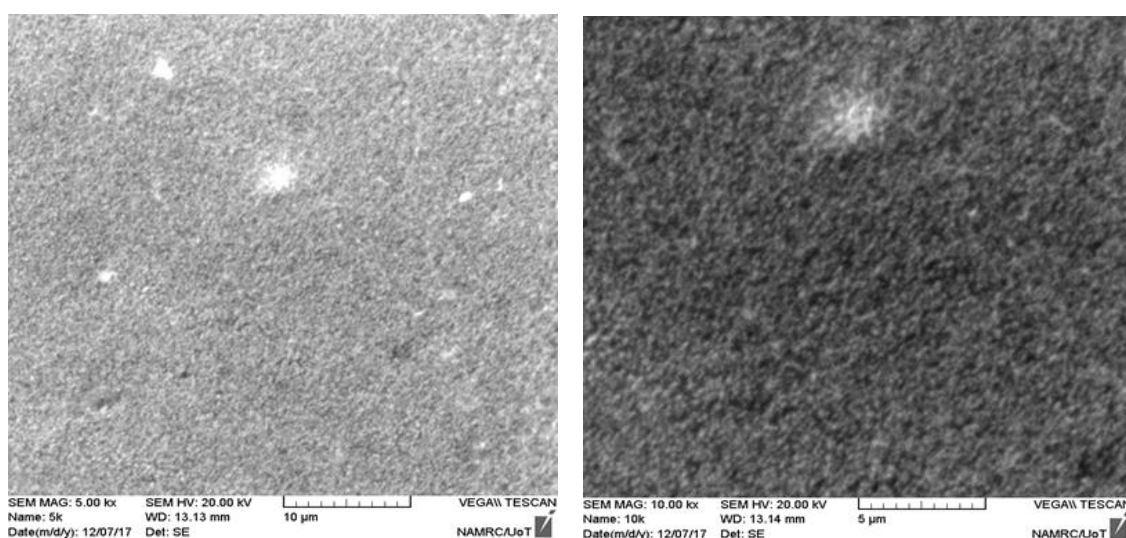


Fig. 2 Different magnifications, SEM pictures of ZnO NRs on quartz substrate; (a,b) drop-cast seed layer.

The Shimadzu / UV-visible- 2450 spectrophotometer) was used to measure the optical properties of ZnO nanostructures. The UV-vis spectrum of the nanorods zinc oxide films on a substrate in the ranges of 300 to 900 nm is shown in Fig. 3 (a). The absorption spectra have a narrow peak near the band edge in the exciton absorption region (UV region) at 351,360 nm and are blue-shifted relative to the bulk exciton absorption (380 nm) [40]. The stronger exciton effect is an important character of

the quantum confinement effect [41]. The results of the transmittance measurements for the ZnO NRs films are shown in Fig. 3(b). The optical transmission of ZnO nanorods is about 80 % in the regions (400-900) nm, as shown in this figure, and gradually increases with increasing wavelength. The high value of transmission of ZnO nanorods film was found in good agreement with the values of another worker [42]. Furthermore, this film is considered a transparent conductive oxide (TCO) material [43]. Using Tauc's plot method [44], the absorption coefficient α was utilized to estimate the band gap energy. Following the relationship:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (4)$$

Where A indicates the constant, $h\nu$ represents the incident photon energy, and E_g represents the energy band gap. Plotting optical absorption versus photon energy and extrapolating the linear section of the curve to $((\alpha h\nu))^2 = 0$ gives the optical band gap. The change of $((\alpha h\nu))^2$ as a function of photon energy ($h\nu$) for zinc oxide nanomaterial is shown in Fig 3(c). The optical energy gap of ZnO was determined to be 3.28 eV, which is somewhat smaller than the bulk energy gap of 3.32 eV. according to other results [45] and is consistent with other published work of the same films [46].

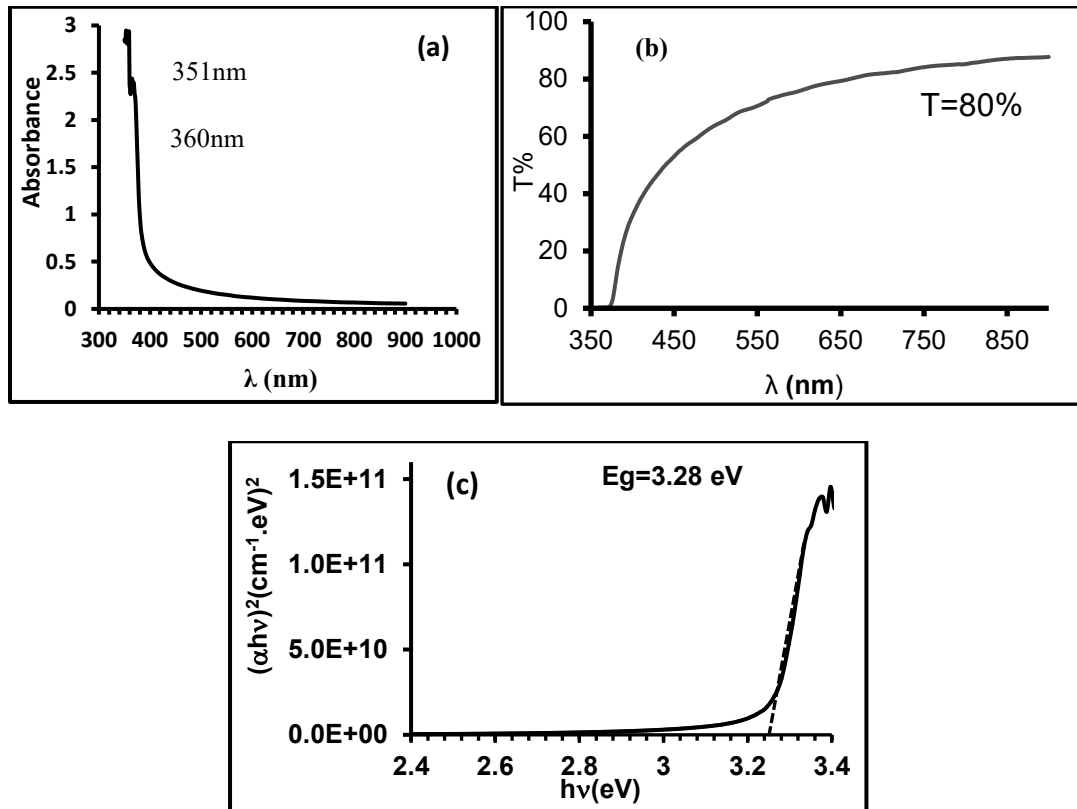


Fig.3 ZnO nanostructures' absorbance, transmittance, and energy band gap curves (a, b, and c, respectively).

Using the handmade measuring stage presented in our previous work, we measured the thermal and electrical properties of the device. The measurements were taken using the two adjustable point probes. The I-V characteristic of ZnO nanostructure at room temperature is plotted in Figure 4. The value of this resistance was discovered to be linear and obey ohms law.

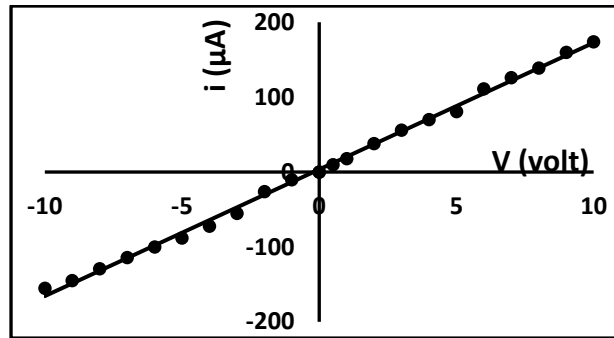


Fig. 4 I-V at room temperature of bare ZnO NRs on the quartz substrate.

Temperature sensor with exponential resistance relation (Type 1)

The as-synthesized ZnO NRs were fabricated as temperature sensor relays on the exponential relation between the resistance variation versus temperature [47]:

$$R = R_0 e^{-\alpha \Delta T} \quad (5)$$

Where α is the temperature coefficient and other parameters are defined above. From the plot of the resistance versus temperature shown in fig. 5, when $R_0 = 319.67 \text{ k}\Omega$, $\alpha = 0.008^\circ \text{C}^{-1}$.

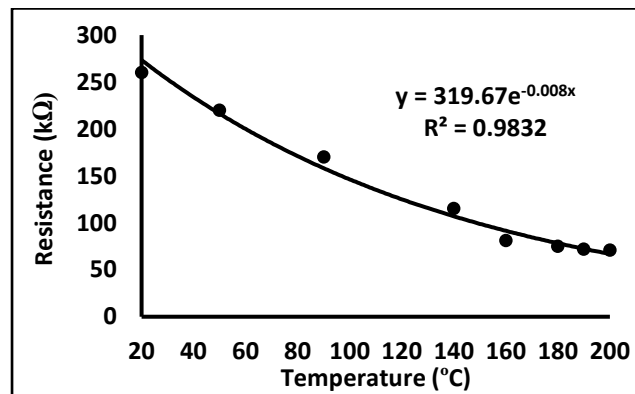


Fig. 5 Resistance versus temperature of ZnO nanostructures on a substrate.

From the plot of the relative resistance $[(R_0 - R)/R_0 \Delta T] \times 100\%$ versus the temperature shown in Fig. 6, the linear relation given the slope $= 0.3378\% / ^\circ \text{C}$ $[(R_0 - R)/R_0 \Delta T] \times 100\%$. This represents the highest average sensitivity of $0.34\% / ^\circ \text{C}$ in the range of $20\text{--}200^\circ \text{C}$. This value is comparable to the reported values of $0.4\% / ^\circ \text{C}$ and $0.33\% / ^\circ \text{C}$ in the temperature ranges of $120\text{--}260^\circ \text{C}$ [48] and $150\text{--}260^\circ \text{C}$ [49], respectively. Our value was also lower than reported values of $3.05\% / ^\circ \text{C}$ and $0.98\% / ^\circ \text{C}$, in the temperature range of $10\text{--}110^\circ \text{C}$ [50].

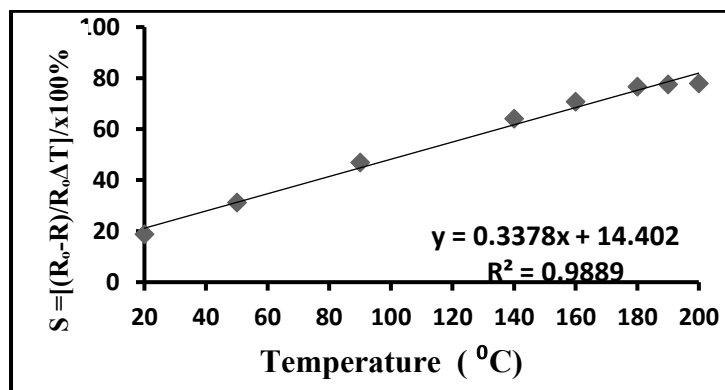


Fig.6 Sensitivity $[S = (R_0 - R)/R_0 \%100]$ versus temperature of ZnO NRs on quartz only.

Temperature sensor with linear resistance relation (Type 2)

The as-synthesized ZnO NRs were coated with gold nanoparticles for two different samples (S01 and S02) to modify the ZnO resistance to create a linear relationship between the resistance variations versus temperature.

The resistance depends on the temperature variations relation is [51, 52]:

$$R_T = R_0(1 + \alpha \Delta T) \quad (6)$$

Where R_T is the resistance at temperature T , $\Delta T = T - T_0$, by considering that $T_0 = 0$ (absolute temperature) when $R = R_0$. So, equation 1 can be written as [53]:

$$R_T = R_0 + R_0 \alpha \Delta T, \text{ where } R_0 \alpha \Delta T = \text{slope} \quad (7)$$

$$R_T - R_0 = R_0 \alpha \Delta T$$

$$(R_0 - R_T) / \Delta T R_0 = -\alpha =$$

According to Equation 6, the resistance can be plotted as a function of the temperature as shown in Fig. 7. These experimental data were linearly fitted with a trend line relation for S01 [54]:

$$Y = -670.24X + 554571 \quad (8)$$

Where the slope value is represented by $R_0 \alpha = 670.24 \Omega / ^\circ\text{C}$ and the intercept = $R_0 = 554571$ ohms, so, $\alpha = 670.24 / 554571 = 0.0012 / ^\circ\text{C}$ (This value represents the thermal coefficient). The minus value represents the resistance decreasing versus the temperature increased.

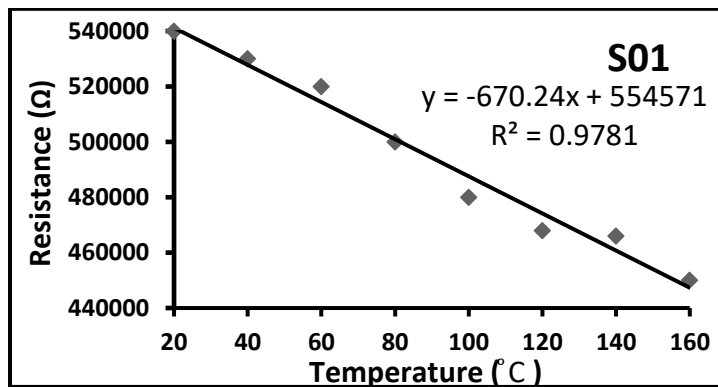


Fig. 7 Resistance vs temperature of Au/ ZnO NWs on quartz substrates.

The resistance can be plotted again by using equation (6) as shown in Fig. 8. These experimental data for S02 were linearly fitted with a trend line relation as shown in Fig.4 [55]:

$$y = -47078X + 1E+07 \quad (9)$$

Where the slope $= 47078 = R_0 \alpha$ and the intercept = R_0 , then, $\alpha = 47078 / 1E+07 = 0.00471 / ^\circ\text{C}$, (This value represents the thermal coefficient). The minus sign indicates the decrease of the film resistance when the temperature increases.

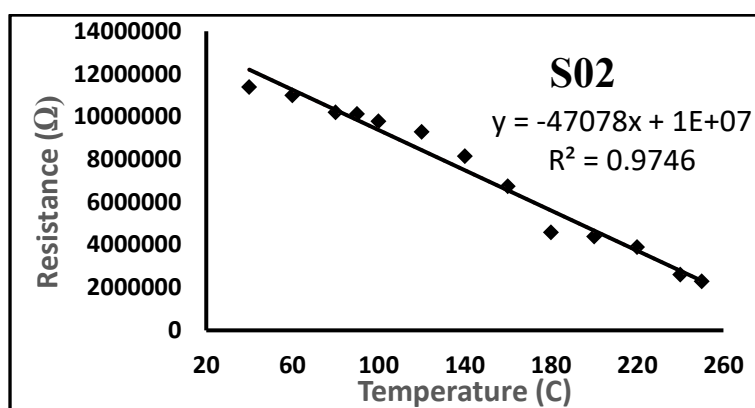


Fig.8 Resistance with temperature for (Au/ZnO NWs) on the quartz substrate.

Table 2 Summarized the suggested temperature sensor results.

ZnO NRs/Quartz					
Sample No.	R _o (M Ω)	T-range (°C)	α/°C	Relation	
S	0.31967	20-200	8*10-3	R=R _o e ^(-αΔT)	
Au/ZnO NRs/Qz					
	R _o (M Ω)	T-range (°C)	/°Cα	y=mx+b	T(°C)
S01	0.55	20-160	1.20*10-3	-670.24X+554571	Low T range
S02	10.0	40-250	4.71*10-3	-47078X+1E+07	THigh range

Conclusion

In conclusion, the conductivity of bare ZnO NRs on quartz substrate was successfully fabricated and investigated by gold coating. Two types of temperature sensors were successfully fabricated based on exponential and linear resistance relations. The SEM images revealed that high-density nanowires were grown via drop cast coated seed layer. The bandgap in the ZnO film was found to be 3.28 eV. The conductivity of bare ZnO nanorods was successfully modified by gold coating. Two types of temperature sensors were fabricated based on exponential and linear resistance relations. The sensor's results were proved to be a good ZnO NRs film temperature sensor. It was concluded that gold metal can play a significant role to tune the semiconductor conductivity. This property has been given an improvement to the temperature sensor device. Due to this study, it was found that the film of ZnO NRs has an exponential relation while the film of Au/ZnO NRs has a linear temperature relation with a negative thermal coefficient as shown in Fig.7. It was also concluded that there is a sensitivity enhancement for Au/ZnO NRs compared with pure ZnO NRs film.

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CHAPTER 4:

Fuel Production

Comparative Analysis and Performance Characteristics of Bio-Additives Induced Fuel Blend

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Abstract. Global demand for efficient transportation and energy dissipation in industries that use engine-powered equipment is enormous and largely supplied by liquid fuels derived from petroleum that power internal combustion engines (ICEs). Since the demand for jet fuel and diesel is anticipated to surpass gasoline consumption in the near future, low-octane gasoline components will become more widely available. As a result, low-octane gasoline components are expected to become more readily available, as demand for jet fuel and diesel is expected to outpace gasoline consumption in the near future. Experimentally, the effects of organic fuel additives (OFAs) on the performance of internal combustion engines were investigated. The findings compare plain, commercially available, neat gasoline samples to pure ethanol and fuel samples injected with OFAs. The development of various fuel blends; the analysis and characterization of fuel samples, including blended fuel samples; and the experimental investigation and comparative analysis of the engine performance powered by the various samples and blends of gasoline on the TQ TD115 MK11 testbed for single-cylinder engines were carried out in the study. The study demonstrated that the nano additions were superior to pure ethanol and undiluted gasoline in terms of performance. and showed that pure ethanol has a high torque value at lower speeds, but at speeds greater than 3000 rpm, D-NA outperformed ethanol additives and neat gasoline in terms of torque. At lower speeds, pure ethanol also had a high brake power value, but as speeds increased, samples containing D-NA outperformed ethanol additive and neat gasoline in brake power. Pure ethanol in a concentration of more than 3 has a high brake thermal efficiency value at lower speeds, but as speeds increased, samples containing D-NA outperformed ethanol additive and neat gasoline in terms of brake thermal efficiency.

1. Introduction

Global demand for efficient transportation and energy dissipation in industries that use engine-powered equipment is enormous and largely supplied by liquid fuels derived from petroleum that power internal combustion engines (ICEs). As a result, low-octane gasoline components are expected to become more readily available in the future, as demand for jet fuel and diesel is expected to outpace gasoline consumption shortly [1]. Commercial transportation will continue to be highly dependent on ICEs powered by petroleum-derived liquid fuels for decades to come since each of these alternatives has a low base from which to grow and confront significant obstacles in their quick and unrestricted growth [2]. To keep transportation costs, energy security, emissions of GHGs, and air quality in check, ICEs must be improved and in reality, the developments in combustion, control, and after-treatment systems, as well as hybridization and partial electrification, will help ICEs continue to improve while using existing market fuels. However, these systems can still be improved by using the advantages of fuel generation and utilizing readily accessible materials [2], [3].

Additives in fuel are primarily used to enhance fuel efficiency and minimize emissions such as smoke, CO, HC, NO_x, and particles to the environment. Most fuel additives contain metals in the form of a soluble organometallic complex, which decomposes in the combustion chamber of the engine while the organic component is combusted, resulting in soot at the moment of combustion. Fuel additives allow the use of greater compression ratios, which increases efficiency and power. They can also serve as corrosion inhibitors and lubricants. Additives include metal deactivators, corrosion inhibitors, oxygenates, and antioxidants [4]. Profit maximization through adulteration or the importing of substandard goods is an issue in Nigeria. This endangers human health and environmental safety in the country, forcing refineries to conduct research and development to find ways to balance fuel composition while taking into account engine performance and efficiency, as well as the health and safety of human life and property [5], [6]. In light of these observations, this study presents a comparative analysis of gasoline samples in the Nigerian market, as well as samples with additives, based on their effect on brake thermal efficiency, torque, brake power, and specific fuel consumption, to determine the country's level of conformity with international requirements for gasoline production.

2. Experimental Methods

Various types of fuel additives for gasoline sold at retail stores were developed and examined in comparison to existing automobile performance-enhancing additives used commercially in Nigeria as well as laboratory-developed bio-additives. Two categories of additive-gasoline blends were considered. They are; Bio-additives mixed with gasoline and Ethanol mixed with gasoline. The blended fuels were prepared in five (5) varying mix proportions of: 0:100 vol%, 1:99 vol%, 4:96 vol%, 7:93 vol%, and 10:90 vol% for additive and gasoline respectively. Engine performance for the best performing Developed- Nano Additive (D-NA) and ethanol fuel blends in comparison with neat or pure gasoline. The experiment was conducted in three phases;

- i. production of additives from agricultural wastes and the development of different fuel blends;
- ii. analysis and characterization of fuel samples, including blended fuel samples; and
- iii. Experimental investigation and comparative analysis of the engine performance powered by different samples and blends of petrol.

2.1 Production of additives

In this research work, wastes generated from the processing of agricultural products were used as feedstock for the production of nanoparticles, oxygenates that will serve as base fluid, and dispersants which were used to stabilize the nanofluid. The most common type of oxygenate used as a fuel additive is ethanol, therefore, the focus is on the production of ethanol from cassava wastes. On the other hand, nanoparticles were synthesized from coconut waste while dispersant stabilizers were produced from seafood wastes. The organic nanoparticle was dispersed in the ethanol base fluid utilizing an ultrasonicator. The stability of the nanoparticles in the fluid was improved by the addition of dispersants.

2.2 Synthesis of additives

Nanoparticles were synthesized from coconut shells via the mechanical ball milling method for about 70 hours according to research conducted by [7], [8], and [9]. After milling the resulting material was mechanically sieved to attain an ultrafine sample as shown in Figure 2. The organic nanoparticle was then characterized by Scanning Electron Microscopy [SEM], and energy dispersive analysis of X-rays [EDS] technique to respectively evaluate the internal and surface structure, morphology, and elemental composition of the nanoparticle.

Ethanol produced from hydrolysis and fermentation of agro-waste materials like bagasse, peels, fibre, and bark from cassava processing industries was used as the base material for ethanol

production in this study. Cassava processing waste is characterized as a source of starch that can be converted into fermentable sugars to produce ethanol. The cassava waste was washed, dried, and pulverized to increase its surface area for chemical and microbial reactions. The dispersant was produced from the hydrolysis of seafood waste by mixing with equal volumes of distilled water in an Erlenmeyer flask. A water bath at 90 °C was used to apply heat to the flask for 10 minutes to deactivate already existing enzymes in the waste. This is followed by the introduction of Alcalase enzymes into the flask at 53 °C for 240 minutes. After hydrolysis, the remnant Alcalase enzyme was desaturated by applying heat to the flask for 10 minutes at 95 °C.

2.3 Analysis and characterization of fuel samples

A preliminary investigation was carried out to characterize and ascertain the characteristics of the raw fuels to be used in this study before blending occurs. A sample of Premium Motor Spirit [PMS]/petrol, to serve as a reference standard, was collected directly from the Nigeria National Petroleum Corporation (NNPC) laboratory. Other samples of PMS were collected at the point of dispensation in randomly selected commercial filling stations within Nigeria. The following fuel properties were determined for each sample as recommended by the American Society for Testing and Materials [ASTM], reported in [10] and [11]. Several methods were used for the analysis of the fuel including the ASTM D1298 used to determine the specific gravity of the fuel samples. Typically, a hydrometer and a thermometer are immersed into a measuring cylinder of known volume, filled with the sample to be tested. The temperature reading is then taken and converted into Fahrenheit [°F]. The hydrometer readings are then corresponded with the converted temperature readings to accurately obtain the specific gravity of the sample. The ASTM D86 test method for distillation of petroleum products at ambient pressure was used to determine the atmospheric distillation values of the fuel samples. The test sample was placed in a round bottom flask containing anti-bombing stones. The stones are necessary to prevent explosions. The flask containing the test sample was placed in a distillation machine with a regulated temperature of 300 °C. Firstly, the initial boiling point temperature of the sample is taken and as the temperature increases, the temperatures of the final boiling point and the total recovery of the sample are recorded.

The ASTM D323 test method for the vapour pressure of fuels was used to determine the Reid vapour pressure (RVP). An adequate amount of the test sample was put into a Reid vapour pressure machine and the machine was subsequently immersed in a Reid vapour pressure bath. The temperature of the bath was regulated at 38 °C and the samples were allowed to reach a similar temperature to the RVP bath. After a while, test sample vapours begin to discharge, and the RVP device will detect the pressure of the escaping vapours, and the reading on the device is registered as the Reid Vapour Pressure. The Research Octane Number (RON) was determined by the comparison of the knock intensity of the fuel under standard conditions with that of blends of two reference fuels. In this study, the appropriate amount of fuel sample was inserted into the carburetor of the RON machine, and the machine switched on to evaluate the research octane number. The machine's selector valve is allowed to operate for an hour to reach a state of equilibrium. The height of the cylinder for reading the knock-meter was initially set between 45 and 47 and eventually set to 50 after the maximum knock fuel level had been found. The reading on the knock meter is then recorded as the research octane number.

2.4 Engine performance test

Engine performance test experiments have been carried out using an air-cooled, single-cylinder, four-stroke spark-ignition engine to determine the efficiency of three categories of fuels;

- a. Standard reference PMS obtained directly from the Nigerian National Petroleum Corporation (NNPC) laboratory in Nigeria;

- b. Commercially sold PMS blended with ethanol additives in the local market; and
- c. Commercially sold PMS blended with additives derived from agricultural wastes

The single-cylinder research engine was preferred to mitigate complexities associated with inadequacies in the fuel/air distribution ratio. The test engine was operated at similar conditions for all evaluated fuel categories. The throttle or rack was held open while the needle valve was gradually adjusted to increase the flow of water through the dynamometer until the needle valve was fully open. Keeping track of the engine speed, the engine was tested between 1000 and 3500 revolutions per minute (rpm), and the engine performance was measured at nine different speeds. The throttle was kept open and the water flow was lowered to a trickle, allowing the engine to resume its maximum speed. When the engine had settled down to a steady output, the speed and torque were recorded. As a result, the fuel tap beneath the pipette was left open, and the engine drew fuel from the pipette to determine the 8ml fuel consumption time.

The water pouring out of the dynamometer was maintained at 80°C or less. When the temperature exceeded 80°C, the water flow was increased to cool the dynamometer bearing seals. The water flows into the dynamometer and is then raised until the engine speed is reduced to the next highest pre-set setting. Because the dynamometer's time reaction was rather slow, the needle valve had to be operated carefully. After that, the engine was stabilized before getting another set of results. If the dynamometer was too sensitive to attain the correct speed, the drain tap had to be partially closed. The procedure was repeated once the fuel composition was changed. The data was gathered and organized into a table for calculating various factors such as braking power, specific fuel consumption, and brake thermal efficiency.

3. Results and Discussion

The results of engine performance for the best performing D-NA and ethanol fuel blends in comparison with neat or pure gasoline are outlined. The engine performance results are further subdivided into four parameters which are Torque, Brake Power, Brake Thermal Efficiency, and Specific fuel consumption. The results in this section are represented graphically under the literature [12]. Each result is accompanied by two-column charts the first is to compare the best performing developed nano-additive and ethanol samples (A_4 and B_4) amongst themselves, whereas, the second is to compare the D-NA samples with neat gasoline (A_0). The results of the experiments are reported below.

3.1 Torque

Torque communicates the amount of power available during engine operation. Similarly, the level of force required to drive a shaft is indicated using torque. The value of torque relative to the engine speed was recorded from the TD 114 indication unit. The Torque of all developed samples is depicted in Table 1. Also, the best performing blends of ethanol and developed nano-additive in relation to neat-gasoline are presented. The percentage to which both ethanol and developed nano-additive is introduced to neat-gasoline is in the step of 3 percentage units.

At 3000 rpm, D-NA and ethanol mix outperformed plain gasoline by roughly 3%, 8%, and 4%, respectively. The engine torque of D-NA is higher than that of ethanol at 3500 rpm, whereas the engine torque of ethanol is higher at 1000 rpm. Studies by [13], [12], [14], [15], [16], Kader et al. (2015), and [17] have identified ethanol as an oxygenate and as a crucial ingredient in enhancing torque at high speeds. Similar to studies by [15] and [16], The ingredients of D-NA, a mix of ethanol and silicon dioxide nanoparticles, influenced the engine's torque. Pure ethanol had the most torque at low speeds, but at 3000 rpm, D-NA surpassed ethanol additive and neat gasoline.

Table 1: Torque at varying speeds of fuel blends A₀, A₁, A₂, A₃, A₄ B₁, B₂, B₃, and B₄.

Speeds Specimen	1000	1200	1400	1600	1800	2200	2500	3000	3500
A ₀	3.7	4	4.2	4.8	4.8	5.6	6	6.6	6
A ₁	3.7	3.95	3.95	4.8	4.75	5.5	6	6.7	6.4
A ₂	3.6	4	4	4.75	4.8	5.5	6	6.7	6.43
A ₃	3.65	4	4.15	4.8	4.8	5.6	5.95	6.75	6.5
A ₄	3.72	4.1	4.25	4.9	4.9	5.75	6.1	6.8	6.5
B ₁	3.6	4	4.2	4.7	4.8	5.6	6.1	6.7	6.05
B ₂	3.72	3.95	4.15	4.7	4.9	5.7	6.1	6.72	5.8
B ₃	3.72	4.1	4.3	4.9	5	5.65	6.2	6.7	6.2
B ₄	3.8	4.2	4.4	5	5.1	5.8	6.2	6.8	6.21

3.2 Brake Power

The power present at the crankshaft during engine operation is referred to as Brake power. The results for the test on brake power were computed using the product of engine speed and torque which in this study was recorded from the TD 114 indication unit. The product of these units was then multiplied with a constant 2π . The Brake Power (BP) of all developed samples is presented in table 2, also the best performing blends of ethanol and developed nano-additive in relation to neat-gasoline. The percentage to which both ethanol and developed nano-additive is introduced to neat-gasoline is in the step of 3 percentage units.

The BP of the nano-additive and commercial ethanol is similar at 3000 rpm. However, at 3500 rpm, the produced nano-additive A₄ has a higher BP value than Ethanol B₄, 2.38 KW against 2.28 KW. Comparing the findings of BP for D-NA and ethanol to those of gasoline at 3000 and 3500 revolutions per minute. At 3000 rpm, D-NA and ethanol blends beat plain gasoline by roughly 3% apiece, followed by 8% and 3% at 3500 rpm. At engine speeds spanning from 1000 to 3000 rpm, ethanol beat all tested fuel mixes, but at 3500 rpm, D-NA outperformed ethanol. In Studies by [13], [12], [14], [17], [15] and [16], Ethanol as an oxygenate is highlighted as a crucial ingredient in enhancing torque at high speeds, which effects the BP. The influence of nanoparticles on engine BP has been studied by [15], [16], [18], and [19]. D-NA, a mixture of ethanol and silicon dioxide nanoparticles generated from crushed coconut waste, may have influenced engine BP. In terms of BP, pure ethanol performed well at low speeds, but as speeds grew, samples containing D-NA outperformed ethanol additive and straight gasoline.

Table 2: Brake power at varying speeds of fuel blends A₀, A₁, A₂, A₃, A₄ B₁, B₂, B₃, and B₄.

Speeds Specimen	1000	1200	1400	1600	1800	2200	2500	3000	3500
A ₀	0.387513	0.50272	0.615832	0.804352	0.904896	1.290315	1.571	2.07372	2.1994
A ₁	0.387513	0.496436	0.579175	0.804352	0.89547	1.267273	1.571	2.10514	2.346027
A ₂	0.37704	0.50272	0.586507	0.795973	0.904896	1.267273	1.571	2.10514	2.357024
A ₃	0.382277	0.50272	0.608501	0.804352	0.904896	1.290315	1.557908	2.12085	2.382683
A ₄	0.389608	0.515288	0.623163	0.821109	0.923748	1.324877	1.544817	2.13656	2.382683
B ₁	0.37704	0.50272	0.615832	0.787595	0.904896	1.290315	1.597183	2.10514	2.217728
B ₂	0.389608	0.496436	0.608501	0.787595	0.923748	1.313356	1.597183	2.111424	2.126087
B ₃	0.389608	0.515288	0.630495	0.821109	0.9426	1.301835	1.623367	2.10514	2.272713
B ₄	0.397987	0.527856	0.645157	0.837867	0.961452	1.336397	1.623367	2.13656	2.276379

3.3 Brake thermal efficiency

Brake Thermal Efficiency (BTE) is a function of fuel usage. The better the brake thermal efficiency, the better the fuel economy and the lower the GHG emissions. Braking thermal efficiency is calculated by multiplying brake power by the quantity of fuel consumed in Kg/h and the calorific value in KJ/Kg. This ratio is then expressed as a percentage. The calorific value of

samples varies depending on the additive fraction. Table 3 displays the BTE of all samples. The ratio of ethanol and the created nano-additive in neat gasoline is around 3%.

Investigating table 3 from the 1000-3500 rpm engine speed range, the BTE range varies per fuel sample. The BTE ranges from 12.9 to 39.52 % in samples A₀, A₄ and B₄ from table 3. The BTE for the developed nano-additive and commercial ethanol is the same at 3000 rpm. Nevertheless, at 3500 rpm, the created nano-additive A₄ has a higher BTE than Ethanol B₄.

Several other studies have shown the influence of additives like ethanol and nano-silicon oxide particles on BTE, including [13] and [12]. BTE is affected by differences in calorific value, according to [12]–[14]. It is possible that the components of D-NA, ethanol, and silicon dioxide nanoparticles from crushed coconut waste, influenced the engine BTE. Ethanol with a concentration above 3% had the highest BTE value at low speeds, but as the speed increased, samples containing D-NA surpassed ethanol additive and unleaded gasoline.

Table 3: Brake thermal efficiency at varying speeds of fuel blends A₀, A₁, A₂, A₃, A₄ B₁, B₂, B₃, and B₄.

Speeds Specimen	1000	1200	1400	1600	1800	2200	2500	3000	3500
A ₀	12.9429	14.86081	14.70545	18.28073	18.82884	23.38101	27.14028	33.43682	31.24148
A ₁	13.5748	15.63184	14.40735	19.05897	19.45571	24.0422	28.44401	37.28639	36.936
A ₂	13.35632	16.02758	14.82057	19.17374	20.01667	24.541	29.06236	38.11498	38.03686
A ₃	13.61706	16.12652	15.49609	19.53386	20.19476	25.24114	29.12677	38.8168	38.91986
A ₄	13.95488	16.63109	15.99213	20.10242	20.79727	26.17797	29.18603	39.52481	39.38878
B ₁	13.05951	15.63184	16.61306	18.97191	20.01667	24.9872	29.54673	36.45781	34.17293
B ₂	13.64818	15.63184	15.61585	19.28191	20.79727	25.95034	30.17539	37.3977	33.47325
B ₃	13.64818	16.22546	16.18027	20.10242	21.22171	25.72271	30.67007	37.28639	35.78175
B ₄	14.25499	17.03673	17.06443	21.17224	22.403	27.45763	31.94799	39.52481	37.63143

3.4 Specific fuel consumption

The amount of fuel consumed with respect to the power produced is referred to as specific fuel consumption. Specific fuel consumption gives the idea of how much fuel needs to be consumed to produce power, the unit of specific fuel consumption is gram per kilowatt-hour (g/KWh). Mathematically, Specific Fuel Consumption (SFC) is derived from the ratio of the mass of fuel consumed in Kg/h to brake power in KW. Mass of fuel consumed is derived using the time it takes for the engine to consume 8ml of feed sample [20]. SFC of all developed samples is depicted in table 4.

The proportion of ethanol and nano-additive added to neat gasoline is around 3%. The SFC range varies with the fuel sample. The maximum SFC value is 642 g/Kwh, while the smallest is 227 g/Kwh. Because SFC informs this study regarding fuel efficiency, it may be assumed that A₄ outperforms B₄ at higher engine speeds, while B₄ outperforms neat gasoline at lower speeds.

Studies by [12], [13], [15]–[20] have shown that additives such as ethanol and nano-silicon oxide particles influence the SFC. [13], [17], [20] found that changes in fuel consumption or fuel mass flow rate impact the value of SFC. The components of D-NA, a blend of ethanol and nanoparticles of silicon dioxide derived from coconut waste, affected the SFC engine. In conclusion, the SFC value of all samples developed in this investigation was greater at lower speeds, but as speeds increased, samples containing D-NA outperformed ethanol additive and regular gasoline in terms of BTE.

Table 4: Specific fuel consumption at varying speeds of fuel blends A₀, A₁, A₂, A₃, A₄ B₁, B₂, B₃, and B₄.

Speeds Specimen	1000	1200	1400	1600	1800	2200	2500	3000	3500
A ₀	632.1473	550.5634	556.3801	447.5652	434.5365	349.9343	301.464	244.6948	261.8896
A ₁	659.6946	572.8835	621.5734	469.8692	460.2878	372.4794	314.8369	240.1741	242.4525
A ₂	670.4859	558.7382	604.243	467.0567	447.3883	364.9087	308.1382	234.9529	235.4354
A ₃	657.6476	555.3104	577.9021	458.4461	443.443	354.7869	307.4568	230.7048	230.0939
A ₄	641.727	538.4628	559.9769	445.48	430.596	342.09	306.8325	226.5722	227.3547
B ₁	685.7242	572.8835	539.0474	472.0254	447.3883	358.3924	303.0868	245.6326	262.0561
B ₂	656.1478	572.8835	573.4703	464.4366	430.596	345.0908	296.7724	239.4592	267.5338
B ₃	656.1478	551.9244	553.4655	445.48	421.9841	348.1447	291.9858	240.1741	250.2735
B ₄	628.217	525.6422	524.7889	422.9701	399.7332	326.1471	280.3064	226.5722	237.9719

Conclusion

The following conclusion can be drawn from the foregoing comparative analysis of fuel samples containing additives with international standards;

- Pure ethanol has a high torque value at lower speeds but at speeds greater than 3000 rpm D-NA outperformed Ethanol additive and neat gasoline in terms of torque.
- Pure ethanol had a high brake power value at lower speeds but as speeds increased, samples containing D-NA outperformed Ethanol additive and neat gasoline in terms of brake power.
- Pure ethanol in a concentration of more than 3% has a high brake thermal efficiency value at lower speeds but as speeds increased, samples containing D-NA outperformed Ethanol additive and neat gasoline in terms of brake thermal efficiency.
- Samples containing more than 3% concentration of commercial ethanol have better Specific Fuel Consumption values at lower speeds but as speeds increased, samples containing D-NA outperformed Ethanol additive and neat gasoline in terms of specific fuel consumption.

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Combined Solid Olive Pomace Waste Biofuel: Heating Energy Enhancement and Comparative Experimental Analysis

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Abstract. In the present study, a solid biofuel based on Olive Pomace Waste (OPW) is manufactured in order to estimate the energy for heating water. A mechanical hydraulic press is constructed in order to create the block of OPW biofuel. To proceed, the standard form is burned to heat water in a tank where a thermocouple is placed to estimate the heating energy created by OPW blocks. Then, the standard OPW blocks are compared experimentally with other mixed biofuel blocks such as, waste Beeswax, oak charcoal, dry olive leaf and waste wood sawdust. It is shown that the standard OPW blocks could increase the temperature of 3 Liters of water to 34 °C whereas with the modified OPW mixed with other constituents temperatures up to 65 °C can be reached.

1. Introduction

The energy management and the use of renewable energy sources became an important objective worldwide. The biofuel production is one of the suggested solution especially that it doesn't depend on the weather conditions such as wind, sun, and hydraulic sources. It depends on the chemical constitutions of the biomass sources. There could be a variety of advantages to switching to biofuels from fossil fuels. Biofuels are created from renewable feedstocks, as opposed to fossil fuels, which are finite resources. As a result, their manufacturing and use might theoretically continue for a long time. Because biofuels may be generated domestically, the importation of fossil fuels may decline. Increasing petroleum consumption abroad could result from decreasing domestic demand for petroleum, which would benefit American consumers economically [1]. Furthermore, compared to traditional fuels, biofuels can result in lower lifecycle Green House Gases emissions, according to academic studies utilizing various economic models [1, 2]. In this context, the main focus point in the present project is based on the solid biofuel that is provided by the olive pomace waste obtained after extraction of the olive oil from bio refinery machines. Olive pits, a byproduct of the manufacture of olive oil, can be recovered and used to generate energy, electricity for use in residential boilers or big industrial plants for cogeneration [3]. In Spain, 50000 tone of olive oil is produced annually which leads to have a large amount of olive pomace waste that is used for generating electricity [4]. Another research project is recently published by García-Maraver et al [5] about an analysis of olive grove residual biomass potential for electric and thermal energy generation in Andalusia. The authors presented an interesting statistic about the primary energy consumption where 48% is based on Biomass source and 2000 tones/year is the olive stone. Miranda et al [6] investigated the characterization and combustion of olive pomace and forest residue pellets. Based on their study they demonstrated that the pellets produced from olive pomace show acceptable values for their thermal use. Abdulyekeen et al [7] explained in their paper the importance of using the municipal solid waste

that could be converted in energy production. In their publication, the authors demonstrated the potential of using the biomass and biofuel for combustion, gasification. In addition, they suggested an enhancement for the chain production of the wasted solid biofuel in order to be used in the correct way. In Andalusia, Marquina et al [8] presented an economic value of olive sector biomass for thermal and electrical uses. Based on their study, 69% wastage of olive sector residues could be available for energy purposes where currently only 2 million tons of biomass are used for energy purposes and it is confirmed by [9, 10]. In Andalusia, 1 ton of olives produces 73% of olive pomace and then 37% of the 73% of olive pomace are solid water biomass that could be converted to block of solid biofuel. A case study was suggested by Kinab et al [11] about the management of olive solid waste in Lebanon where the energy management and the electricity production is on corruption till now. They mentioned in their study that 79000 tons of olive waste can be obtained in a high season where 25 % are converted to stone which is dried and used for heating purposes. Accordingly, the main purpose of the present study is the enhancement of the energy that could be provided by the olive pomace waste for heating. The enhancement will be made by mixing the olive waste stone with other biomass such as the wasted beeswax, which representing around 50% of the gross weight after obtaining honey and recycling of beeswax to be reused for other applications [12]. Moreover, the OPW will be mixed with dried olive leaf, oak charcoal and wood sawdust at different mass ratio. The investigation in the present paper is based on experimental study. A homemade hydraulic press is designed in order to produce the biofuel blocks. In addition, a small chimney is also designed in order to convert the solid biofuel to combustion. The chimney is used in order to heat a water tank where a thermocouple is placed in order to estimate the energy recovered from the varied biofuel as mentioned previously. Accordingly, the energy is estimated based on the evolution of the temperature of heated water. Consequently, the wasted beeswax mixed with the olive pomace demonstrates around 50 % of energy enhancement. Based on the experimental measurement, the temperature of water increases by around 28 °C when using the wasted beeswax with the olive pomace waste.

2. Experimental Setup

The experimental setup in the present project is subdivided into two main parts. The first part is the biofuel samples forming and the second one is the water heating process. In order to prepare the samples, a hydraulic press is used where the provided force is at 250 kN. The samples have a diameter of 12 cm and a height of 22 cm. The mold is designed in order to have an air gap at the center with 2 cm of diameter. The air gap allows to have a chimney effect during the combustion process in the chimney that is used later on for water heating. The mass of each sample is maintained at 1 kg. In addition, when the olive pomace waste is mixed with other biofuel, the sample weight is always conserved rationally. The schematic that is presented in the fig.1 demonstrates the hydraulic press in addition to the dimensions of mold and the biofuel samples.

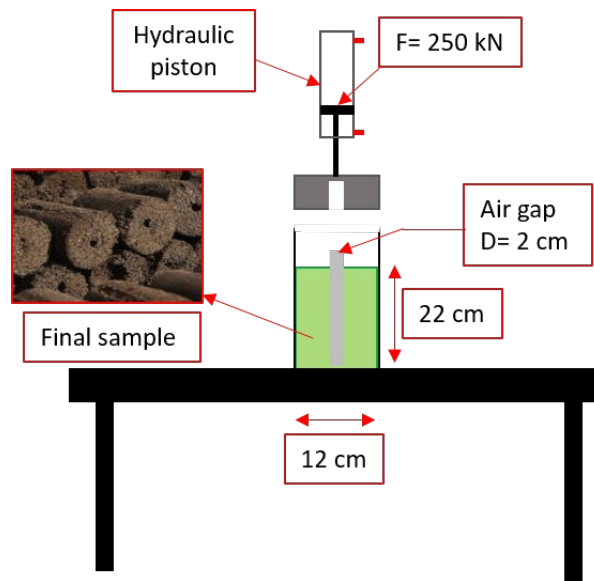


Fig. 1. The hydraulic press used to form the biofuel samples based on olive pomace waste.

In order to study the rate of combustion, the chimney designed has a water tank that contains specific quantity of water (11.5 Liters) during all the experiments. A thermocouple of type K is inserted in the water of the tank and connected to a digital data logger as shown in figure 2. However, a collection of temperature every 2 min is recorded during the combustion reaction and the water heating process.

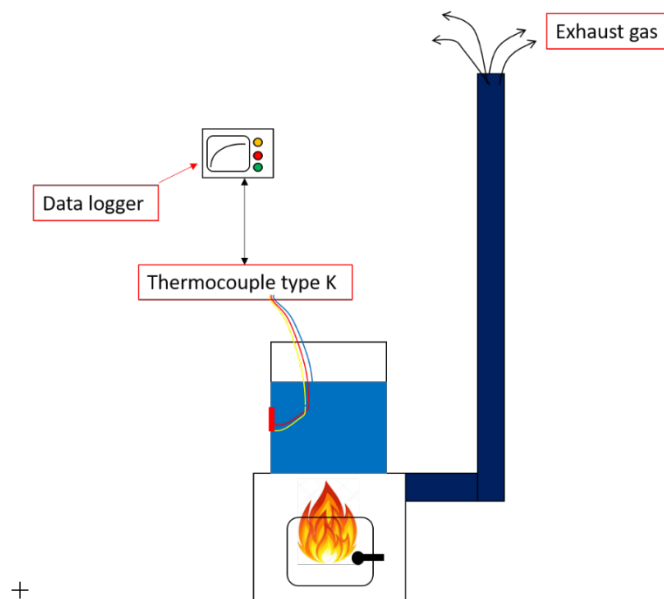


Fig.2. Water heating process and the designed chimney for biofuel combustion process.

3. Methodology

As mentioned previously, the experimental study is subdivided into 14 different experiments that can be categorized into 8 main biofuel mixed cases. All of the mixed cases will be based on olive pomace waste where the mass of other biofuel is changed in order to clarify the effect of each one on the water temperature and the provided energy. Accordingly, the experiments are under the same external condition where the ambient temperature is around 21 °C and the initial water temperature is maintained at 18 °C. The purpose of the present methodology is studying the feasibility of increasing the energy of combustion by mixing the olive pomace waste with other biomass constitution (beeswax, dry olive leaf, wood sawdust and oak charcoal). After forming the block samples of biofuel using the hydraulic press, it will be combusted in the chimney in order to heat 11.5

liters of water (11.5 kg of water). During the combustion process, the used thermocouple that is placed into the water tank permits to record the temperature variation during the water heating process. According to the temperature evolution of each case, a comparative study with the reference sample that contains only olive pomace waste will be presented. The mixed biofuel cases are presented as follows:

- **Case 1:** Two samples are prepared; one contains 800 g of olive pomace with 200 g of dry olive leaf while the second contains 700 g of olive pomace with 300g of dry olive leaf.
- **Case 2:** two samples are prepared; one contains 800 g of olive pomace with 200 g of wood sawdust while the second contains 700 g of olive pomace with 300g of wood sawdust.
- **Case 3:** Two samples are prepared; one contains 800 g of olive pomace with 200 g of oak charcoal while the second contains 700 g of olive pomace with 300g of oak charcoal.
- **Case 4:** one contains 800 g of olive pomace with 200 g of beeswax waste.
- **Case 5:** Three samples are prepared; one contains 800 g of olive pomace with 200 g of oak charcoal while the second contains 700 g of olive pomace with 200g of oak charcoal and 100g of beeswax, Then, the third one contains 600 g of olive pomace with 200g of oak charcoal and 200g of beeswax
- **Case 6:** two samples are prepared; one contains 800 g of olive pomace with 200 g wood sawdust. Then, one contains 700 g of olive pomace with 200 g wood sawdust and 100 g of beeswax.
- **Case 7:** two samples are prepared; one contains 700 g of olive pomace with 300 g of dry olive leaf while the second contains 600 g of olive pomace with 300 g of dry olive leaf and 100g of beeswax
- **Case 8:** Two samples are prepared; one contains 600 g of olive pomace waste, 200 g of oak charcoal, 100 dry olive leaf and 100 g of beeswax. The second contains 600 g of olive pomace waste, 100 g of oak charcoal, 100 dry olive leaf and 200 g of beeswax.

4. Results and Discussion

In the present section the experimental results obtained from the experimental setup that are presented previously will be presented and described.

4.1 OPW mixed with dry olive leaf

Figure 3 presents the experimental evolution of water temperature as a function of time when the mass of dry olive leaf is added to the pomace olive waste sample. According to the curves, the combustion time during the phase of heating water is between around 50 to 60 min. It was noticed that the combustion time to reach the highest water temperature decreases around 6 minutes when the mass of dry olive leaf increase from 200g to 300g. Meanwhile, the maximum water temperature increases with the addition of dry olive leaf from 33 °C to 36 °C. This could explain the decreasing of combustion time because of increasing of combustion temperature into the chimney.

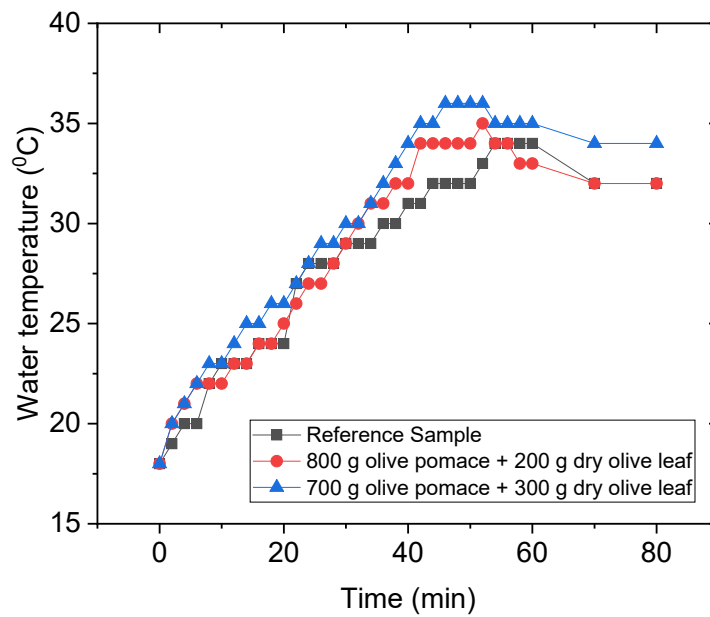


Fig.3. Evolution of temperature of heated water with respect to time presenting the mass effect of dry olive leaf.

4.2 OPW mixed with wood saw dust

Figure 4 is presented in order to study the effect of wood sawdust on OPW sample. Focusing on temperature evolution, it was noticed from the obtained measurement that the water temperature is increased slightly to reach maximum 37 °C where there is only 3 °C of water temperature enhancement.

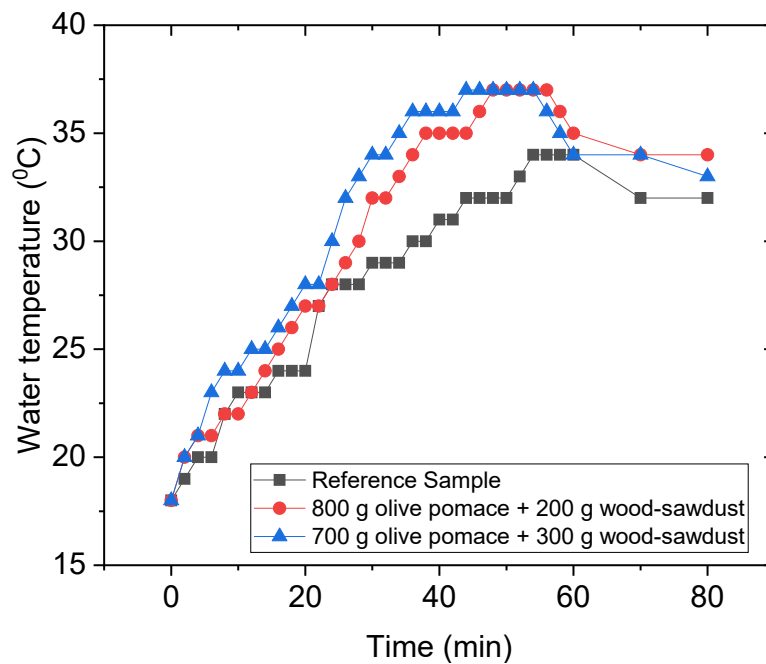


Fig. 4. Evolution of temperature of heated water with respect to time presenting the mass effect of wood-sawdust.

4.3 OPW mixed with Oak Charcoal

In this part, Figure 5 demonstrates the effect of oak charcoal on the OPW sample. The mass of oak charcoal is increased in two tested samples. According to the results, a significant enhancement in increasing the water temperature is obtained. Consequently, the temperature of water is increased by around 8 °C. The more significant enhancement in this case is not only the water temperature but also the time of temperature increasing. In the present case, it could be noticed that the maximum temperature in the three cases is reached approximately at the same time after around 60 min of combustion.

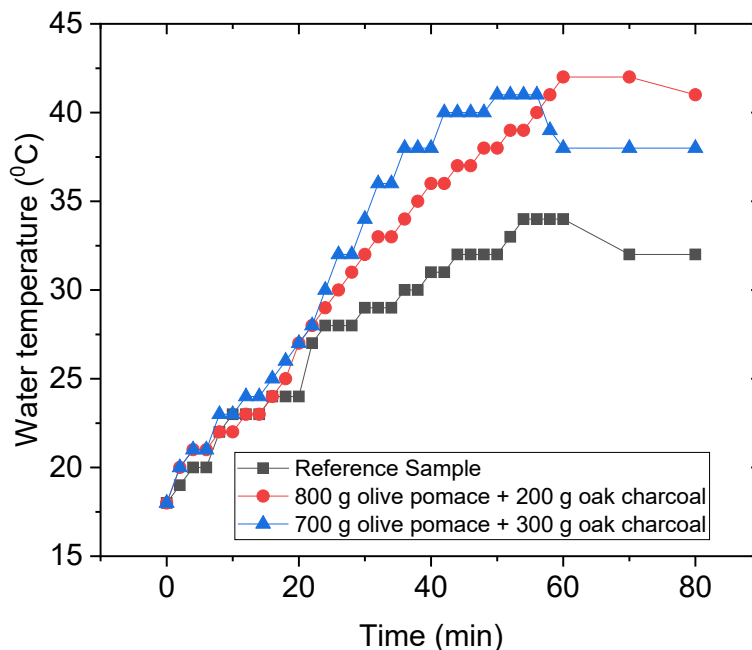


Fig. 5. Evolution of temperature of heated water with respect to time presenting the mass effect of oak charcoal.

4.4 OPW mixed with wasted beeswax

The most significant effect in the present study is the use of the beeswax waste mixed with the OPW sample. According to Figure 6, the temperature of water is increased to reach 52 °C after 50 min. In addition, the maximum temperature increases 34 % compared with the case of reference sample. This increase of temperature demonstrates that the wasted beeswax has a potential energy to enhance the combustion of OPW and especially for heating applications. However, the time occurred to reach the maximum water temperature when the OPW is mixed with the beeswax is decreasing around 10 min.

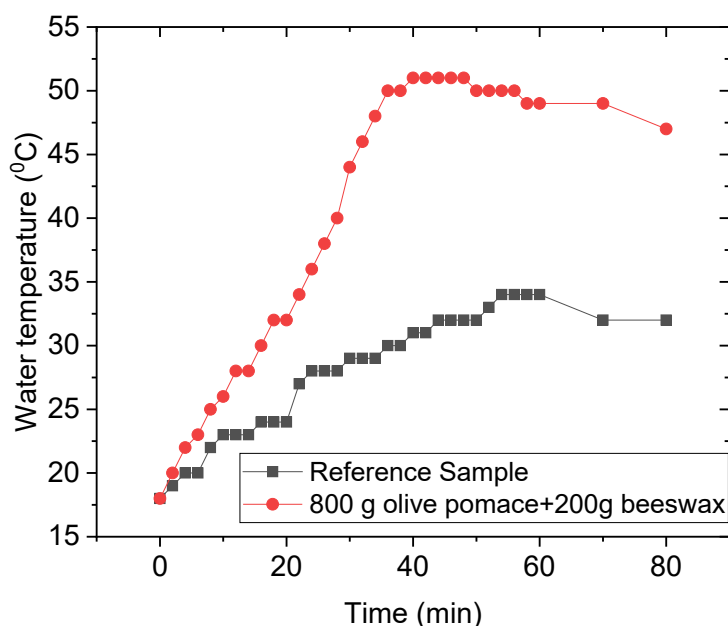


Fig. 6. Evolution of temperature of heated water with respect to time presenting the mass effect of waste beeswax.

4.5 OPW mixed with Oak Charcoal

According to the obtained results in Figure 6, it will be interesting to mix the beeswax and the oak charcoal in the sample samples and then to be compared with only the OPW sample. Figure 7 demonstrates the importance of coupling the oak charcoal and the beeswax with OPW only. The results show that the water temperature increases with increasing the beeswax and oak charcoal mass. The curves demonstrate that the beeswax effect of the water temperature is more significant especially when the blue and red curves are compared. It is because in both cases the quantity of oak charcoal is the same. In addition, the curves blue and green demonstrates the effect of adding the beeswax where the maximum water temperature reaches around 59 °C where it is a significant enhancement of combustion temperature. The presence of oak charcoal in this case improve slightly the time of heating water compared with OPW sample. This could be obtained by comparing the green curve of Figure 7 and red curve presented previously in Figure 6.

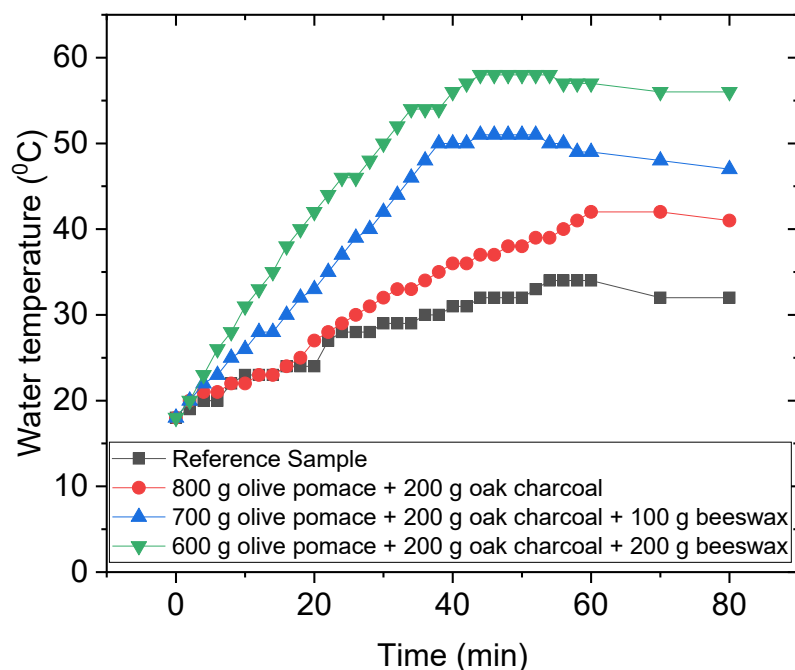


Fig. 7. Evolution of temperature of heated water with respect to time presenting the mixing of beeswax and the oak charcoal

4.6 OPM mixing with wood saw dust and wasted beeswax

Figure 8 represents the effect of mixing the bees wax and the oak charcoal with the OPM. The temperature of water increases by 5 °C when a 200 g of oak charcoal are only added to the OPW. Moreover, it could be clearly noticed that the maximum temperature reaches 40 °C when the beeswax is mixed with the OPM and the oak charcoal. In other terms, the presence of beeswax enhances the energy of combustion where the total gain of temperature reaches 10 °C.

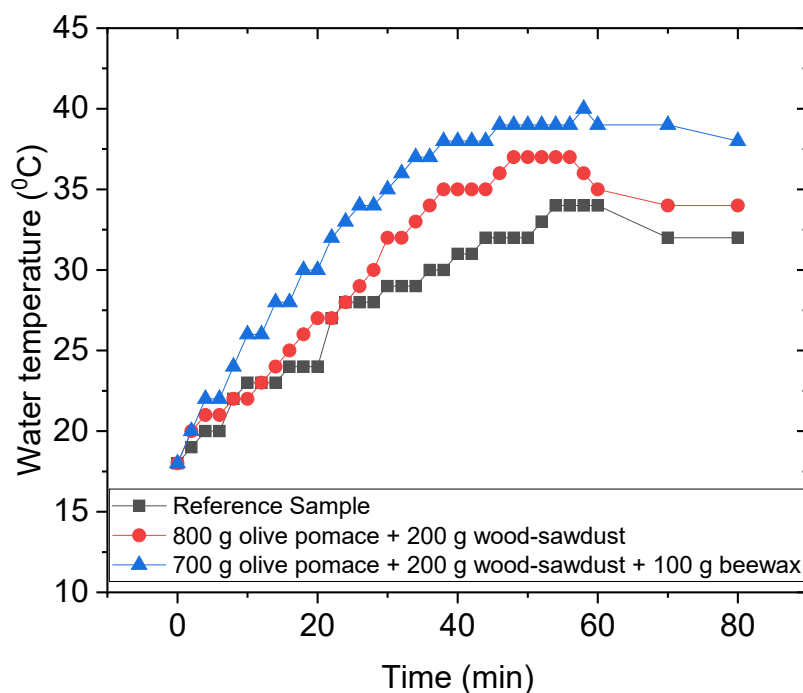


Fig. 8. Evolution of temperature of heated water with respect to time presenting the mixing of sawdust and beeswax.

4.7 OPW mixing with dry olive leaf and wasted beeswax

Figure 9 presents the evolution of water temperature after mixing the OPW with only dry olive leaf and then the OPW with dry olive leaf and the wasted beeswax. Based on the experimental results, the dry olive leaf increases the maximum temperature by around 3% when it is compared with the reference sample. On the other hand, the maximum temperature increased to reach 42 °C when the beeswax is mixed with the OPW and the dry olive leaf so that around 16 % of relative enhancement in the temperature is noticed.

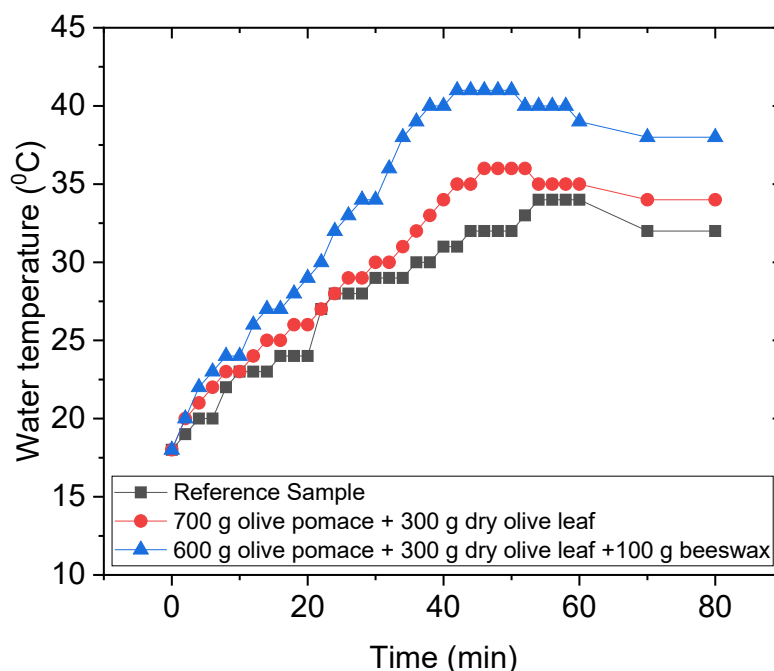


Fig. 9. Evolution of temperature of heated water with respect to time presenting the mixing effect of dry olive leaf and the beeswax.

4.8 OPW mixed with Oak Charcoal, dry olive leaf and wasted beeswax

In this case, a mixing of OPW with all used biomasses is studied. The black curve of Figure 10 represents the reference sample. The red curve and the blue curves represent the mixing of all used biomasses with the OPW. The only difference between the red and the blue curve is the increasing of the mass of wasted beeswax by 100g. Based on the results, the maximum temperature is enhanced significantly to reach a maximum value of 65 °C or 47% when it is compared with the reference sample. Moreover, when the red and the blue curves are compared, it could be noticed that when only 100g of wasted beeswax is added, the relative enhancement of maximum temperature increased around 8 %. The present mixing in the present case demonstrates an enormous enhancement of energy for heating applications.

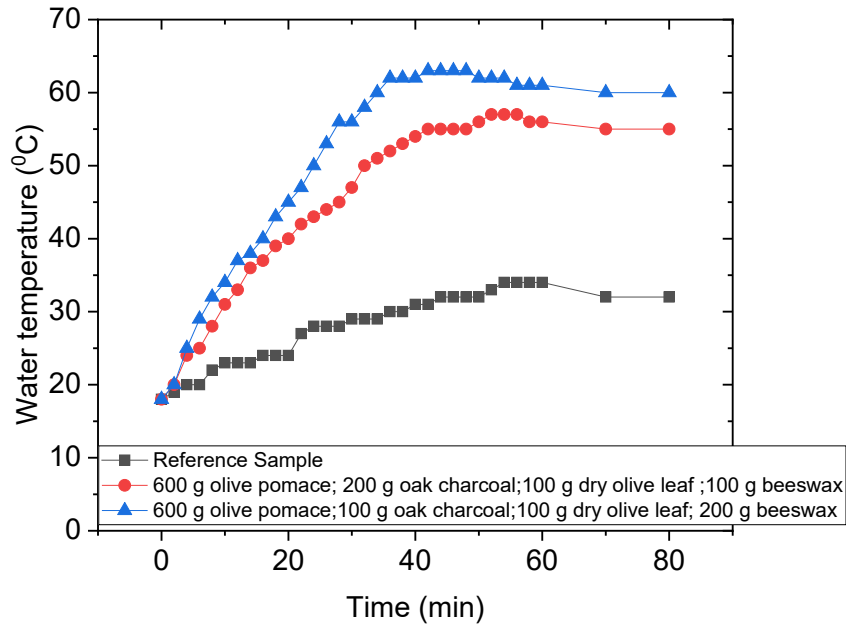


Fig. 10. Evolution of temperature of heated water with respect to time presenting the effect of mixing the oak charcoal with the dry olive leaf and the beeswax

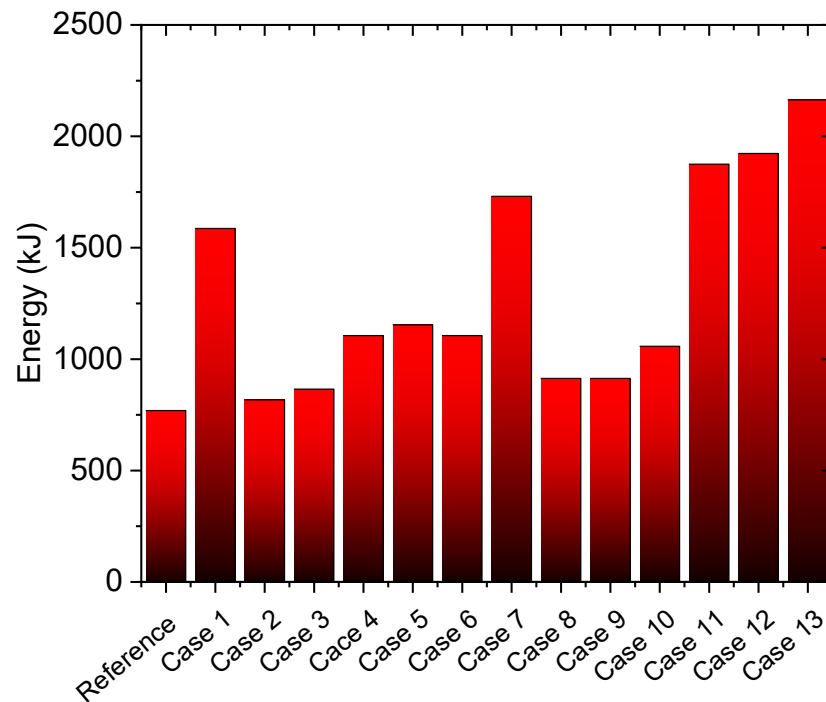
5 Heating Energy Analysis

Figure 11 summarizes the calculated energy from the experimental measurements. The energy is calculated using the collected data from the thermocouple that is installed in the water tank. The equation below presents the energy equation and it was used to calculate the energy provided by the solid biofuel to heat the water:

$$E = \rho V C_p (T_{\max} - T_{\text{initial}}) . \quad (1)$$

Where V is the volume of water in m^3 , C_p is the specific heat of water fixed at $4180 \text{ kJ.kg}^{-1}.\text{k}^{-1}$, ρ is the density of water fixed at 1000 kg/m^3 . $T_{\max}$ is the maximum temperature in each case and T_{initial} is the initial temperature of water equal to 18°C .

As shown in Figure 11, the energy provided by the sample reference is estimated at around 750 kJ and increases significantly when the OPW is mixed with other biofuels. In addition, case 1 where the wasted beeswax is added, the energy increases to reach around 1600 kJ so that the energy is almost doubled. Moreover, the results obtained in case 1 is similar to that obtained in case 7 where 100 g of wasted beeswax is added to the 200g of oak charcoal. The significant energy enhancement of the present cases is those obtained in the last three cases where the energy increases to reach 2200 kJ in case 13.



Reference: Reference sample, only OPW

Case 1: 800g olive waste and 200g beeswax

Case 2: 800g olive waste and 200g dry olive leaf

Case 3: olive waste and 300 g dry olive leaf

Case 4: olive waste and 300g dry olive leaf and 100g beeswax

Case 5: olive waste and 200g oak charcoal

Case 6: 700g olive waste and 300g oak charcoal

Case 7: 700g olive waste and 200g oak charcoal and 100g beeswax

Case 8: 800g olive waste and 200g wood sawdust

Case 9: 700g olive waste and 300g wood sawdust

Case 10: 700g olive waste and 200g wood sawdust and 100g beeswax

Case 11: 600g olive waste and 200g oak charcoal and 100g dry olive-leaf and 100g beeswax

Case 12: 600g olive waste and 200g oak charcoal and 200g beeswax

Case 13: 600g olive waste and 100g oak charcoal and 200g beeswax and 100g dry olive leaf

Fig. 11. Evolution of energy for each studied case.

6 Conclusions and Recommendations

In the present study, an experimental setup is built and well implemented in order to study the energy provided by solid biofuels based on OPW. The experimental setup consists of a chimney that permits to burn solid biofuel in a chamber and to heat water at the same time. In the water tank, a thermocouple is placed to measure the temperature of water during the heating process. The objective of the designed experimental setup is to demonstrate the feasibility of the heating energy enhancement of solid biofuels based on OPW by mixing it with other biofuels such as, wasted beeswax, oak charcoal, wood sawdust and dry olive leaf. To proceed, a reference sample based only on OPW is used to heat the water and then it is compared with 13 cases of study. The cases are the mixing OPW with the other proposed biofuels. According to the obtained results, the maximum water temperature reaches only 34 °C when the reference sample is burned. Moreover, the wasted beeswax has a significant potential to enhance the heating energy of solid biofuel based on OPW where the energy is multiplied by two. In addition, the mixing of OPW with all proposed biofuels increase the temperature of water to reach 62 °C and the energy was multiplied by three.

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Effect of Biowaste Materials on the Physical Properties of Blended Fuel for Industrial Application

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Keywords: PMS Fuel; physical properties; density; oxygenates; nano additives; ethanol

Abstract. In this study, PMS gasoline gotten from randomly selected commercial fuel stations was blended with ethanol gotten from agricultural waste and developed nanoparticles Additives (D-NA). The blended samples were analyzed for their physical properties using methods recommended by the American Society for Testing and Materials (ASTM). The tests were carried out on the fuel's density, oxygenates, benzene content, research octane number (RON) and sulphur content. The results shown in the physical property tests done on these blended fuels when compared with the neat gasoline gotten from the Nigerian National Petroleum Corporation (NNPC), industry standards (DPR/SON) and global markets (United States US & United Kingdom UK) shows that the blended fuels meet all required standards and specifications. The additives had little effect on the fuel's density but showed a sharp drop in its benzene content levels which makes it a healthier choice of fuel. Ethanol blended fuel had a higher oxygenate level than neat gasoline and the D-NA blended fuel. The research octane number for the three fuel samples showed favorably high numbers that fit the standards of the global market. The most interesting result is the Sulphur content which showed an increase in its values for the blended fuels although the values are within industrial and global limits.

1. Introduction

Premium Motor Spirit (PMS) fuel is a fractional distillation derivative of crude oil and the sample form of fuel used in this experiment. PMS is primarily used in the internal combustion of engines and It consists mostly of aliphatic hydrocarbons obtained by the fractional distillation of petroleum [1,2]. Naphthenes and olefins are among the more than 1500 hydrocarbon chemicals found in PMS (gasoline), a complicated mixture. Its overall hydrocarbon makeup consists of 20-50% aromatics with C₅-C₁₂ carbon atoms per molecule, 4-8% alkanes, 2-5% alkenes, 25-40% isoalkanes, 3-7% cycloalkanes, and 1-4% cycloalkenes [3].

This paper aims to do a comparative analysis of the physicochemical properties of neat PMS gasoline fuels and blended PMS gasoline fuels against international standards and global market standards [4]. The physical properties considered in this paper are density, sulphur content, benzene, research octane number and oxygenates. In a conference delivered by Vallinayagam [5]. It was discovered that the effect of physical properties of fuels in internal combustion engines is rarely reported. In his findings, he discovered that the different physical properties of the different types of fuels show marked differences in their effects on the combustion engines which goes on to show the effects of the physical properties of PMS on the engine's overall efficiency. Fuel additives are chemicals created and added to fuel to improve the quality and effectiveness of the fuel in the corresponding engines [1,6]. They can be powder, liquid or pill. They increase fuel octane number, inhibit corrosion and allow for the proper workings of the engine components [5].

There are three different types of PMS Fuel based on their octane ratings: regular PMS, which has an octane rating greater than 85 but less than 88; mid-grade PMS, which has an octane rating greater than 88 but less than 90; and premium PMS, which is more expensive and has an octane rating greater than 90 [7,8]. Octane rating is a measure of a fuel's ability to withstand compression before detonating [9]. The Research Octane Number (RON) and the Motor Octane Number (MON) are the two most popular types of octane ratings, respectively. In addition to improving combustion, removing sludge, controlling soot, and removing dangerous yeast and fungus from the fuel, fuel additives also serve as biocides [10].

Nano additives on the other hand are products of nanotechnology. Nanotechnology is a recently discovered but exciting field of research that has contributed a lot to the field of science and technology. Due to its vast application, it is regarded as a multidisciplinary field [11]. Nanoparticles (a general name for nanotechnology products) have unique properties that help them stand out. One is the ease of dispersion. Unlike bulk material, nanoparticles have a larger surface area and better electrical, optical and mechanical properties [12]. At present, nanoparticles and by extension nanoadditives have multiple applications in every field of science and technology, from food and drugs to oil and gas to manufacturing and production and even beyond [13]. Nano additives are materials that are one dimension less than 100nm added to their host materials to improve or help improve their qualities and efficiency.

In nutrition, for example, nanoadditives are incorporated into food to improve the dispersibility of water-insoluble additives such as flavours, colours, nutrients and preservatives without the need of a surfactant. Because of their huge surface area, these nanoadditives improve the nutritional value, absorption, and flavour of components into the body [11]. The primary function of nano additions as lubricant additives is impacted by their excellent thermal stability at high temperatures. Nanoparticles' small size allows them to cling to and smooth out imperfections in contact surfaces. Consequently, their high surface area to volume ratio allows contact with their surroundings [14]. Nanotechnology has a wide range of applications in the petroleum business. It involves everything from the use of silica particles to improve hydraulic fracturing fluids and drilling to better oil recovery, oil well cementing (including foam, transport studies and emulsion stability), and logging activities and corrosion inhibition [15]. According to research, an optimal quantity of nanoparticles improves the evaporation of fuel droplets, whereas an excessive concentration reduces the evaporation rate [12].

Furthermore, the nanoadditives enhance the fuel's thermo-physical properties, and its physicochemical properties are more enhanced than that of its base fuel [12]. A major challenge to using nano additives is clogging. Due to their small size, they easily aggregate together and sediment causing clogging to the fuel injector. A good solution to that is developing and adding a surfactant to the fuel. There are different types of fuel additives, they include metallic additives, metal oxide additives, carbonaceous additives, carbon-based fuel additives, organic nanoparticles, and nanofluid additives [16].

2. Experimental Methods

Three fuel samples were considered in this study. Sample A₀ which contains no additive was purchased from NNPC fueling station Nigeria. Sample A₄ contains a 10% vol of a developed bioadditive created for this study. Sample B₄ contains 10% vol of ethanol additive. The developed bioadditive was created using a two step process which consisted of a ethanol base fluid created from fermented bagass and crushed coconut nanoparticles. The developed additive was ultrasonicated to ensure homogenous mixture of nanoparticle.

Physical property tests on fuel samples

For the physical property tests done on the blended fuel samples, the 10% additive and 90% fuel sample variables were used. Appropriate ASTM methods such as ASTM D1298, ASTM D1552, ASTM D5580, ASTM 2699 and ASTM 6293-98 respectively were used to test for the five physical property parameters which include, Density, Sulphur content, Benzene content, Research Octane number and oxygenates.

Specific gravity

To determine the API Specific gravity. Typically, a hydrometer and a thermometer are immersed into a measuring cylinder of known volume and filled with the sample to be tested. The temperature reading is then taken and converted into Fahrenheit [17F]. The hydrometer readings will then be aligned with the converted temperature readings to accurately obtain the specific gravity of the sample.

Reid vapor pressure

For the Reid vapor Pressure test, an Adequate amount of the test sample was put into a Reid vapor pressure machine and the machine was subsequently immersed in a Reid vapor pressure bath. The temperature of the bath had been regulated at 38 °C and the samples were allowed to reach a similar temperature to the RVP bath. The RVP gadget detected the pressure of the fleeing vapors after a period, and the reading on the device was recorded as the Reid Vapor Pressure. Soon after, test sample vapors started to discharge.

Research Octane Number Test

For the research octane number test, the carburetor of the RON machine was filled with the appropriate volume of fuel sample, and the machine was then turned on to determine the research octane number. The selector valve of the machine had been run for an hour to bring it into equilibrium. Initially set between 45 and 47, the height of the cylinder for reading the knock-meter will eventually be set to 50 once the maximum knock fuel level has been identified. The reading on the knock meter is then recorded as the research octane number.

3. Results

To further investigate the physical properties of the blended fuels, the results are shown in figures 1-figures 5.

Figure 1 compiles the result of the specific gravity or density of three samples A₀, A₄ and B₄. A₀ represent neat gasoline, A₄ represent samples containing gasoline blended with 10% developed Nano-additive and B₄ represents a sample blended with 10% ethanol. Samples A₄ and B₄ have lower densities compared to Sample A₀. Sample A₀ had a result of 0.769, and Samples A₄ and B₄ have results of 0.762 and 0.763 respectively. This shows that the blended gasoline is less dense than the neat gasoline and more so that ethanol-blended gasoline is denser than D-NA blended gasoline. While in the Sulphur content [see figure 2], there is an increase in the Sulphur presence in the blended fuels. Sample A₀ has a Sulphur content value of 0.023 and Samples A₄ and B₄ have their Sulphur content values to be 0.05 and 0.048 respectively.

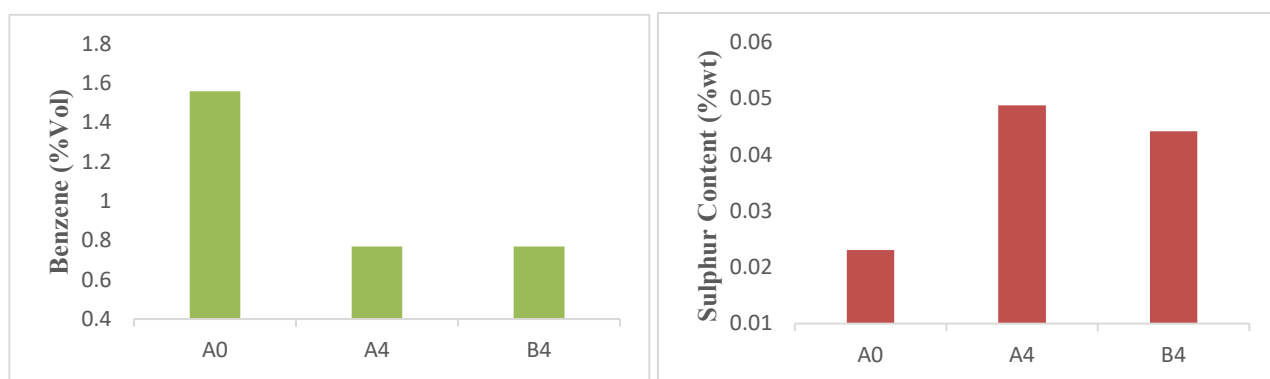


Figure 1: Density of fuel blends A₀, A₄ and B₄ Figure 2: Sulphur content of fuel blends A₀, A₄ and B₄

After testing for the benzene content in the sample fuels, it was observed that the blended fuels have fewer amounts of benzene present as compared to the neat gasoline. The neat gasoline had a benzene content value of 1.6 while the blended fuels both had the same benzene content value of 0.8. The research octane number of the sample fuel did not appear to follow a pattern. It was observed in its results that Sample A₄ had the lowest RON Value of 91.2 followed by sample A₀ with a value of 91.4 and sample B₄ had the highest value of 92.3. In testing for the presence of oxygenates, the results as shown in figure 5 shows that sample A₀ has a negligible amount of oxygen present while sample A₄ and B₄ have noticeable amounts. Sample B₄ however has a significantly higher amount of oxygen present as compared to sample A₄.

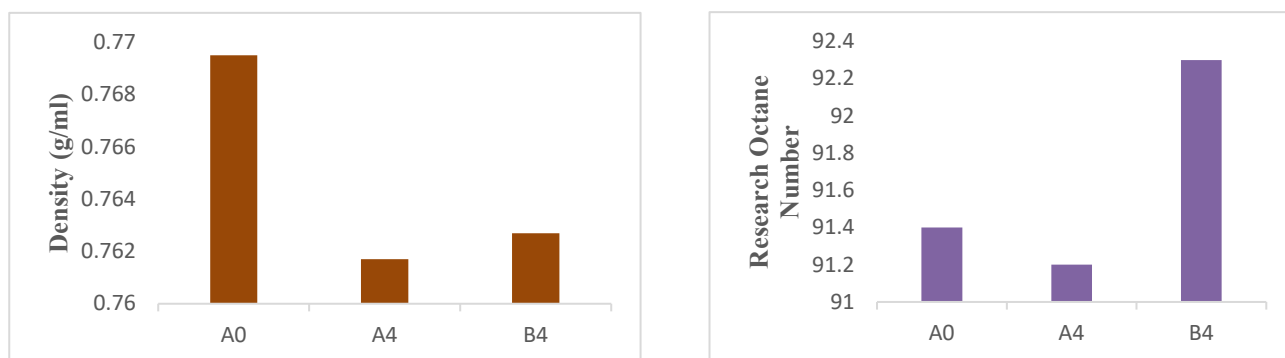


Figure 3: Benzene content of fuel blends A₀, A₄ and B₄ Figure 4: RON of fuel blends A₀, A₄ and B₄

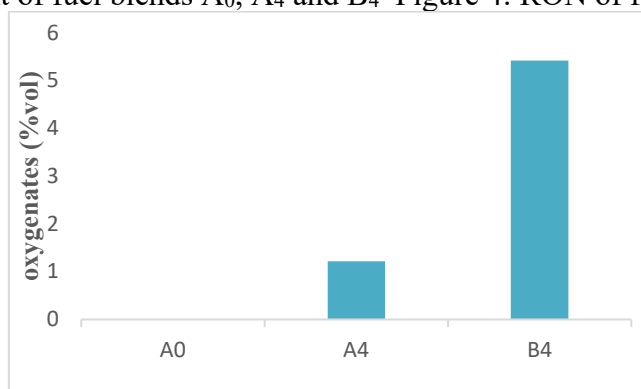


Figure 5: Oxygenate value of fuel blends A₀, A₄ and B₄

4. Discussion

It is impossible to overstate the impact of the physicochemical properties of the fuel. It is used to assess how well the fuel is burned in a combustion engine [7,18]. It can be also used to determine

the price of fuel in the market [23], especially with API Specific gravity, benzene content and Sulphur content [8]. It is also important to note that in a world where the focus is clean energy and control of pollution from these fuel types, these physiochemical properties are tested, and standards are set on them to determine the standard of the PMS gasoline fuel [30].

4.1 Analysis of fuel density

Density is referred to as the mass per volume of the fuel. Density affects the energy present in the fuel which is why diesel fuel has 15% more energy than petrol fuel [25]. Europe reports on a vehicle in use that there is a 40% increase in diesel efficiency over a spark ignited petrol fuel and this is because diesel is heavier than PMS gasoline fuel since it contains heavier carbon molecules [12,18]. The average density of PMS gasoline fuel is 0.8 but the global market accepts a density range of 0.71- 0.77 with a mean density of 0.75 [18]. In this experiment, it was found that the densities of the blended gasoline fuels were lower than those of neat gasoline. These values are in accordance with the Department of Petroleum Resources (DPR) and Standard Organization of Nigeria (SON) requirements, whose range of values is between 0.75-0.77.

4.2 Analysis of fuel Sulphur content

Just as its name implies, Sulphur content is the amount of Sulphur present in the fuel. Sulphur is a naturally occurring element while drilling for oil and it must be removed in the fuel treatment process. Sulphur affects the emission control systems, and it causes pollution. In 2017, the EPA adopted the Tier 3 Gasoline Sulphur Program, which required that all US gasoline have an average Sulphur content of 10ppm. This regulation was in line with the 2009 British Standard BS 2869 for gas oil, which stated that gasoline or diesel fuel must have a maximum Sulphur content of 10ppm [4, 24]. Because 38% of emissions in the UK come from fossil fuels, new guidelines were created to reduce emissions (the United Kingdom Petroleum Industry Association) [8, 27, 29] and in 2021, statistics show that about 3.21 billion barrels of gasoline were consumed on only motor gasoline [29]. In % weight, US and UK standards are 0.001% for the amount of sulphur to be present in PMS fuel while in Nigeria, the permissible limit for Sulphur content is 0.1% weight. In this experiment, it was observed that Sample A4 has the highest amount of Sulphur content present, and this can be attributed to the source of nanoparticles used which is coconut shells. Studies done in Article [22] show that there is a presence of Sulphur although in small amounts present in coconut shells.

4.3 Analysis of fuel Benzene content

Same as Sulphur content, benzene content is representative of how much or how little benzene presence is in the fuel. Benzene is naturally occurring in crude oil production and because of its aromatic component, studies that it improves octane number and fuel efficiency [7]. Despite its useful benefits, benzene is a cancerous element, so it must be completely removed from fuels, sadly it is very difficult to remove [9]. The United States Environmental Protection Agency (USEPA) states benzene content in its fuels should not be more than 1% wt volume but the Health and Safety in the United Kingdom pegs benzene content permissible limits to be 2% to 3% which is also the same as Nigeria's DPR. In this body of work, the blended gases show reduced benzene content which is a good one because it shows that the blended gases are health-friendly as compared to the neat gasoline so they can be used locally and sold globally.

4.4 Analysis of fuel Research Octane Number (RON)

RON is described as the octane rating used for vehicle fuel [2] Octane rating is now the percentage by volume of iso-octane in a mixture of iso-octane and n-heptane that knocks with some intensity as the fuel is being tested [15]. The closer the octane rating is to 100, the better the fuel because it shows a greater percentage of iso-octane and less unpredictable combustion at high temperatures and pressures [17,9]. According to USEPA, Retail gasoline stations in the United States sell three main grades of gasoline based on the octane level; Premium (octane range of 91–94), Midgrade

(octane range of 89–90) and regular (octane number of 87) [7, 8, 11]. All automobiles constructed in the UK are designed to operate effectively on fuel with a RON value of 95. Fuels with a higher-octane rating can have RON levels of up to 97, 98, and even 100. These have a higher price tag and are typically preferred by drivers of high-performance cars. [23,25] In Nigeria, the average octane rating is 84 although the reason is not clear why the value is so low [17] however Nigeria as a hub of reused cars and low-performance vehicles may be a reason in addition to the poor refineries and lack of proper regulations. In this project, the blended fuel samples had ratings of 91.2 and 92.3 which is a good one and is within the global standard. The DNA blended fuel however has a lower octane rating as compared with the ethanol-based fuel additive. This can be attributed to the ratio between ethanol and the dispersant used in the developed nanoadditives as this RON value for sample A4 did not follow the regular pattern for D-NAs.

4.5 Analysis of fuel Oxygenates

This is the amount of oxygen present in the fuel mostly in form of ethanol and methanol (alcohol) [20, 21, 27]. USEPA defines oxygenates as fuel additives that contain oxygen, usually in the form of alcohol or ether [31]. Oxygenates can enhance fuel combustion and thereby reduce exhaust emissions. Some oxygenates also boost gasoline octane [17]. Despite its usefulness, the USEPA has discovered that it is contaminating the groundwater, so it is fast disappearing from use and research is going on how to ban it or give it strict restrictions in the clean water act.[11] In the UK, there is a new type of fuel called E10 and which means the fuel contains 10% bioethanol in its mixture [24]. Bioethanol helps cut emissions when cars burn petrol and is a renewable source of energy — as it's a byproduct of sugar fermentation [6, 8,31]. In this study, ethanol fuel additive has a higher oxygenate value than developed fuel additives while neat gasoline has less oxygenated. Studies show that the DPR/SON has no local standards or permissible limits for oxygenates but the value of the fuel samples shows that they can be used as they conform to global standards.

Conclusion

To be able to compare and analyze the different physical properties of blended PMS gasoline fuel against neat PMS gasoline, industry and market standards, a series of experiments were carried out using the ASTM Methods in addition to the additives developed under standard conditions. The major findings are as follows

- The addition of the additives has very little effect on the density of the fuel and the difference is not as beneficial since the blended fuel is now less dense although still within the required standards and limits.
- The addition of additives to the PMS fuel blends increased the amount of Sulphur present in the PMS Gasoline fuel due to the source of the additives. The Sulphur content level in the blended fuels was higher than the one in the neat gasoline.
- Benzene, a cancerous element is discovered to be in reduced quantities in the blended PMS fuel making it a health-friendlier choice for consumers. The benzene content in the blended PMS fuels was 50% less than that of the reference fuel.
- The research octane number did not follow a pattern in this experiment as the D-NA blended fuel had the lowest RON Value followed by the neat gasoline and the ethanol blended PMS fuel had the highest RON Value
- The ethanol-blended PMS fuel had the highest level of oxygen present followed by the D-NA PMS fuel blend. The neat PMS gasoline was very dry as no value was recorded for its level of oxygen present.

In conclusion, the diverse physicochemical parameters examined showed that the fuel additives used had varying impacts, which supports the effects of additives in PMS. To create PMS with the best physicochemical qualities, additional research and comparative study on the various fuel blend types can be conducted with an emphasis on their percentage ratio.

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CHAPTER 5:

Wastewater Treatment and Waste Recycling

Facile Synthesis of Robust Metal-Organic Framework (MOF-5) for Chromium (VI) Decontamination from Wastewater

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Keywords: Zinc Metal-Organic Framework (MOF-5), Cr(VI) Decontamination, Isotherm and Kinetics, Recyclability.

Abstract. Herein, for the first time, we investigate the adsorption performance of nano-Zn benzenedicarboxylate metal-organic framework (nano-MOF-5) as an efficient adsorbent material for Cr(VI) decontamination from polluted water. The synthesized Zn MOF-5 was fully characterized *via* FT-IR, XRD, HRTEM, BET, and TGA techniques. Moreover, the prepared Zn MOF-5 revealed a prominent surface area of 1169.32 m² g⁻¹, demonstrating its ability to be utilized as a capable adsorbent material. The adsorption profile of Cr(VI) onto the fabricated Zn MOF-5 was performed against the various parameters such as contact time, dosage, and initial Cr(VI) concentration. The optimum dosage from the Zn MOF-5 for 81.03% adsorption of 25 ppm Cr(VI) was 0.5 g L⁻¹ at pH=7 after 15 min. The Cr(VI) decontamination performance of the synthesized Zn MOF-5 recorded the maximum monolayer adsorption capacity of 91.22 mg/g. These data demonstrated that the synthesized nano-Zn MOF-5 is a promising adsorbent material for the removal of Cr(VI) from wastewater.

1 Introduction

Metal-organic frameworks (MOFs) are crystallized compounds formed consisting of ionic species that are linked together with organic linkers to create unlimited single-, or multi-dimensional frameworks [1-3]. Recently, many MOFs with remarkable porosity, large surface area, high pore volume, and exquisite pore size have attracted great interest in a wide range of applications, including adsorption, catalysis, drug delivery, sensors, and ion exchange [3, 4]. Among the various applications of MOFs, wastewater treatment is considered one of the critical applications because of the frank growth in water contamination. Where half of the world's people may suffer from water stress in 2025. Consequently, the synthesis of profitable, outstanding, and effective adsorbent materials such as MOFs for wastewater remediation is urgently required for a cleaner and sustainable environment [5-7]. MOFs were utilized in the adsorption of harmful materials such as dyes, organic compounds, benzene, and heavy metals from aqueous solutions [2, 3].

Because of their hazardous and bioaccumulation effects, the high discharge of toxic heavy metals into the aquatic environment has gained global attention. Chromium is a hazardous metal released from industrial processes such as plating, steel, and pigment production. The toxicity of hexavalent chromium is 1000 times greater than that of the trivalent form [8]. Cr(VI) levels should not exceed 0.05 ppm according to WHO environmental regulations [9]. To eliminate Cr(VI) from aqueous solutions, many procedures are used such as photocatalytic degradation, reverse osmosis, precipitation, separation, and adsorption [3, 10, 11]. Adsorption is considered a promising and useful technique in the removal of Cr(VI) among the other traditional techniques because of its high efficacy, ease of operation, and low energy needs. The adsorption process directly depends on the type of the utilized adsorbent. Adsorbents with a large surface area, high porosity, and high pore volume are preferred [6, 7, 12].

In the present study, nano-MOF-5, as a participant of the Zn-based MOF cluster was fabricated and used to adsorb chromium (VI) from aqueous solutions. The influence of contact time, dosage, and initial Cr(VI) concentration on the adsorption performance was investigated. Also, equilibrium isotherm and kinetics were performed to evaluate the adsorption behavior.

2 Experimental Procedure

2.1 Synthesis of Zn benzenedicarboxylate MOF

4.0 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.0 mmol 1,4-benzenedicarboxylate were dissolved under continuous stirring at room temperature in 30 mL of N, N-dimethylformamide (DMF). The mixture containing 2.2 mL of triethylamine and 11.0 mL of DMF was gradually poured into the above solution under strong stirring. Subsequently, a white precipitate appeared. At that point, 0.15 mL of 1.5 mmol hydrogen peroxide was added to the reaction with stirring for 2 h. Then, the mixture was filtered and washed several times with DMF and CHCl_3 . Finally, the resulted powder was immersed in 30 mL of CHCl_3 overnight and vacuum-dried at 100 °C.

2.2 Characterization of the fabricated Zn benzenedicarboxylate MOF

The infra-red absorption spectra of the synthesized MOF-5 were recorded using FT-IR (Thermo-Scientific Nicolet). X-ray spectra were conducted by Shimadzu XRD-6100 (Cu-K_α radiation, $\lambda=1.54 \text{ \AA}$). The morphological structure of the synthesized MOF-5 was examined *via* high-resolution transmission electron microscopy (HRTEM) (JEOL JEM-2100). The specific surface area of the prepared MOF-5 was detected using BEL Japan. Where the prepared material was degassed for 6 h at 250 °C under vacuum, and then the N_2 adsorption-desorption isotherms were measured. The thermal stability of the fabricated MOF-5 was assessed by a thermal gravimetric analyzer (TGA-50, Shimadzu). The temperature was raised from 30 °C to 1000 °C in the presence of nitrogen gas, and the weight loss was monitored during the process. The flow and heating rates were respectively 40 mL/min and 10 °C/min.

2.3 Adsorption of Cr(VI) onto the synthesized Zn benzenedicarboxylate MOF

The Cr(VI) adsorption affinity of the prepared MOF-5 was evaluated *via* batch technique. 100 mg of MOF-5 was mixed under continuous stirring with 100 mL from a different initial concentration of Cr(VI) at 25 °C. The influence of different parameters, such as contact time (0-120 min), pH (1-11), adsorbent dosage (0.5-10 g/L), and initial Cr(VI) concentration (10-100 ppm) on the adsorption process was investigated. The MOF-5 was then separated to detect the final Cr(VI) concentration by UV spectrophotometer at 365 nm. The Cr(VI) adsorption percentage was calculated from the following equation [12]:

$$\text{Removal \%} = ((C_o - C_e)/C_o) * 100 \quad (1)$$

Where, C_o is the initial concentration of Cr(VI) (mg/L); and C_e is the concentration of Cr(VI) at equilibrium (mg/L). The adsorption capacity (mg/g) was determined from Eq. (2) [2]:

$$q_e = V * (C_o - C_e) / m \quad (2)$$

Where V is the volume of the solution in liters; and m is the weight of the fabricated MOF-5 in grams.

2.4 Equilibrium and kinetics of Cr(VI) adsorption onto MOF-5

To examine the nature of the removal process of Cr(VI) using the synthesized MOF-5, the equilibrium of the decontamination procedure was evaluated using Langmuir, Freundlich, and Temkin isothermal models. Moreover, the kinetics were assessed *via* pseudo-first-order, pseudo-second-order, and Elovich equations.

2.5 Reusability of the synthesized MOF-5

To enhance the affordability of the utilization of the prepared MOF-5 in the wastewater decontamination process, the used MOF-5 was regenerated by washing five times with deionized water and ethanol then dried in air for extra recycling.

3 Results and Discussion

3.1 Characterization of the fabricated MOF-5

Fig. 1 shows the FT-IR spectra of the prepared MOF-5. Broadband was observed around 3400 cm^{-1} which corresponds to the stretching of the hydroxy groups. The two sharp peaks are shown at 1590 and 1478 cm^{-1} are related to the carboxylic group of the 1,4-benzenedicarboxylate [13]. The symmetric stretching vibration of ZnO was displayed at 609 cm^{-1} [14]. Therefore, FT-IR spectra demonstrate the existence of the characteristic bands of the prepared MOF-5 with high agreement with the previous studies [14, 15].

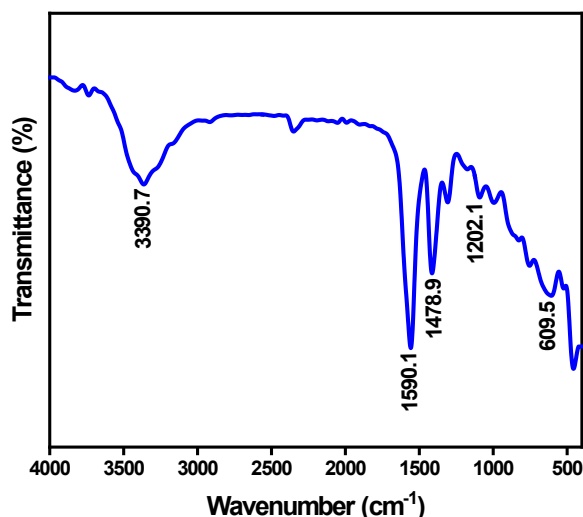


Figure 1. FT-IR of the synthesized MOF-5.

The PXRD patterns of the fabricated MOF-5 were displayed in Fig. 2. The PXRD shows strong characteristic peaks of MOF-5 at 9.6° , 17.5° , and 29.8° . Meanwhile, three small peaks at 20.4° , 22.8° , and 28.2° , observed at the PXRD of the prepared MOF-5, indicating that traces of zinc species were tricked to the framework. These characteristic patterns correspond to the most distinguished diffraction peaks of the simulated MOF-5 structure [13-15].

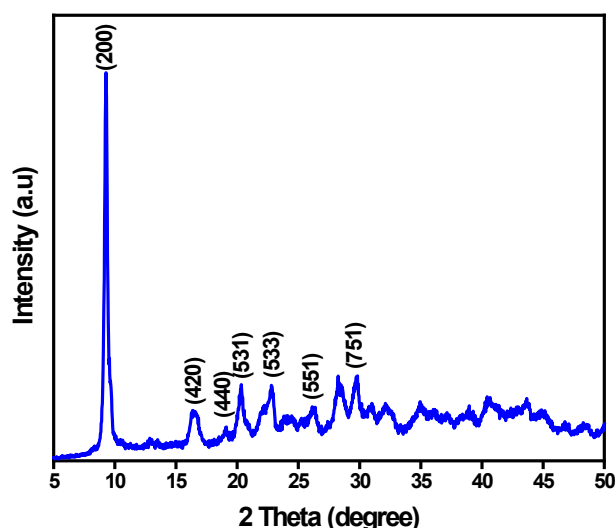


Figure 2. Illustrated XRD patterns for MOF-5.

The morphological structure of the synthesized MOF-5 was investigated *via* HRTEM, as shown in Fig. 3. The HRTEM images prove the nanomorphology of the prepared MOF-5 with homogeneous distribution and small particle size, which is very useful in the adsorption application and varies from the previously presented MOFs that were fabricated in a large micro-scale size [2, 3]. The average particle size of the spheric MOF-5 nanoparticles was determined as 25-35 nm.

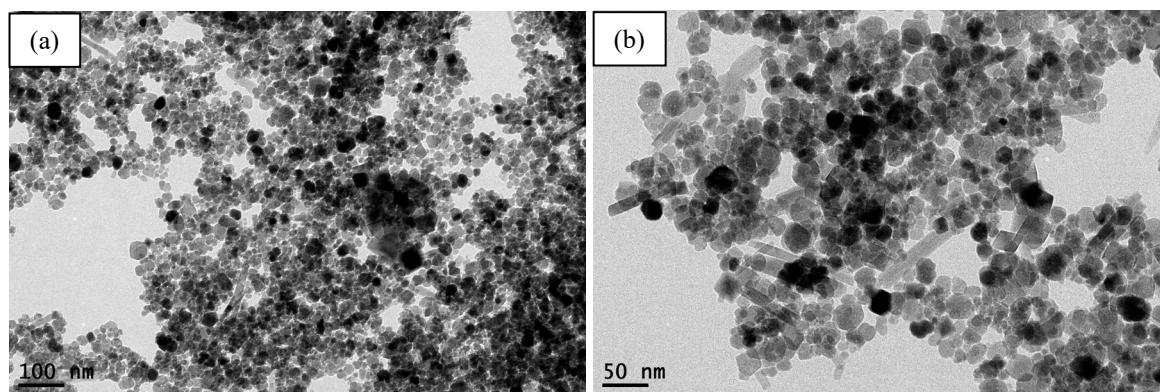


Figure 3. TEM images of the synthesized MOF-5.

The surface area outline of the prepared nano-MOF-5 was determined by Brunauer Emmett Teller (BET), as presented in Fig. 4. The BET surface area, pore diameter, and pore volume of the fabricated MOF-5 were recorded 1169.32 m²/g, 3.9 nm, and 1.21 cm³/g, respectively. The recognized large surface area of the synthesized nano-MOF-5 is useful to apply as a promising adsorbent material for Cr(VI) from aqueous solutions [2, 3].

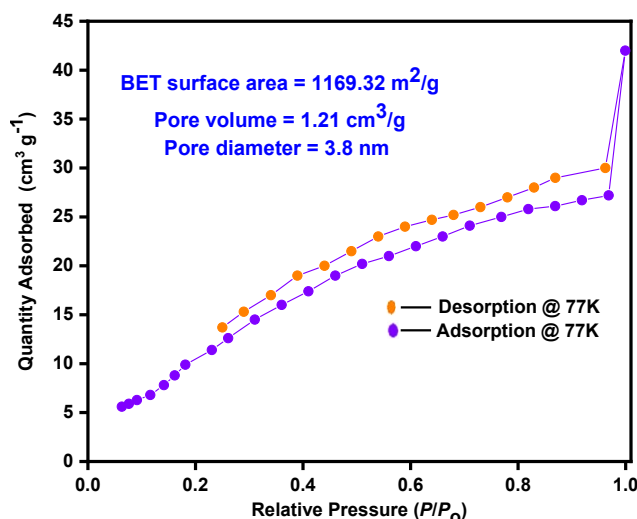


Figure 4. N₂ adsorption-desorption isotherms of the prepared nano-MOF-5.

To evaluate the thermal stability of the fabricated nano-MOF-5, TGA was utilized as shown in Fig. 5. It is clear that the synthesized MOF-5 nanoparticles display high thermal stability till 300 °C. Where different weight-loss phases were detected. The first loss phase (~18%) at a temperature range less than 300 °C, that may correspond to the loss of water molecules and atmospheric gases suspended to the MOF's pores [3]. The second weight-loss phase (~59%), which may be attributed to the degradation of the organic framework from 200 °C to 510 °C [2]. These data established the excellent thermal stability of the prepared MOF-5 compared with the other MOFs utilized in water treatment processes [2, 3].

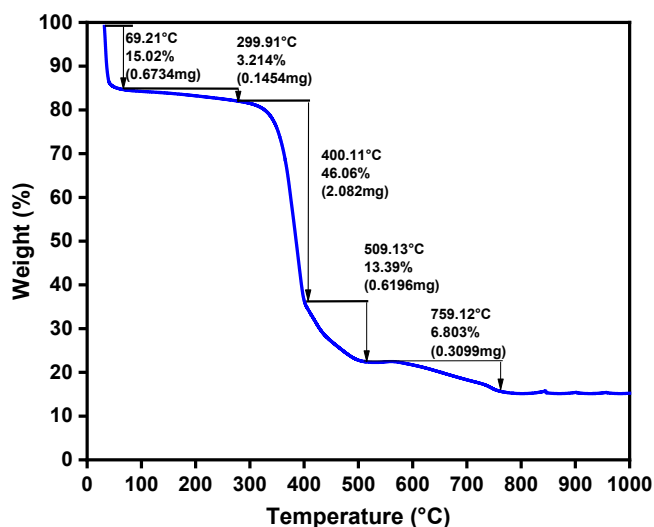


Figure 5. TGA of the synthesized nano-MOF-5.

3.2 Assessment of the synthesized MOF-5 nanoparticles for Cr(VI) decontamination from wastewater

The performance of the fabricated MOF-5 nanoparticles was tested for the adsorption of Cr(VI) from polluted water *via* batch technique.

3.2.1 Impact of contact time on Cr(VI) decontamination process onto nano-MOF-5

Figure 6 presents the effect of contact time on the Cr(VI) removal percentage onto the fabricated MOF-5 at a time range from 0 to 120 min. It was demonstrated that the adsorption of Cr(VI) onto the prepared MOF-5 enhanced with increasing the time until the equilibrium time. The high Cr(VI) removal rate in the first phase may be according to the high surface area and functional groups of the synthesized nano-MOF-5. The optimum contact time of the Cr(VI) adsorption process was recorded at 15 min, with a maximum decontamination percentage of 87.03%. At the second stage of decontamination, the MOF-5's active sites were more saturated with Cr(VI) and unnoticeable removal was observed [2, 3].

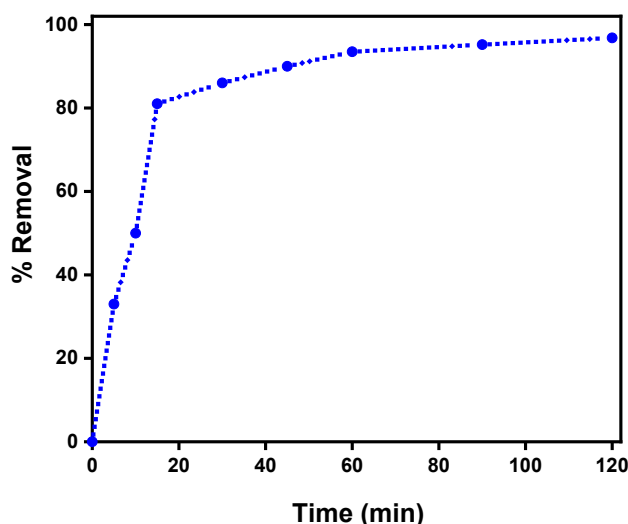


Figure 6. Influence of contact time on Cr(VI) removal *via* nano-MOF-5 at adsorbent dosage = 0.5 g/L, pH = 7, stirring = 250 rpm, temperature = 22 °C, and initial Cr(VI) concentration = 25 ppm.

3.2.2 Impact of nano-MOF-5 dosage on the Cr(VI) decontamination process

Because of its effects on the adsorption performance, the adsorbent dosage is regarded as one of the most important elements in the decontamination process. The effect of the produced MOF-5 dose on Cr(VI) adsorption processes was assessed at 15 min. The Cr(VI) decontamination process was improved when the amount of prepared nano-MOF-5 increased from 0.10 to 4 g/L, as shown in Figure 7. On the other hand, increasing the dosage of MOF-5 reduced the adsorption capacity [7, 12]. As a result, the optimum MOF-5 dosage was determined to be 0.5 g, which was selected to be an affordable dosage for the Cr(VI) removal process.

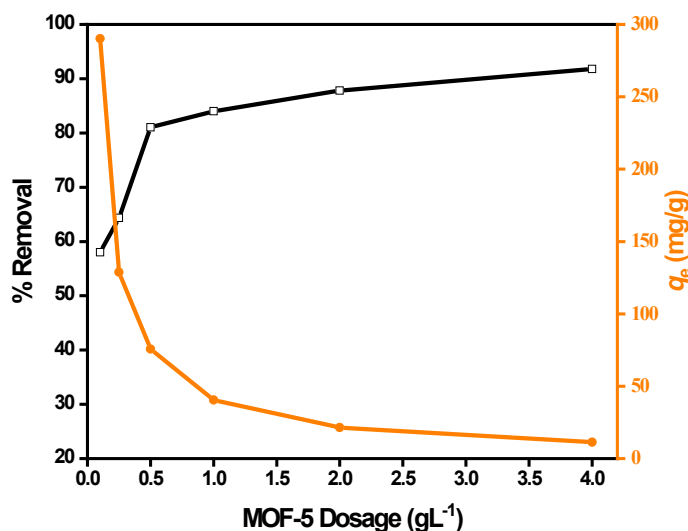


Figure 7. Influence of nano-MOF-5 dosage on Cr(VI) adsorption at time = 15 min, pH = 7, temperature = 22 °C, stirring = 250 rpm, and initial Cr(VI) concentration = 25 ppm.

3.2.3 Impact of initial concentrations of Cr(VI) on the decontamination process

After 15 minutes, the influence of Cr(VI) concentration was investigated, with beginning concentration levels ranging from 10 to 100 mg/L and 0.5 g/L as the optimum dosage. Figure 8 shows that raising the starting Cr(VI) concentrations from 10 to 100 mg/L decreased the Cr(VI) decontamination performance, which is consistent with our prior findings. This could be due to the active sites of the fabricated MOF-5 being saturated as the Cr(VI) concentration increased [5, 6]. According to these results, the prepared nano-MOF-5 was found to be effective for Cr(VI) adsorption from aqueous media at various beginning concentrations.

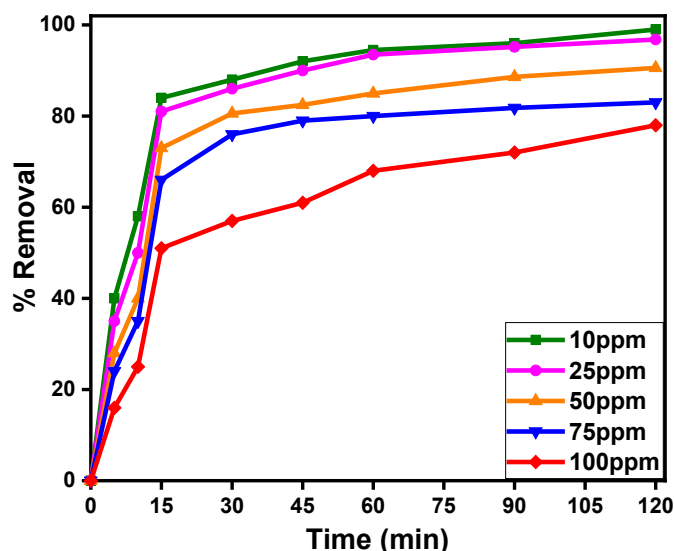


Figure 8. Influence of initial concentration of Cr(VI) on decontamination process at pH = 7, dosage = 0.5 g/L, temperature = 22 °C, and stirring = 250 rpm.

3.2.4 Equilibrium isotherm for Cr(VI) decontamination process onto nano-MOF-5

The behavior of Cr(VI) decontamination onto nano-MOF-5 was studied using Langmuir, Freundlich, and Temkin equations. When the correlation coefficients of the three examined models are compared in Table 1, it is clear that the Langmuir and Temkin models are the best fit for describing the Cr(VI) decontamination on the fabricated MOF-5. Furthermore, the separation factor (R_L) value ranges from 0 to 1, demonstrating the favorable removal of Cr(VI) using the Langmuir model [2]. However, the Freundlich intensity (n_F) of Cr(VI) on MOF-5 was 0.227, which is less than unity, indicating that the adsorption process is unfavorable. The strong Temkin correlation coefficient indicates that the equilibrium data of Cr(VI) adsorption onto synthetic nano-MOF is matched with the Temkin isothermal model. As a result, the Langmuir and Temkin models are the most suitable for describing monolayer chemical adsorption.

Table 1. Isothermal parameters for the Cr(VI) adsorption onto the prepared nano-MOF-5.

Langmuir parameters			Freundlich parameters			Temkin parameters		
q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n_F	R^2	A (L/g)	B (J/mo)	R^2
91.225	0.028	0.998	0.651	0.227	0.789	30.681	1.787	0.999

3.2.5 Comparison of decontamination capacity for nano-MOF-5 with other adsorbent materials

The Langmuir decontamination capacity of the fabricated MOF-5 was compared to the adsorption capabilities of the other adsorbent materials indicated in Table 2. In comparison to other published adsorbent materials in the literature, this table shows that the prepared nano-MOF-5 exhibits adequate and prospective performance for Cr(VI) removal from polluted water.

Table 2. Comparison of mono-layer adsorption capacities of Cr(VI) *via* different adsorbent materials.

Pollutant	Adsorbent material	Optimized conditions	Adsorption capacity (mg/g)	Reference
Cr(VI)	The prepared nano-MOF-5	Time = 15 min Dosage = 0.5 gL ⁻¹ Conc. = 25 ppm	91.22	This work
	JLU-MOF-60	Time = 10 min Dosage = 1.0 gL ⁻¹ Conc. = 80 ppm	72.01	[16]
	MIP-202 MOF	Time = 30 min Dosage = 2 gL ⁻¹ Conc. = 50 ppm	19.01	[3]
	Butylacrylate@chitosan	Time = 30 min Dosage = 0.2 gL ⁻¹ Conc. = 50 ppm	17.15	[17]
	Magnetic graphene	Time = 30 min Dosage = 0.1 gL ⁻¹ Conc. = 3 ppm	17.29	[18]
	Azadirachta leaves	Time = 60 min Dosage = 1 gL ⁻¹ Conc. = 75 ppm	10.20	[19]

3.2.6 Kinetic models of Cr(VI) decontamination process onto nano-MOF-5

The pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion kinetic models were used to investigate the Cr(VI) decontamination mechanism onto the fabricated MOF-5. The correlation coefficients for the linear graphing of the examined models were compared in Table 3. The strong R^2 of Cr(VI) decontamination from wastewater was detected when plotting t/q_t versus time. This shows that the Cr(VI) decontamination process onto the manufactured nano-MOF-5 agrees with the pseudo-second-order kinetic model. Moreover, the predicted and experimental constants are extremely similar. The correlation coefficient of the Elovich equation, on the other hand, was a high 0.996, indicating that the Cr(VI) adsorption process can be successfully explained using the Elovich model [2]. These findings support the hypothesis that the Cr(VI) elimination examined on the prepared MOF-5 is mainly described using chemisorption.

Table 3. Pseudo-first order, pseudo-second-order, Elovich, and intraparticle diffusion kinetic parameters for Cr(VI) decontamination onto nano-MOF-5.

Kinetic model	Parameter	Value
Pseudo-first order	$q_{\text{exp.}}(\text{mg/g})$	88.14
	$q_{\text{theor}}(\text{mg/g})$	41.17
	$K_1(\text{min}^{-1})$	0.021
	R^2	0.784
Pseudo-second order	$q_{\text{exp}}(\text{mg/g})$	90.17
	$q_{\text{theor}}(\text{mg/g})$	89.85
	$K_2(\text{g/mg}\cdot\text{min})$	0.084
	R^2	0.993
Elovich kinetic model	$\alpha(\text{mg/g}\cdot\text{min})$	-11.125
	$\beta(\text{g/mg})$	8.131
	R^2	0.996
Intraparticle diffusion kinetic model	$C(\text{mg/g}\cdot\text{min})$	0.455
	$k_i(\text{g/mg})$	0.038
	R^2	0.812

3.3 Reusability of the fabricated nano-MOF-5

One of the most essential variables is the adsorbent reusability studies, as it has an impact on the total cost of real-world applications [2, 12]. As a result, the manufactured nano-MOF-5 was reused six times for Cr(VI) decontamination in batch studies in order to evaluate its reusability affinity. As presented in Figure 9, the adsorption/desorption results demonstrate MOF-5's capability to recycle after six cycles, in which the decontamination reduced to 52.07%.

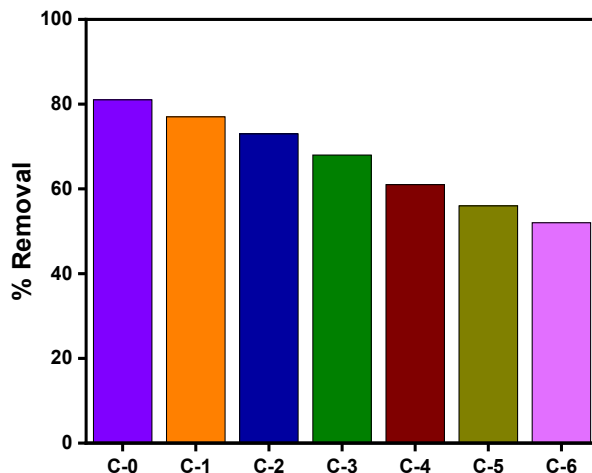


Figure 9. Recyclability of nano-MOF-5 for Cr(VI) decontamination.

Conclusion

In conclusion, we demonstrate in this study for the first time the efficacy of nano-MOF-5 in the decontamination of Cr(VI) from wastewater. The produced MOF-5, which is highly robust and processable, displayed effective Cr(VI) removal from wastewater. FTIR, XRD, HRTEM, BET, and TGA were utilized to characterize the functional groups, surface area, and thermal properties of the synthesized MOF material. The maximum monolayer adsorption capacity was recorded at 91.22 mg/g, and the Cr(VI) decontamination behavior was well-matched with the Langmuir model, indicating monolayer adsorption onto the synthesized nano-MOF-5. The best kinetic model for the description of Cr(VI) decontamination was a pseudo-second-order model. According to the above-mentioned data, nano-MOF-5 is a viable candidate for decontamination of Cr(VI) from polluted water due to its easy fabrication and recyclability.

Acknowledgments

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Metallic Oxide Nanoparticle from Agricultural Waste: A Review on Composition and Application

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Keywords: Fuel additives; ethanol; brake power; Internal combustion engine; fuel

Abstract. The rapid advancement in the extraction method of metallic oxide nanoparticles from agricultural waste has led to the significant use of agriculture waste in the nanotechnology industry because the use of chemical procedures in the production of metallic oxide nanoparticles produces hazardous toxic compounds that are dangerous to the ecosystem. In particular, this article examines the creation of silicon dioxide (silica) nanoparticles from agricultural waste. Environmental cleanup and wastewater purification are only two examples of the many areas where sand-sized silica particles (SNPs) have shown promising results. rural, agricultural, etc. The lack of toxicity of these particles has been demonstrated, making them an excellent tool for biomedical study. Additionally, because of the particles' ability to mobilize molecules onto their interior and external surfaces, they constitute good transporters for both biotic and non-biotic substances. In this regard, the current paper provides a thorough assessment of the sources of agricultural waste used in producing silica nanoparticles as well as the processes used to create it. The report also examines SNPs' most recent applications in a number of fields and discusses the technology's potential for the future.

1 Introduction

The creation of distinctive nanoscale particles is the subject of nanotechnology. These particles have found ground-breaking uses in a variety of sectors, including electronics, health, and consumer goods. One use of nanotechnology is the widespread adoption of silica nanoparticles in the industrial, food, and agricultural sectors in recent years. Normal methods of creating nanoparticles include chemical and physical processes. Some examples of physical processes include pyrolysis, high-energy ball milling, gas condensation, extreme plastic deformation, ultrasonic peeling, and shot peeling [1]. Usually, these methods are used to create metallic nanoparticles. On the other hand, chemical approaches include pulse electrodeposition, chemical coprecipitation, chemical vapor condensation, chemical reduction of chemicals and phytochemicals, and electrochemical treatments [2-4]. In contrast, chemical procedures use a variety of dangerous and toxic compounds that are bad for the ecosystem. Fossil fuels may not be as economically viable in the long run. Thus, it is intriguing to create a technology for commercially viable nano silica production from a silicon-containing biomass component.

This allowed for the development of green nanotechnology, which produces nanoparticles via biological and environmentally beneficial methods. In general, green nanotechnology creates nanoparticles using microorganisms (fungi, bacteria, and algae) and naturally sourced substrates (plant extracts). These techniques are not only environmentally beneficial but also reasonably priced [4, 5]. Typically, silicon alkoxides are dissolved in alcohol to create silica nanoparticles.

Researchers have found that metal oxides are crucial to the research of many different types of nano-materials. The size of an oxide's particles is very important to the structure, size, and other properties of a substance. For example, the chemical reactivity and electrical conductivity of metal oxides are highly dependent on their particle size [6, 7].

Surface qualities have a significant influence in the solid-liquid and solid-gas transformations, thus they are also crucial [8]. Sensors, coatings, agrochemicals, anti-corrosives, fuel cells, and catalysts are just few of the many applications [9, 10] for the metal nano-particles SiO₂, ZrO₂, CeO₂, and TiO₂. Iron oxide NPs, for instance, have found several uses thanks to their strong magnetic characteristics, such as in cell-component separation, drug delivery, nano-coating, and even food packaging [11–13]. The remainder of this study is a literature assessment on the feasibility of using leguminous agricultural waste as a source for producing silicon nanoparticles. Rice husk and corn waste are the agricultural wastes discussed in this article. Rice and corn waste were selected due to their availability in abundance as it is readily being consumed around the world.

2 Review

2.1 *Silica nanoparticles synthesis*

Silicon dioxide, more commonly known as silica due to its common usage, is an oxide of silicon that can be found in nature as quartz and in many different types of organisms [5] [6]. In many parts of the globe, silica is the predominant component of sand. Silica, which occurs naturally and may also be produced, is one of the most varied and widespread classes of materials. Notable examples include aerogels, opal, fused quartz, fumed silica, silica gel, and opal. It is utilized as an electrical insulator in microelectronics, structural materials, as well as pharmaceutical and food industries. There are two methods of synthesising silica nanoparticles. These include; chemical methods and biogenic methods.

2.1.1 *Synthesis of SNPs (Chemical Methods)*

Some of the most typical ways that silica nanoparticles are created include through sol-gel synthesis, Stober's approach, the "renowned synthesis," and microemulsions [14]. These chemical pathways are simple to use and can have their parameters changed, but they can be expensive and challenging to manage. In a reverse microemulsion, for instance, the water-soluble surfactant molecules dissolve to create micelles, which are then re-dispersed throughout the emulsion. It is necessary to separate the surfactants in the end goods, which can be costly and labour intensive even if the method is successful [15]. Nevertheless, the nanoparticles created in this way were successful in serving as coatings for functional group attachment [16, 17].

Another prominent method for creating silica nanoparticles is called chemical vapour condensation (CVC) [18]. This procedure calls for the combination of silicon tetrachloride, oxygen, and hydrogen. In this approach, the nanoparticles' desired qualities can be tailored by controlling their size and form. It is common practice to create nanoparticles using this method [19–21]. Similar to this, silica and silica gel are frequently synthesized using the well-known sol-gel process [22, 23]. Inorganic salts like sodium silicate and metal alkoxides like TEOS are hydrolyzed and condensed with the help of a catalyst, the acidic or basic action [24, 25]. The hydrolysis of the metal alkoxides (TEOS, TMOS) used to create silica particles results in silanol groups, which polymerize to create the silica structure. Werner Stober pioneered a new method, now commonly referred to as "Stober's method," and published his findings. By adding ammonia as a catalyst, he was able to turn a solution of silica alkoxide alcohol into spherical silica particles. Particle sizes varied from 5 to 2000nm [26]. This technique has improved throughout time, becoming much more adaptable and efficient in terms of setting parameters and achieving desirable features [27, 28]. Stober's approach typically results in monodispersed silica particles, whereas acid-catalyzed systems typically create gel structures [26]. Chemical synthesis methods have their advantages, but they are also very energy-intensive, resource-intensive, and prohibitively expensive, hence the development of biogenic processes was essential [29].

2.1.2 *Synthesis of SNPs (Biogenic Methods)*

Natural substrates and microorganisms like bacteria, fungi, algae, and plant extracts/metabolites are used in the biogenic methods of silica nanoparticle production [30]. For instance, the biosilicification process, which generates silica via silicatein and silaffin, has allowed for the

development of synthetic cationic polypeptides. In addition, numerous studies had looked at the viability of fungi for the production of silica. Aqueous anionic complex, for instance, was combined with the fungus *Fusarium oxysporum* and heated to create silica [31, 32]. Rice husk, sugarcane bagasse, and rice straw are a few examples of biomass that have recently been studied for the synthesis of silica nanoparticles [33–36]. First, silica from the biomass is extracted in order to make a sodium silicate solution [37]. Temperature, pH, and time are just a few examples of process factors that can and should be adjusted [38]. This method of processing biomass into products like silica nanoparticles, which are finding an ever-expanding range of applications, is commendable [39]. To remove any lingering contaminants before silica synthesis can begin, biomass is often treated with leaching agents after being cleaned with distilled water. [40]. Leaching is a process used to get rid of metallic contaminants that are present in biomass [41].

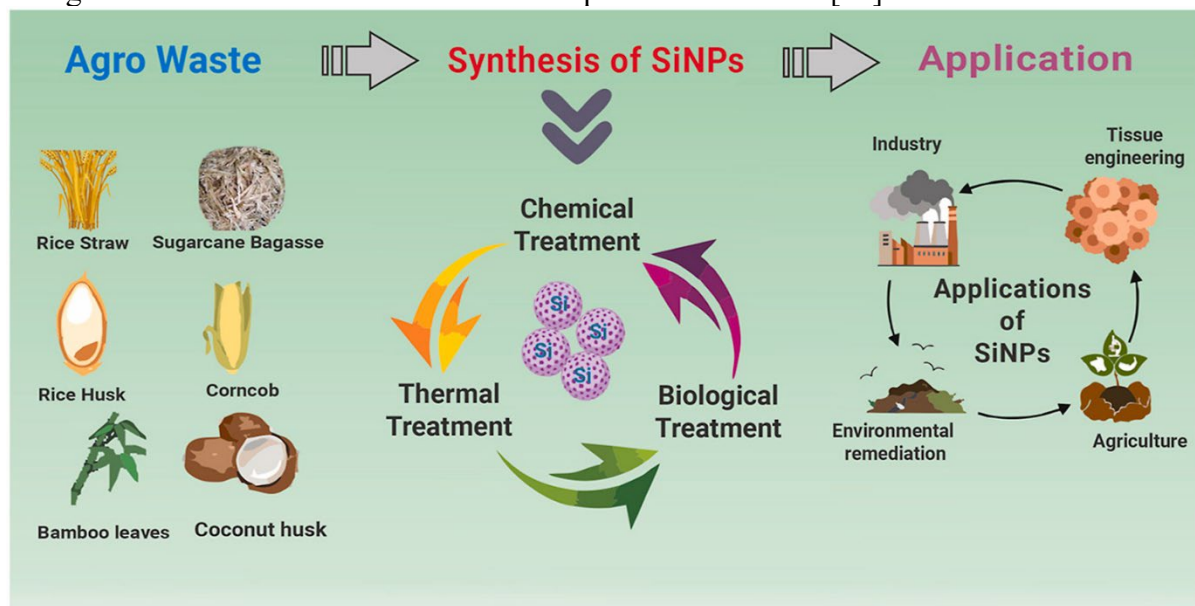


Figure 1. Sources of agricultural waste from which silica nanoparticles can be isolated [42]

2.2 Agro-waste availability

Manure, oil, silage plastics, fertiliser, pesticides, herbicides; poultry house, and slaughterhouse wastes; veterinary medicines; horticulture plastics; these are all examples of agricultural waste, which is the undesirable result of crop cultivation and animal husbandry [43]. There is a correlation between agricultural waste production per ton and the type of agricultural activity a country engages in [44]. So counties with a more crop-dominant agricultural sector produce more crop-based waste while others with more animal-dominant waste produce more animal-dominant waste [45]. The disposal of this waste also depends on the scale to which the farming sector is developed. If a farm field is mono-cultural, farmers may be tempted to let these waste materials fallow on their field in an attempt to replenish the lost soil nutrient. In areas with a good farming ecosystem, waste from a crop-dominant region is followed down to an animal-dominant region, where crop waste is used as feed for farm animals and animal manure is used as fertilizer for the field. Furthermore, excess plant waste could be used as roofing materials in some cases, but this type of application is discouraged because it is prone to fire and disease spread. Cash crops referred to crops that have high demand and these crops account for a lot of agricultural activity. Cash crops like wheat, corn, cotton, rice etc. are associated with the majority of agricultural waste [46-51]. Agricultural waste refers to the trash that accumulates from a wide variety of farming processes [52]. Before using wastes, it is necessary to thoroughly characterize them by looking into their physical and chemical characteristics [56]. Agricultural residues are used or reused depending on their availability. Limited knowledge of fuel feeding, combustion, and emission characteristics is the main obstacle to using these leftovers [57]. Depending on their availability and chemical makeup, the majority of agricultural wastes are regarded as appropriate and favourable for energy production. According to research, the ash concentration of rice straw and maize stalk is high (12.7 per cent and 9.31 per cent,

respectively), which is consistent with the high silica content of rice and maize [53–55]. But according to [58], sugarcane bagasse contains 2.4 per cent ash. The silica contents of the various bio-waste products vary [59].

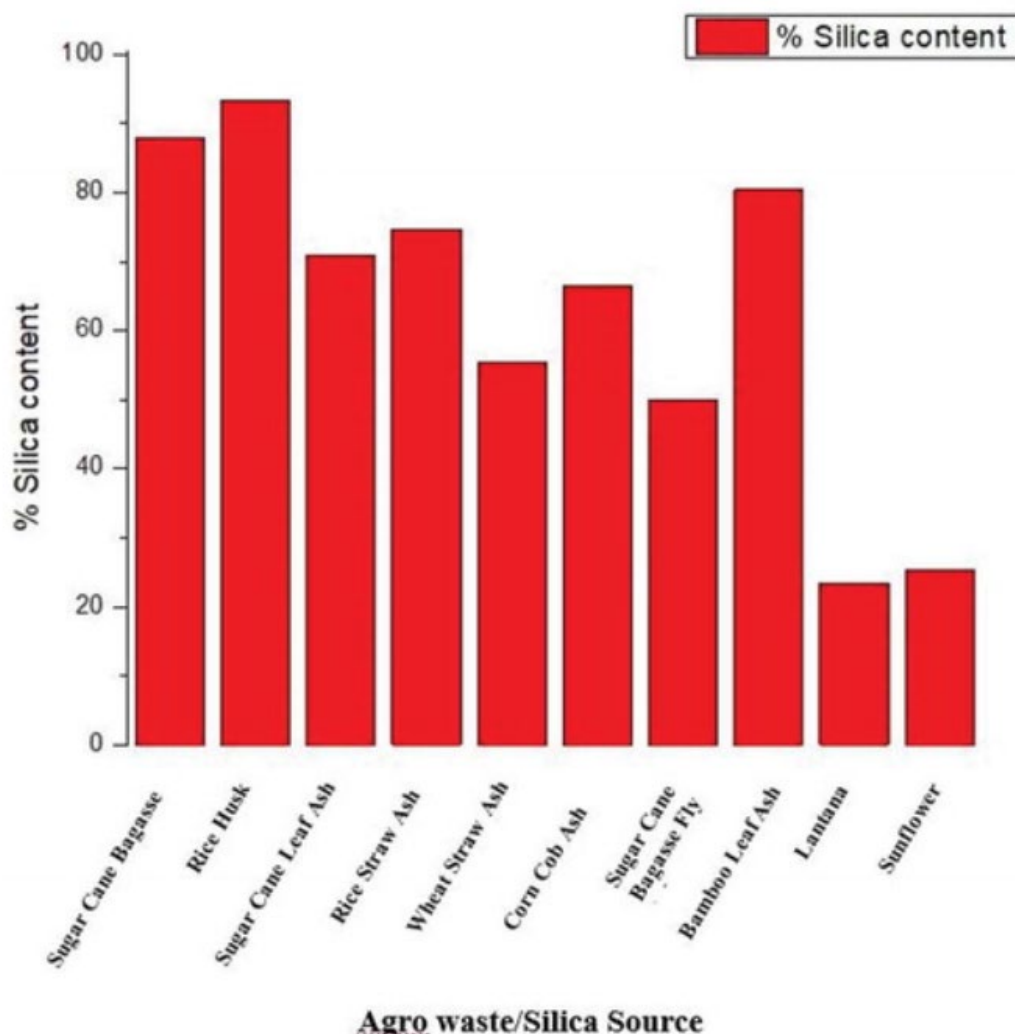


Figure 2. Percentage of silica in selected biowaste ashes [60-67].

2.3 Agro-waste sources for nano-silica and silicon

The potential of agricultural leftovers as a source of raw material for silicon composites has been gaining traction in recent years. Agricultural by-products are a cheap source of silica production [68]. Natural silica is safe to handle and inexpensive, among other advantages [69]. Numerous authors [70–74] have suggested various possible approaches and justifications for using agro-waste to produce silica. These include (i) the low cost of raw materials, (ii) the high concentration of silica in compost, (iii) the quality of the silica being equivalent, (iv) due to the amorphous material's tiny size, (v) a high energy content, and (vi) low energy consumption.

2.3.1 Rice husk ash

Rice husk ash is a major natural source of silica (SiO_2). It is a useless by-product of milling rice but an unavoidable by-product of farming. To the tune of roughly 90%, amorphous silica can be found in rice husk ash [75]. Nano-silicon crystalline particles are produced by treating rice husk ash with a sodium hydroxide solution and subsequently reducing the material in a magnesiothermic reactor. A solution of sodium silicate is produced after one hour of heating the combination (Na_2SiO_3). Later, sulfuric acid was used to precipitate the Nano silica. Hydrofluoric acid and distilled water were used in a washing procedure during the production of solid Nano-silicon particles, with the final stage

being a vacuum filtration of the residue. Silicon was ashed on a nanoscale and dried at 110 °C to create solid silicon [76].

In [77], it was described how to extract Nano silica from rice husk ash using an alkali-leaching technique. Metallic contaminants were dissolved by treating rice husk samples with strong hydrochloric acid. After that, they were washed with distilled water and air-dried. The samples were dried, and then any leftover organic material was burned off in a muffle furnace. Sodium silicate solution was made by heating ash and 1.5 M NaOH solution together at 100 °C for an hour while stirring constantly. It was determined by neutralising a sodium silicate solution with hydrochloric acid, sulphuric acid, citric acid, and oxalic acid which acid was most effective at precipitating nanosilica. Researchers [78] employed an acid leaching technique to extract the Nano silica from the rice husk ash, and then [79] thermally treated the ash after testing it with a variety of acids (sulphuric acid, hydrochloric acid, oxalic acid, and an ionic liquid). As a group, they investigated how silica could be refined from rice husk to increase its purity. In a muffle furnace at 800 °C for 48 hours, the chemical residue was pyrolyzed to produce nano silica. After hydrothermally activating rice husk ash (RHA) in 2 M NaOH, Mor et al. [80] observed that a sodium silicate-containing supernatant solution was produced, which they used to produce nano-silica particles.

2.3.2 Corn cob ash

Corn cob ash is one of the agricultural wastes used to create nano silica. Every year, people eat a lot of corn, which turns into a lot of ash from corn cobs. Corn is burned on the cob and consumed as the ashes are being piled up. Nano-silica could be made from corn cob ash, as has been discussed in a number of articles. Two investigations used corn cob ash as a source material for creating nano silica [76, 81]. Corn cobs were roasted for three hours at 650 °C to act as an activating agent in a reaction that was then carried out using a 1 M NaOH solution. The cooled ashes were mixed with 1 M sodium hydroxide to create a sodium silicate solution. After stirring in 3 M HCl, the pH was titrated down to 7. It was washed and dried as a precipitate. According to [82], Nano silica was extracted from corn cob ash at a range of pH values using Sol-gel technology. Again, [81] explains how to make nanostructured silica using the sol-gel process and the template concept. After vigorously mixing the hexadecyltrimethylammonium bromide (CTAB) and distilled water for 5 minutes, the solution was clear and colourless. After letting it sit for 20 hours, we added the extracted silica and then slowly poured in some ammonium hydroxide while stirring. After that, the nano silica was cleaned and dried. The following phase involved heating the Nano silica to 550 degrees Celsius within a muffle furnace.

2.3.2 Wheat straw ash

Wheat straw, a common agricultural byproduct with a high silica content, has been the subject of substantial research. Wheat straw production exceeds 500 million tonnes annually. Wheat straw fires in the field pose serious risks to wildlife, pedestrians, and motor vehicles [83]. Nearly a third of the world's population, or 2.45 billion people, eat mostly wheat for sustenance. The Nano silica in wheat straw was removed using acid leaching and subsequent combustion [84]. Combustion was placed at 500 °C for 8 hours, and wheat straw was burned in a muffle furnace. Silica's real nature as the ash cooled made itself known. Wheat straw (10 grammes) was acid treated by combining it with 100 millilitres of a 4:1 concentrated HNO₃ and H₂SO₄ aqueous solution at 60 to 70 °C for 24 hours, after which it was centrifuged and washed multiple times. Powder was extracted and then dried. Additional methods for producing Nano silica from designated agro-waste types are detailed in Table 1.

2.3.3 Sugarcane bagasse ash

Sugarcane bagasse is an interesting part of this study because it is a by-product of the ethanol and sugar milling industries. Sugarcane bagasse ash (SCBA) is a by-product of the sugar and bioethanol industries that has the potential to replace more expensive natural silica. Researchers from all over the world are exploring the potential use of silica derived from bio-waste, particularly sugarcane bagasse ash [93]. However, the location and climate in which the sugarcane is grown, in addition to the farming practises employed, have the greatest impact on the silica concentration of the resulting

bagasse ash. Sugarcane bagasse ash, which has excellent pozzolanic abilities, can be used in place of cement to improve the properties of concrete and keep the desired strength [94]. Several authors have demonstrated that sugarcane bagasse ash can be used as a partial substrate in the production of concrete [95, 96]. The amount of silica present in sugarcane bagasse ash is particularly important for concrete mixes. This is because it has an effect on the quality of the concrete production.

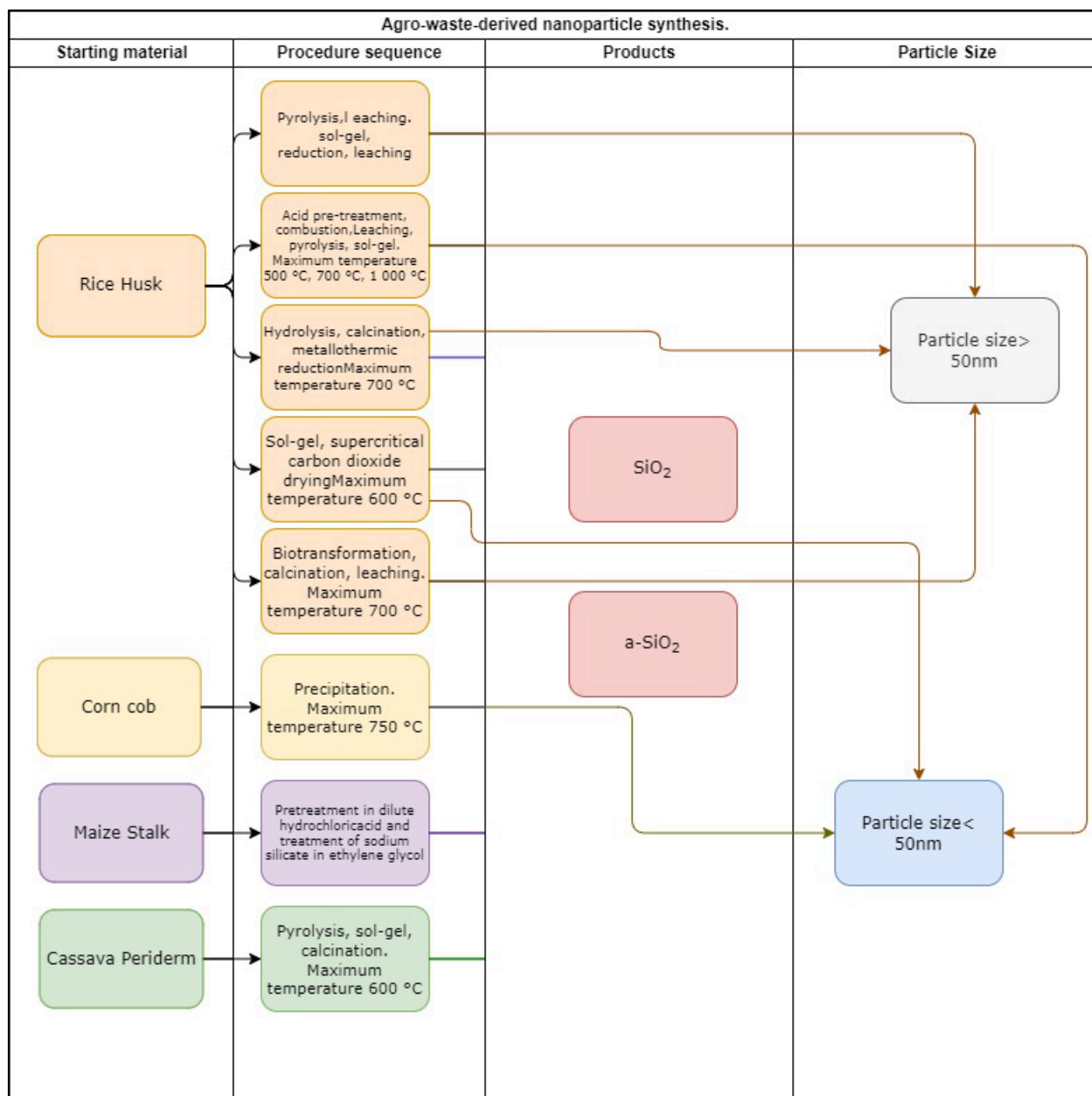


Figure 3. Agro-waste-derived nanoparticle synthesis [70],[76],[85-92].

2.4 Method of preparing nanosilica

Silica has been produced from biomass using two frequently used methods: thermal and chemical.

2.4.1 Thermal methods

Thermoprocessing tools include muffles, fixed-bed furnaces, fluidized-bed reactors, rotary kilns, and inclined-step grate furnaces, among others. Some of the drawbacks of thermal technology include longer reaction times, the potential for hot spots to form, and the inability to fully oxidise carbon due to a lack of circulating air.

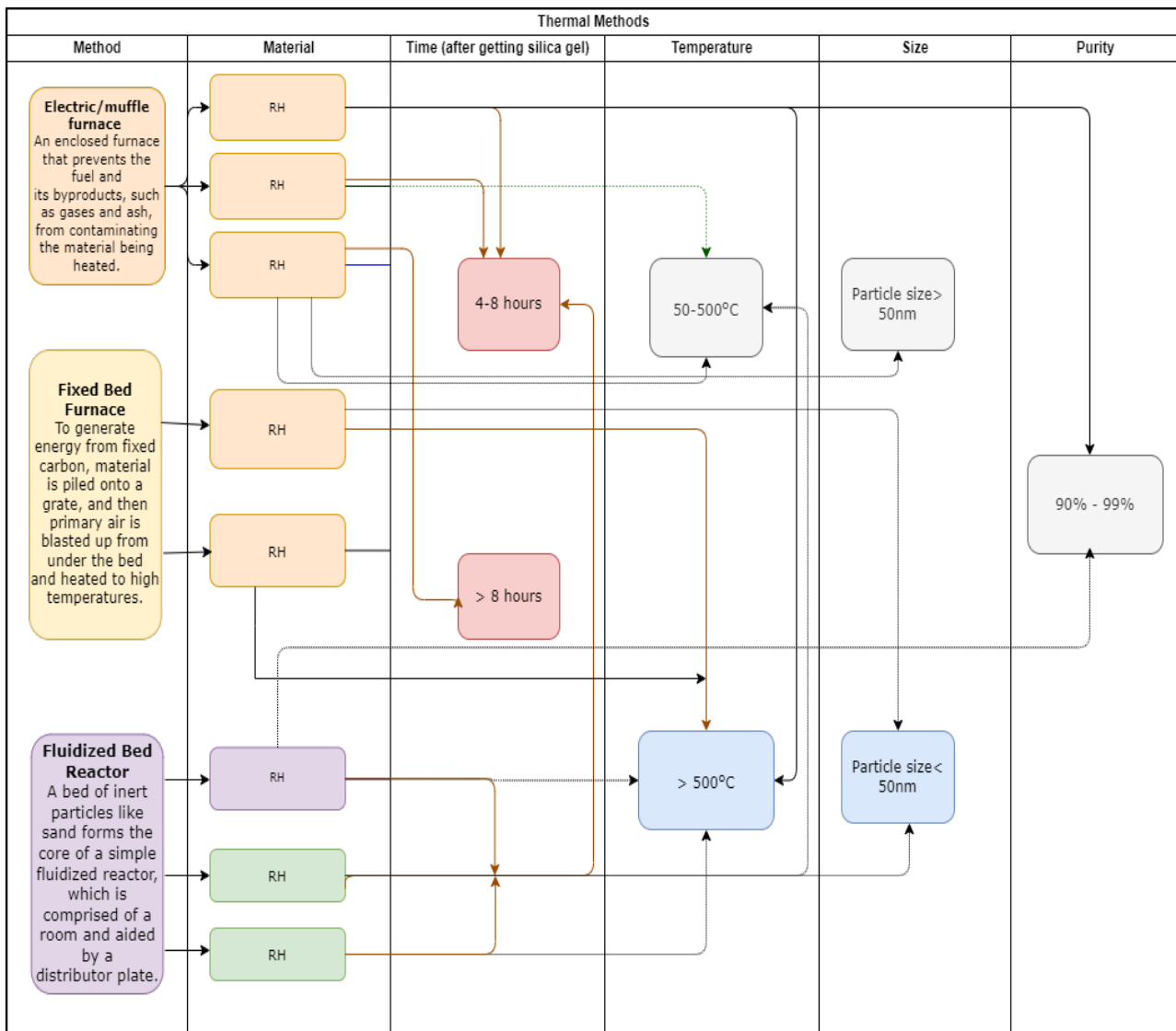


Figure 4. Thermal Methods of preparing nanosilica [84], [97-104]

2.4.2 Chemical method

Pure and large volumes of silica can be extracted chemically using methods like alkaline extraction. This strategy is more costly because it takes longer to complete (24-48 hours) and requires more processes and different kinds of chemicals. Before any chemical processes are applied, RH is often subjected to a thermal procedure (incineration) in order to obtain RHA.

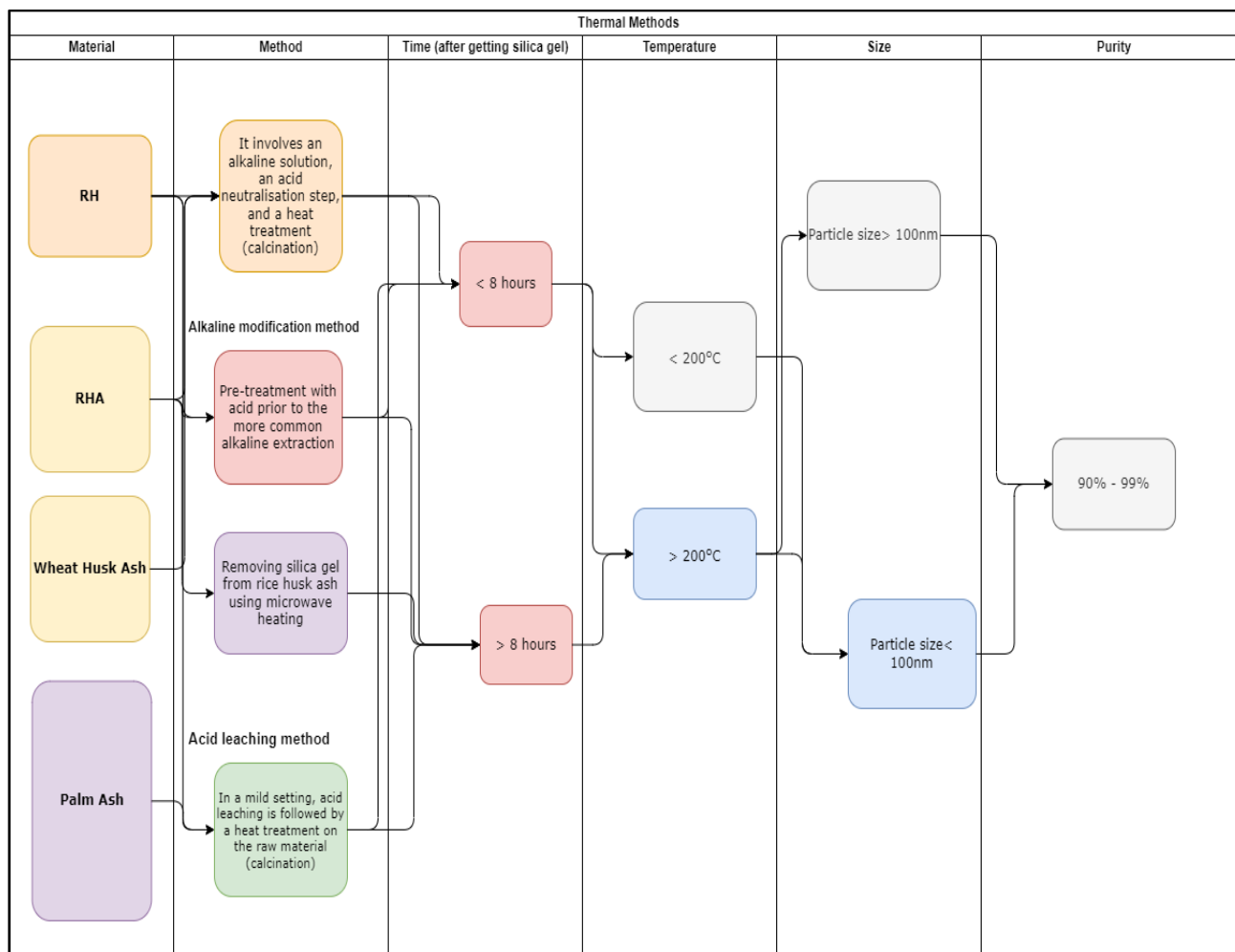


Figure 5. Chemical method of preparing nanosilica [105-120]

2.5 Application of silica nanoparticles

Increased agricultural output assures the survival of the world's expanding population. Sadly, insect and microbial attacks can significantly lower its output. Using pesticides to remedy this problem has worsened the situation due to health and environmental issues. Pesticide abuse is bad for the environment and people's health in addition to the soil. If pesticides are sprayed directly onto crops, they may be absorbed and stored inside the plants. This can lead to a range of health problems in humans, including asthma, neurological disorders, hormone imbalances, and even cancer [121]. This has prompted scientists to create an environmentally friendly insecticide. In addition, boosting seedlings' resistance to microbial assaults is another strategy to do away with pesticides. By utilizing mesoporous silica nanoparticles (MSNs), this has been made achievable [122, 123].

Torney et al [125] used a chemical inducer to successfully load MSNs with genetic material, which the cells of maize seeds and leaves subsequently absorbed. Treatment of maize seeds with silica nanoparticles before to planting increased their nutrient content, germination rate, and resistance to disease. In a similar vein, Siddiqui et al. [126] found that using 8g/L of silica nanoparticles (SNPs) increased the germination rate by 22.16%. This exemplifies the relationship between silica nanoparticle concentration and germination rate. Maryam et al. [127] conducted a recent study that highlights the importance of mentioning poly-ethyleneimine (PEI) coated MSNs. The particles included pDNA, which enabled efficient and effective transfection of the genetic material into plant cells when subjected to ultrasound therapy.

It has been discovered that SNPs can be used to increase the storage life of food, which is only one of their many potential uses. As a result, several types of fruits can now be coated with silica-based hybrid films to keep them fresher for longer [128]. Several experts have analysed this fresh strategy, and they all recommend it. By combining nano-silica and chitosan, for instance, Mirzadeh et al

[129] made a hybrid composite film. The longan fruits' shelf life was significantly extended when the film was applied to them. The film also lessened the fruits' tendency to lose weight and become brown. The same hybrid film coating was applied to loquat in a different study [130], and the results showed improved enzymatic activity, a longer shelf life, and higher quantities of reducing sugars.

A serious issue on a global scale is lead air pollution [131]. In order to study lead absorption from the atmosphere, a group of researchers led by Yang [132] used SNPs with electrical charges and subjected them to two lead-contaminated plants. The study found that SNPs who were exposed to toxic plants absorbed significantly more lead from their surroundings than those who were not. It was also the pioneering study of its sort. Nashwa et al. [133], who biosynthesized silica nanoparticles from rice husk, undertook one of the most current studies in this field. The *Trichoderma harzianum* MF780864 was utilized to induce the particles, which were then employed to remove lead from water. The expense and thorough research are obstacles to the use of nanoparticles in environmental clean-up. He et al [134] engineered mesoporous amorphous silica nanoparticles (MSNPs) with larger pores and more surface area. Trace amounts of mercury were successfully eliminated from aqueous solutions using the produced nanoparticles.

Numerous investigations have shown that silica nanoparticles are effective at removing heavy metals from aqueous solutions, lending credence to their prospective application in the purification of industrial effluent [135]. It has also been shown that the SNPs can cut or even eliminate the need for biological oxygen. This type of BOD activity is superior to older, non-SNP based methods [136]. In a study, Park et al. investigated the efficacy of silver nanoparticles combined with SNPs against a bacteriophage and a murine norovirus in water samples gathered from the ground, the surface, the faucet, and deionized water.

Conclusions and Future Prospects

The use of silica nanoparticles (SNPs) has already made a significant contribution to nanotechnology. The material's versatility is due in major part to its mesoporous structure, vast surface area, adaptable particle size, pore size, and shape, and biocompatibility. These nanoparticles have made significant contributions to many different areas, including agriculture, food preservation, biomedicine, and catalytic reactions. In vitro studies have shown that SNPs are effective encapsulating materials for a variety of bioactive substances, making them well suited for the secure delivery of targeted pharmaceuticals. The versatility of SNPs has been further expanded by their capacity to form hybrid composites with both polymeric and non-polymeric materials. In chemotherapy, mesoporous silica nanoparticles (MSNPs) are utilised to target specific cancer cells due to their exceptional carrier properties. Overall, SNPs have shown to be a secure, trustworthy, and beneficial option, and their significance is expanding across virtually all markets. The authors conclude from their in-depth examination of this amazing material and its rapidly expanding applications that further research is warranted in the following areas:

1. More investigation is required to find more MSN-compatible immobilizing compounds that can be used for catalytic reactions in single-pot systems without compromising system environment or mutual reactivity. Additionally, it is necessary to define the optimization parameters for such multi-immobilized MSN species employed in single-pot catalytic reactions.
2. SNPs have the potential to entrap colourless and poorly water-soluble medications for targeted delivery, but more research is needed.
3. More seeds, like maize seeds, need to be made available to the public so that SNPs can be used to increase antifungal capabilities.
4. Investigate whether some crops' SNPs increase their ability to withstand stress in saltwater environments, whereas other crops' SNPs cause a decrease in chlorophyll.

5. A hybrid chitosan-silica film has been found to extend the shelf life of loquat fruit. In this regard, it is necessary to use more fruits that, when combined with the same hybrid flower, can create a longer shelf life.
6. Additional enzymes must to be researched and tested for encapsulating onto MSN fibres.

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CHAPTER 6:
Building Materials

Use of Insulation and Phase Change Material in Building Structures – Experiments and Physical Analysis

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Abstract. The present work concerns an experimental study of the utilization of insulation and phase change material PCM in building structures. It particularly presents an efficient heating system modulated with thermal insulations and phase change materials where an appropriate experimental setup is devised to help in making energy management possible. The experimental setup consists of insulated and non-insulated room models that enable direct observation of different heat transfer results between a well-insulated room with PCM (paraffin wax) and a non-insulated room. The integrated heating-insulation-PCM set-up proved that it can work toward a more comfortable and efficient system where energy bills are 74% lower with an average improvement factor reaching 50% in comparison with the non-insulated room model.

Introduction

In an economy burdened by the costs of increasingly scarce oil and natural gas, and a planet suffering the impact of fossil fuel and climate change, the technological revolution of this era is renewable energy [1-5]. Sunlight, wind, water, geothermal heat and plant biomass are all essentially limitless resources and they are all proven technologies that work at any time used. Each region of the earth has its renewable sources from the vast wind potential to the solar mother lode that in the Middle East, and when they are used all together, renewable energy offers a clear global solution to many problems. This technology works but a renewable future requires a political will and a new way of thinking in which a farm harvests wind, fuel and solar energy [6-8]. Regarding energy management, residential and commercial buildings are responsible for nearly one third of total energy usage and carbon dioxide emissions [9-12], and making these buildings more energy efficient [13] will have a significant impact on climate and economy and that would be done by converting buildings into high performance facilities [14].

Phase Change Material PCM is known mainly as a heat storing material as well as an insulation-supplement that can be placed in the concrete floor during construction [15-18], not only to minimize the fluctuation in the floor surface temperature, but also to reach sufficient heat charging [19] so that heating can be done during the off-peak periods [20-24].

The diversity of heating systems shows a lot of differences in the heat distribution method, away from primitive heating system, radiators are considered to be a popular heating system and is used widely in Lebanon. When it comes to energy management, it is not efficient to work with radiators because of their functions' high temperature requirement and the smaller area of heat exchange;

unlike underfloor heating which has a greater heat exchange area to categorize underfloor heating system as a low temperature gradient system [25-29]. Besides, radiators do not offer even heat distribution in the heated space [30]. On the contrary, under floor heating offers a comfortable temperature gradient in the room which is distributed evenly. Underfloor heating also allows the freedom of designing the room layout without compromises [31-32]. It is a more flexible and safer system as no space is lost to radiators and external heaters.

Schwartz et al. [33] used multi objective genetic algorithms to find optimal design for refurbishment of a residential complex case study in terms of life cycle carbon footprint and life cycle cost, where life-cycle impacts of insulating thermal bridges and the importance of using different heating systems and fuels were emphasized. Berger et al. [34] proposed a novel top-down methodology for generating aggregated load curves on heat demand with a focus on residential space heating. Jin et al. [35] explored the potential of adaptive insulation by means of a parametric study on a specific building topology, where properly designed and controlled adaptive insulation can significantly improve the insulation performance. Ramakrishnan et al. [36] fabricated thermal energy storage cementitious composite TESC based on paraffin and expanded perlite to study the thermal performance of an experimental room during summer in order to prove how TESC can provide remarkable annual energy savings. V. Rao [37] reviewed details including different PCM-mortar combinations in addition to their thermal and mechanical properties in the field of synergy of PCM achieving energy efficiency in buildings. El Mais et al. [38] tested a well-insulated house prototype with application of petroleum jelly as PCM with electrical underfloor heating system to save electricity consumption with the presence of PCM.

As shown above, use of PCM and insulation in building structures is becoming a necessity in modern buildings rather than an option or a luxury. In this context, this study highlights the importance of utilizing thermal insulation and phase change materials PCMs in building structures. It particularly presents an underfloor heating system modulated with thermal insulation and PCMs with an appropriate experimental setup devised.

To prove the homogeneity and effectiveness of thermal insulation and PCM in construction, two room models are built and tested. One model is insulated with PCM presented by paraffin wax installed in the floor next to hot water pipes of the underfloor heating system. The other room in contrary is not insulated and no PCM will be installed in the floor. This project aims to prove technical results that show the difference between the insulated- equipped with PCM prototype and the non-insulated prototype, all to prove how insulation and PCM can work together toward a more efficient design.

Materials and Methods

The components that are used in the experimental setup (Figure 1) are:

1. Underfloor heating system
2. Wall insulation system
3. Paraffin wax as PCM

Planning an applicable design is carried out in such a manner to harmonize with the performed calculations and assumed constants where picking the listed components is a crucial part to have a successful design and reliable experimental results.

Underfloor Heating System. Underfloor heating (Figure 2) works by establishing special tubing in a concrete foundation or in a thin concrete mixture on top of a wood-framed floor. Heated water flows through this tubing, warming the thermal mass of the concrete. The Floor area is typically warmed to between 25°C and 35°C, providing an even distribution of heat at only slightly higher than room temperature. The system is then controlled by one or more thermostats which control the manifold and boiler as required [39]. Water pipes can be installed in different patterns for concrete or timber floors where reverse spiral or helical layout is chosen for even distribution of temperature.



Fig. 1. The final room prototype from an outer view.



Fig. 2. Spiral water loop pipes installation.

Insulation System. On account of improving the energy consumption of buildings' heating systems, thermal insulation is used. It is known as a material made to be provided with thermal properties including thermal conductivity and resistance. When heat always flows from warmer to cooler surfaces, the basic requirement for thermal insulation is to provide a significant resistance path to the flow of heat through the insulation material. This is a very important element for estimating comfort and increasing the efficiency of the heating systems [40-41]. Many types, forms and installations of thermal insulation are used to minimize heat loss to outer colder atmosphere in winter and heat gain during summer [42]. Polystyrene foam panels are used in this project [43] to insulate the wooden walls in one of the prototypes built (Figure 3). The choice of ply wood to construct the room is due to its lighter weight compared to brick and the lower thermal conductivity of wood [44-45].

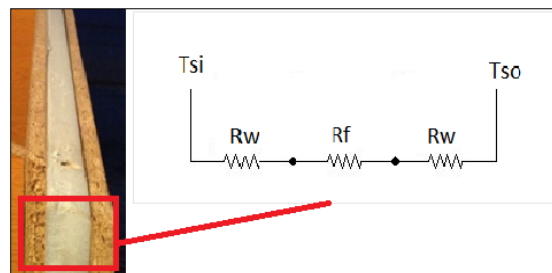


Fig. 3. Insulated wall construction and a representative conduction thermal resistance circuit.

To get the thermal conductivity values of walls experimentally, the linear heat conduction unit shown in Figure 4 was used in linear heat conduction test to measure the temperature distribution for steady state condition of energy through a uniform plane wall of foam and wood, that is to demonstrate the effect of insulation materials. Two specimens were used and both are of the same

radial dimension to fit into the specimen gap. Rigid polystyrene foam specimen has a 25mm radius and 16mm thickness, while wood specimen was of 12.7mm thickness. For both rigid polystyrene and wood, the conductive coefficients were 0.13 W/m.K for wood and 0.3 W/m.K for polystyrene foam insulation.



Fig. 4. H111 Heat Transfer Service Unit and Data Logger

PCM (Paraffin wax). Energy storage is one of the most critical areas that energy management is counting on presently, which makes engineers interested in ways to developing electrical and thermal energy storage technologies. To store thermal energy, sensible and latent heat storage materials are widely used. Latent heat thermal energy storage systems use phase change materials (PCM) that are useful because of their ability to charge and discharge a large amount of heat from a small mass at constant temperature during a phase transformation. The latent heat storage method provides much higher storage density, with a smaller temperature difference between storing and releasing heat unlike the sensible heat storage method [46-47].

To sum up, thermal storage technology uses phase change material which changes from solid to liquid at certain temperature, and in this process, it stores latent heat which is a considerable amount of heat storage in a small volume. Paraffin wax has been chosen in this project since it is widely available, chemically and thermally stable and is not corrosive. Paraffin wax is encapsulated in PEX pipes identical to the hot water pipes as shown in Figure 5, and are installed in the concrete floor next to hot water pipes as shown in Figure 6 so that when the heating system is on, the wax would store latent heat as it melts to be unleashed when hot water no longer flows in the pipes when the system is turned off.



Fig. 5. Paraffin wax pipe installed in the floor



Fig. 6. Paraffin wax pipe installed in the floor.

Configurations and Conditions. Testing the two room models under various conditions is necessary. This design includes two room models that are one-meter cube in volume each and differ by insulation and phase change material. The sample design for the two room models from an outer view is the same and is represented as shown in Figure 7.

At this point, two weather conditions are considered by setting two different outdoor conditions. One test is performed in a refrigerated warehouse having an ambient constant temperature of 5°C that represents a cold winter day. Another test is performed in normal weather conditions of a spring night at temperatures ranging from 13°C to 16°C. Values of temperature at critical settings are quantified using thermocouples and the main setting that is crucial in the heating process is the inner atmosphere of a room. The temperature of the inner surface and outer surface of the walls is also recorded to check the validity of the insulation used compared to the non-insulated walls. The locations of thermocouples used are provided in Figure 7.

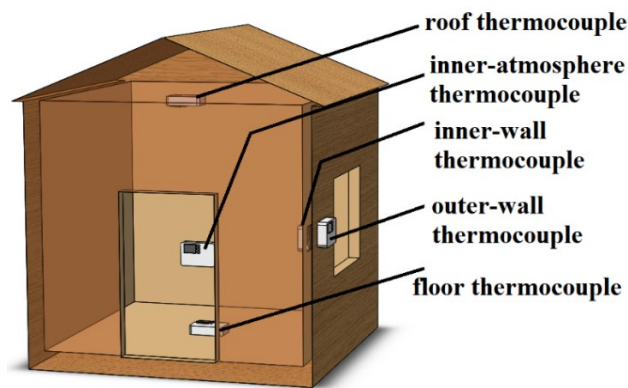


Fig. 7. Locations of thermocouples for both room models.

The procedure is simply summarized by pumping hot water from a water tank that uses an electric water heater to underfloor heating pipes. After about 10 to 20 minutes, the temperature rises in the room to stabilize at 22°C. That is when the heating system is turned off and temperature starts falling, the role of insulation and PCM comes here to preserve the heat inside the room model. Accordingly, using underfloor heating imposes controlling the floor temperature to procure comfort of occupants stepping on the floor and the inner wall temperature to control the heat lost through walls. These values are to be compared for insulated room furnished with PCM and the non-insulated room.

Results and Analysis

The temperature variation of the critical settings of the insulated and non-insulated rooms is shown in Figure 8 tracked for 33 minutes after the heating system is turned off.

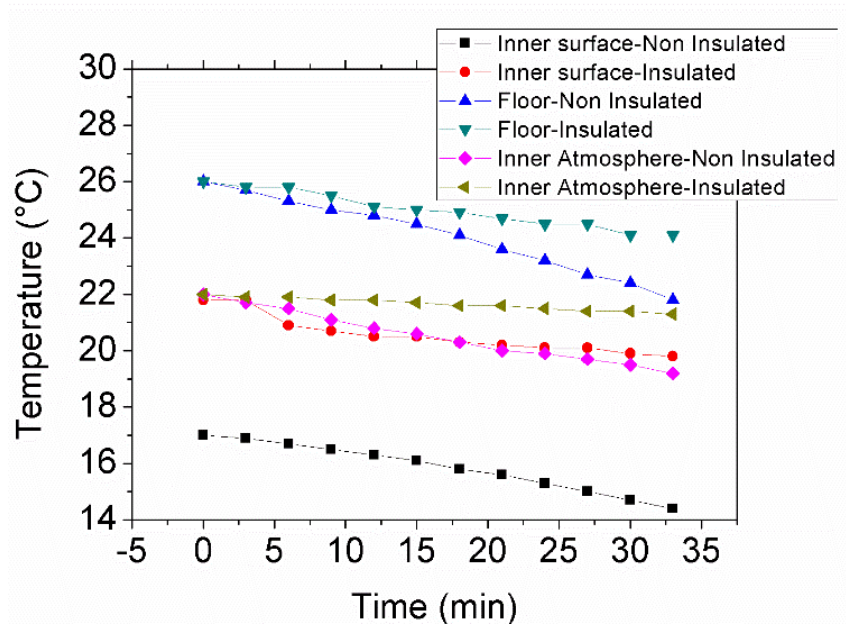


Fig. 8. Temperature temporal variation for insulated and non-insulated rooms for 5 °C of ambient temperature.

It can be noticed clearly how the insulated room with PCM is able to preserve heat where the drop in temperature was slighter compared to the non-insulated room. Considering the atmosphere temperature as the most influential parameter on the comfort factor, the temperature drops from 22°C to 21.3°C after 33 minutes in insulated room, unlike the non-insulated where temperature drops from 22°C to 19.2°C. It is also important to perceive that inner wall surface temperature, in the insulated room at minute 0, reached 21.8°C which is almost equals to that of inner atmosphere and drops to 19.8°C, conversely to the non-insulated room inner wall that had an initial temperature of 17°C that drops rapidly to 14.4°C after 33 minutes.

The noticeable difference between the wall surface temperature at time 0 of the insulated and non-insulated models respectively (21.8°C and 17°C) where the heating system was still providing heat, is directly owing to the foam insulation mounted in the insulated room model. This helped in maintaining heat while and after the system was on. Moreover, the thermostat placed in the floor has a critical use since occupants will step on the floor and it is much important to reach an acceptable temperature underneath to prevent any annoyance or dysfunction. The floor temperature must not exceed 30°C which is the absolute maximum in comparison with blood temperature which is 37°C and in this test, the maximum floor temperature reached and stabilized at 26°C for both rooms and started to dropping as the system was turned off. This proves that underfloor heating is more energy saving since it requires lower temperature values to operate in comparison to radiator heaters. After 33 minutes, the floor temperature of the insulated room dropped slightly to 24.1°C compared with the non-insulated room floor's temperature that reached 21.8°C. Taking into account that both room models have insulation boards beneath the hot water piping system, the floor temperature of the insulated model is retained by dint of the paraffin wax installed in the floor.

The heat rate (heat lost by conduction through the structure from the inner space to the outside of the room) variation is represented in Figure 9 as a function of time.

It can be observed in Figure 9 that the heat transfer values for the non-insulated room are higher constantly with respect to the heat transfer of the insulated room which is considered significantly low. At time 0, the heat transfer rate for the non-insulated room was 378 W which is almost double the value of heat loss through the insulated room which is 176 W. Furthermore, heat transfer rate decreases rapidly for the non-insulated model to reach 273 W after 33 minutes. On the contrary, the heat transfer rate of the insulated room drops slightly to reach 153 W after 33 minutes. Thus, the variation of heat transfer in the insulated room is almost constant compared to the non-insulated

model which shows the function of insulation and phase change material that is to reduce heat loss and generate latent heat to recoup the temperature drop inside the room.

This huge difference in values of heat rates between the insulated and non-insulated rooms is directly related to thermal insulation used to preserve heat inside the heated space and reduce heat transfer effect in the system.

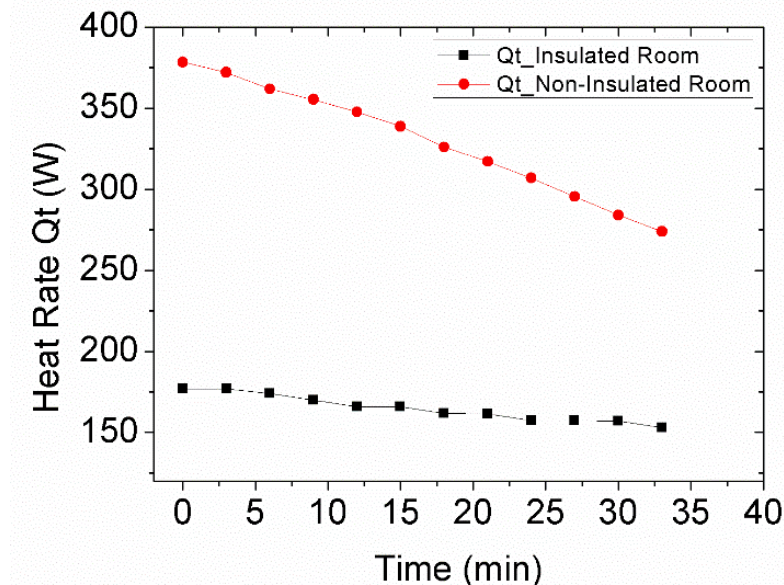


Fig. 9. Heat transfer temporal variation for insulated and non-insulated rooms.

In natural ambient conditions, the temperature cannot be controlled and fixed to a specific constant. Spring weather did not help in performing this test according to the set assumptions. Starting from temperature analysis for the two models in natural-ambient conditions testing presented in Figure 10, inner atmosphere temperature starts dropping from 22°C for both insulated and non-insulated rooms and decreases harmonically for 25 minutes to reach 21.8°C. The non-insulated room curve decreases more sharply reaching 18°C compared to the insulated room curve that reached 20.8°C after 90 minutes. The insulation installed in the wooden walls helped in retaining a higher temperature of inner space, while the non-insulated room lost heat faster. Moreover, the PCM installed in the floor generated heat throughout 90 minutes when the heating system is turned off by releasing the energy it stored.

The inner surface temperature curve shown in Figure 10 starts from 21.8°C for insulated room model and starts decreasing slightly as time passes to reach 20.2°C after 90 minutes. For the non-insulated room, the temperature of the inner surface was 18.9°C and decreased to 16.4°C 90 minutes later. The inner surface temperature of the non-insulated model is relatively lower than the insulated model inner surface temperature since thermal insulation helped in dwelling the heat by diminishing the effect of heat transfer by conduction through the walls, unlike the non-insulated room model that has a relatively low inner wall temperature even when heating system was still tuned on. The floor temperature curves presented in Figure 10 started with a high temperature at zero minutes for insulated and non-insulated for 28.6°C and 28.1°C respectively. The larger decrease for the non-insulated model reaching 22.1°C after 90 minutes compared to the insulated model reaching 25.8°C might be due to re-solidifying PCM that causes energy emission which helps in keeping higher temperatures in the insulated room. That is, the floor surface lost heat more rapidly in the non-insulated room due to the absence of thermal insulation and PCM.

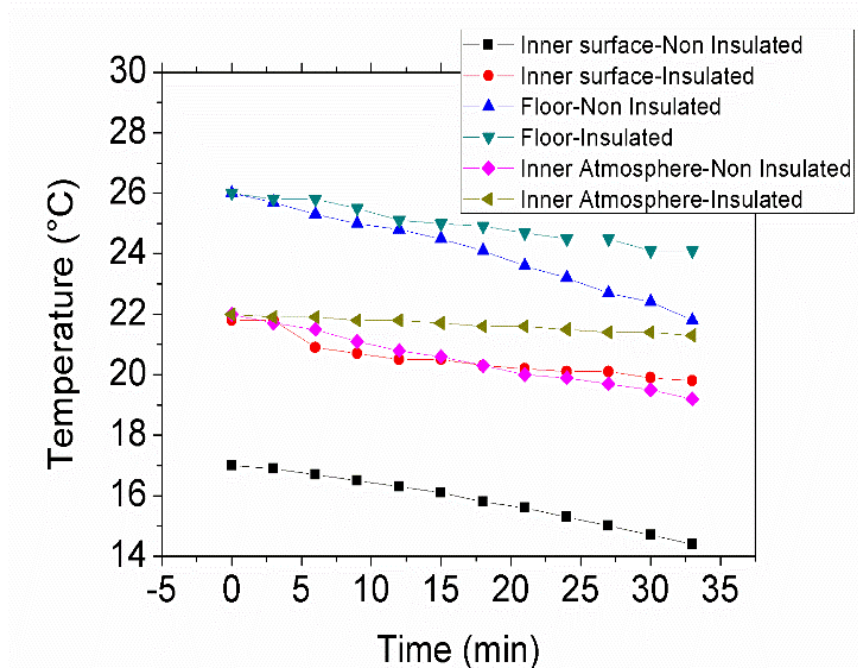


Fig. 10. Temperature temporal variation for insulated and non-insulated rooms for natural ambient conditions.

The heat transfer rate presented in Figure 11 shows the difference in values between insulated and non-insulated rooms with a fine value for insulated room of 16.22 W which is almost one tenth the heat rate value for the non-insulated room 147.744 W. The curves fluctuate in accordance to outer temperature fluctuations which directly affects the total heat transfer value reaching a final value of 11.42 W for the insulated room and 88.211 W for the non-insulated room after 90 minutes. Hence, the difference between the curves is clear and can be related to the existence of phase change material that helps in storing energy to be supplied when the system is off and the wall insulation that prevents heat from transferred to the cooler region. One more possible reason that the heat flux decreases with time might be due to the lower values of temperature as time elapses since the heat rate is directly proportional to temperature.

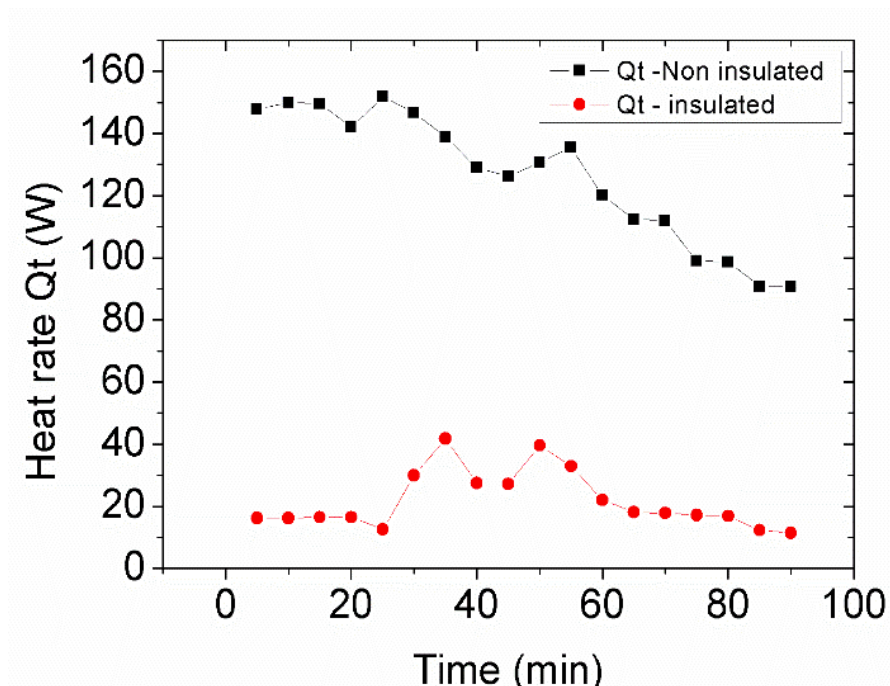


Fig. 11. Heat transfer temporal variation for insulated and non-insulated rooms for natural ambient conditions.

Economic Considerations

The world is in a race to determine energy future where energy challenge is about finding unconventional alternatives to power our houses, vehicles and factories. Many experts believe that half the planet's recoverable oil has been burned through and eventually it will run out. This means that as supplies dwindle, prices will soar, the cost of power will make it a luxury item and energy will be so hard to generate. Technically, executing the models was important to provide more evidence that insulation and phase change material can eliminate about half the value of the heat loss compared with the non-insulated room model, and by reducing energy loss, power is being saved.

The values of heat transfer rates of the two models can be underpinned using the improvement factor scale that can be obtained by comparing the insulated and non-insulated room models according to different heat transfer rates and is presented by:

$$\alpha = \frac{(Qt)_{ins}}{(Qt)_{non-ins}} \times 100 \quad (1)$$

Eventually, two values can describe the success of the design attained after testing the models to have an average improvement factor of 50.25 % shown in Figure 12 comparing the insulated and non-insulated model and is increasing overtime.

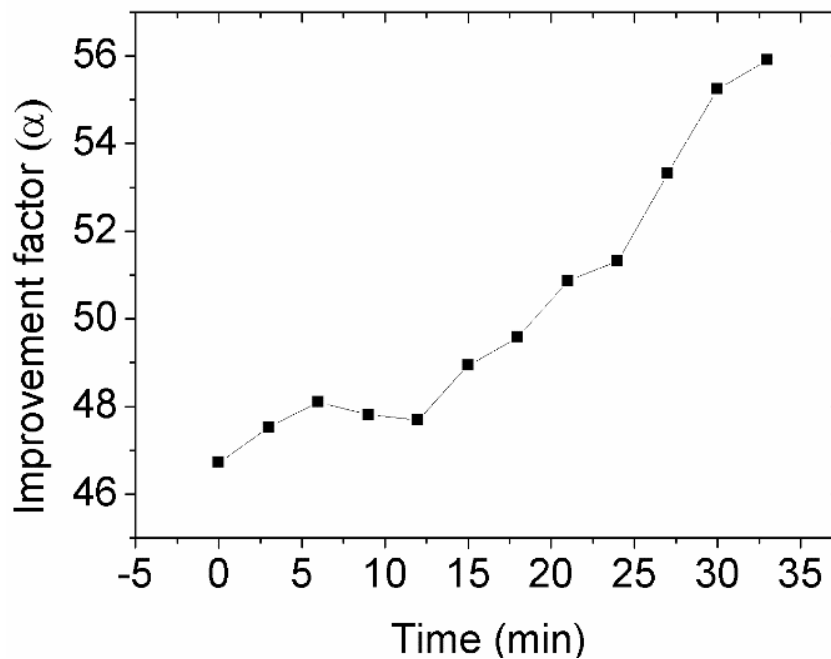


Fig. 12. Improvement factor versus time.

The energy reduction (Figure 13) is a standard for saving money and reducing pollution due to the non-renewable energy sources. This can be calculated using the following formula.

$$\rho = \frac{(Qt)_{non-ins} - (Qt)_{ins}}{(Qt)_{non-ins}} \times 100 \quad (2)$$

The energy consumption reduction started at a high value at time 0 (at the moment of turning off the heating system) which is 53.3%. The reduction percentage decreases as the difference between heat rate transfer of the two models is diminished. The value of energy consumption reduction is also considered elevated at 44.1% after 33 minutes.

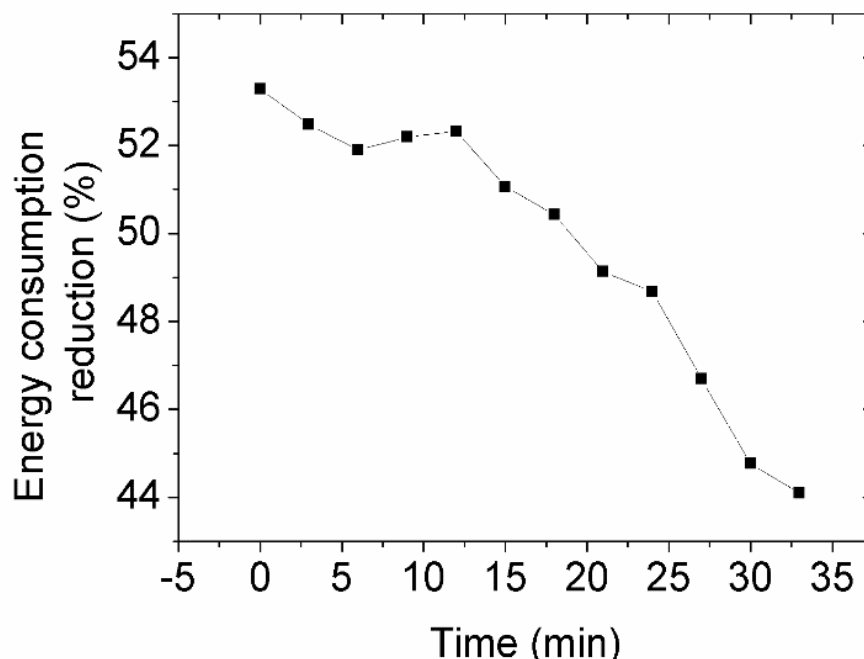


Fig. 13. Energy consumption reduction versus time

Conclusions

The need for energy conservation has become critical due to economic and environmental concerns. The main objective of this study was to design and construct effective residential buildings in a way to reduce energy consumption and control indoor temperature automatically in order to preserve heat and save energy.

Executing the room models was important to prove that insulation and phase change material can eliminate about half the value of the heat loss compared with the non-insulated room model.

For cold ambient conditions of 5°C, the heat rate for the insulated room was almost 2 times less than that of the non-insulated room model. As for natural ambient conditions, the heat rate of the insulated room model was almost 6 times less than that of the non-insulated room model with no installed PCM.

With an average of 50.25% of improvement and 49.7% of the energy consumption reduction, it can be clear how insulation and PCM improved the preservation of heat in a certain space during winter which in turn served efficiently in decreasing thermal losses to save energy, money and environment. It was noticed that the heat loss by conduction through the roof was 40% of the conduction heat loss. Thus, for future research it is recommended to insulate the roof to minimize the heat loss as much as possible. Moreover, it is advised to build a third model to show the basic role of the phase change material in the building sector.

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Experimental and Theoretical Study of Adsorption/Desorption Isotherms of Straw Earth Material Used in the Construction of Shell Huts in the Far North of Cameroon

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Keywords: Adsorption / desorption isotherms, Hygric properties, local materials, Earthen material, straw, Experimental study.

Abstract. Earth-based materials (EBM) provides a valuable avenue for improving thermal comfort, energy consumption, indoor air quality and humidity regulation. However, in the literature, very few studies have addressed hygrometric characteristics of shell huts in EBM from the far north region of Cameroon. The use EBM is hampered by the non-availability of databases related to their intrinsic properties and through unfamiliarity of their behavior over time. In the meantime, these shell huts in EBM are known for their moisture which regulates properties and thus contributes to the comfort of their occupants. This study aims to determine experimentally the adsorption/desorption isotherms at 30, 40 and 50 °C of the straw earth material carried out by the static gravimetric method for eight saturated salt solutions (LiCl, MgCl₂, Mg(NO₃)₂, NaBr, IK, NaCl, KCl and K₂SO₄). The experimental curves obtained for absorption / desorption show that for a given water activity, the equilibrium water content W_{eq} increases inversely with temperature (i.e. decreases with increasing temperature, and vice versa). In addition, the absorption curve does not overlap with the desorption curve. As a result, these shell huts in EBM display interesting humidity regulation characteristics.

Introduction

To ensure comfort in a building, the relative humidity of the surrounding air is an important factor. The use of a moisture regulating material is an effective way to stabilize the ambient humidity without consuming energy and thus ensure a satisfactory level of comfort. Building materials that absorb and release moisture can be used to positively reduce extreme differences in humidity levels within the wall. Recently, there has been a resurgence of interest in green building using natural renewable materials. Ecological or bio-based materials proved to be an interesting alternative to conventional building materials, thanks to their hygroscopic capacity as well as their thermal insulation quality, they contribute to a reduction in energy consumption and ensure thermal comfort in winter and summer. In addition, the so-called ecological or bio-based materials improve the thermal and hygrothermal quality as well as the air quality in the living space [1].

In general, earth-based materials (EBM) are known for their undeniable ecological and economic advantages. EBM are one of the oldest and most modern building materials and the use of raw earth

as a building material dates back ten thousand years. About 50% of developing countries population and at least 20% of the urban population live in earthen housing [2]. EBM are perfectly in line with the rules of eco-construction. As a local, universal, abundant, and easily accessible material, EBM are used during the construction phase of building, and requires very little energy. Its availability reduces the energy required for extraction, processing, and transport. The method of producing EBM also reduces energy consumption compared to the costs of producing conventional materials [3]. While building, EBM are exposed to an environment with varying temperature and relative humidity. It is observed that EBM have an important capacity to adapt to external conditions due to their thermal storage and water regulation properties. EBM contribute to the regulation of indoor thermal comfort, even though they suffer from a high sensitivity to water. Variations in ambient water conditions can strongly affect EBM durability. Besides, EBM are characterized by a complex mechanical behavior that results in plastic deformation and mechanical damage. Stabilization through additives in the production of EBM is considered the best way to overcome this sustainability deficit. Soil can be stabilized using stabilization method and the nature of the stabilizers used in developing EBM strongly influences thermal and water properties of these materials. Yet, EBM weaknesses to be addressed include, high drying shrinkage, limited liquid water sustainability and low ductility [4]. The use of renewable stabilizers such as cement or lime, or plant aggregates such as straw, hemp or wood chips, reduces these drawbacks. The use of fibers and dung to improve soil properties are based on empirical knowledge. To date, approximately twenty studies only deal with raw earth bricks in which plant aggregates have been incorporated [5] and few studies deal specifically with the addition of hemp in the soil matrix. From the literature, the addition of hemp (either in the form of fibers) modifies the mechanical performance of the material. For example, the compressive/compression strength is increased by 16% by addition of 0.4% by mass of hemp fibers of 3 cm length [6]. However, other studies with different plant materials showed that the compressive strength could decrease, especially with the addition of straw [7]. The literature also shows that tensile and flexural strengths are improved by the addition of hemp fibers as well as the ductility of the material. It has also been found that the addition of hemp fiber limits shrinkage cracks by resisting deformation, thus limiting soil contraction [8]. As far as thermal conductivity is concerned, the few results available on the subject show the same trend: thermal conductivity decreases with the addition of plant aggregates. For example, the thermal conductivity of a mud brick was decreased by 20% by adding 0.8% by mass of hemp fibers [6].

In the far north of Cameroon, construction using EBM has been the subject of limited studies. Recent studies on adobes reinforced with millet and neem fibers [8],[9] have shown advantages related to thermal comfort, cost and environmental protection. However, the construction technique in cob, very original and specific to the Musgum people, renowned for its aesthetics and which was at the origin of tourism was disinterested for some time. At length, research studies of hut shell of Musgum people living in the Logone plains, remained unexplored. This study aims to enhance the rich heritage of the Musgum habitat through a characterization of the hygroscopic properties of the materials used for the construction of shell huts. This study will provide the scientific data needed to understand thermal comfort enjoyed by shell hutches in a dry tropical climate where temperatures often reach 45 °C. EBM reinforced with grass fibers are extracted from the locality of Mourla where craftsmen build huts in shells. Grass fibers containing 0, 5, 10 and 15% are added to EBM (soil matrix) to characterize the composites used for the construction of the shell hutch.

Materials and Methods

EBM consisting of earth mixed with straw, came from Mourla, whose geographical coordinates are 10°54'0" N and 15°4'60" E in the Maga district of the Far North region of Cameroon (Fig. 1), where housings are essentially shell huts (Fig. 2).

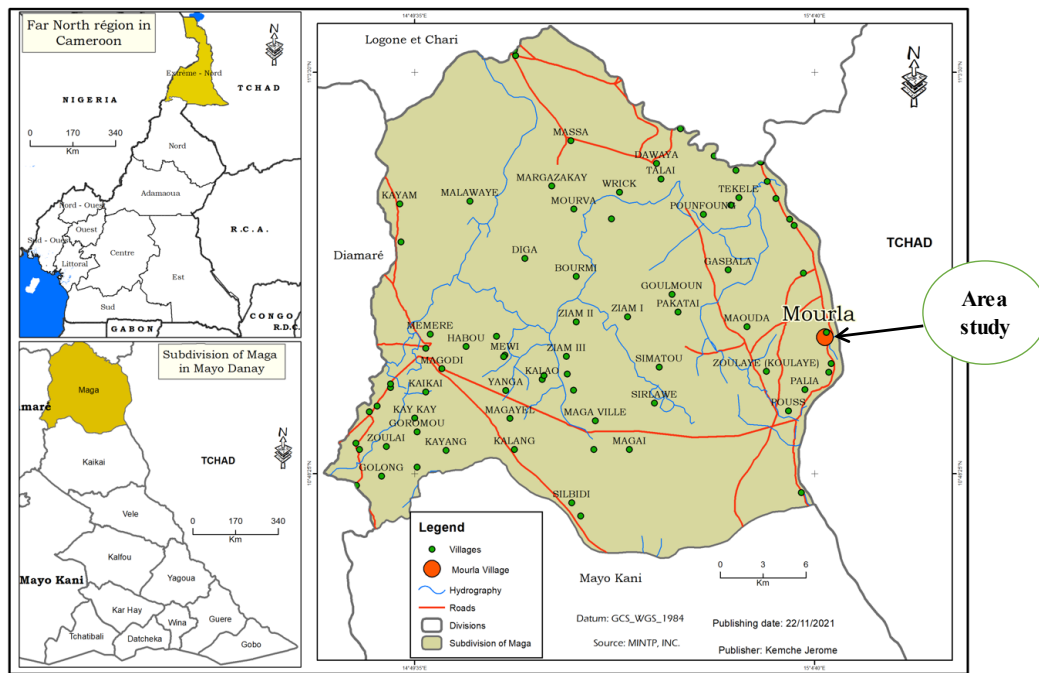


Fig. 1. Geographical location of study area



Fig. 2. Hut shell

The experimental apparatus consists of a temperature and humidity-controlled chamber (Fig. 3), a ventilated oven (Fig. 4) and an electronic balance (Fig. 5). This soil is chosen because of its abundant use in the construction of traditional huts by the local population. The mixtures are made with different proportions of earth and straw. Four different types of mixtures (Fig. 6) are prepared to make the samples for the different trials: one type of sample composed only of soil (control), another type containing 5% straw by mass, another type containing 10% straw and the last type containing 15% straw. The water content of the mixtures is between 15% and 20%. The samples correspond to the dimensions $10 \times 10 \times 3 \text{ cm}^3$. The mixtures are placed in the moulds using the following steps: pour the mixed soil and straw into the mixer bowl, pour in the water, the quantity of which ensures a moist state, mix for 1 minute, place the mixture in the previously oiled moulds, packing it in several layers. Flatten the moulds to obtain even surfaces. Immediately unmould the bars and place them on a ventilated rack. The samples are stored for 14 days in a controlled atmosphere, in a room where the temperature is maintained at $25 \pm 2 \text{ }^\circ\text{C}$ and the relative humidity is set to 60 ± 10 .



Fig. 3. Temperature and humidity-regulated enclosure



Fig. 4. Ventilated oven



Fig. 5. Electronic scale



Fig. 6. Samples of research materials

Experimental method for determining adsorption/desorption isotherms

Hygroscopic sorption describes the exchange between the water vapor content of the material and the relative humidity of the ambient air up to an equilibrium point. Sorption and desorption isotherms were determined according to the requirements of NF EN ISO 12571 (NFENISO12571, 2000; NFENISO12572, 2001). The moisture storage capacity of the material is determined at several relative humidity levels. Prior to the test, the material samples are dried at 105 °C to a constant weight. The samples are then placed in a climate chamber (Fig. 3.), where the temperature is set at 23 °C and the relative humidity (RH) varies in steps of 33, 43, 50, 70, 90 and 97% RH. However, the samples are weighed regularly until the difference between two consecutive measurements 24 h apart is less than 1%, so that the RH of the climate room varies. For the desorption curve, the reverse procedure is followed with decreasing levels of relative humidity from 97 to 33% RH. The experimental method is the saturated salt solution method (Table 1). This method is based on the principle of static gravimetric method and consists of placing the sample whose adsorption and desorption curves are investigated above a saturated salt solution in a chamber placed in an oven regulated at the temperature T of the experiment. The role of the saline solution is to keep the relative humidity RH of the chamber constant. The sample is weighed at regular time intervals until it reaches its equilibrium mass. The latter mass is recorded and used to calculate the water content of the sample

at the temperature T of the experiment and at the relative humidity RH imposed by the saturated saline solution. The equilibrium water content W_{eq} is given by Eq. (1)[10]:

$$W_{eq} = \frac{M_h - M_s}{M_s} \quad (1)$$

Where M_h and M_s represent the masses of the wet sample and the equilibrium sample respectively

Table 1: Saturated salt solutions

Salts	30 °C	40 °C	50 °C
LiCl	11.3	11.2	11.1
MgCl ₂	32.4	31.6	30.5
Mg(NO ₃) ₂	43.2	48.4	45.4
NaBr	56	53.2	50.9
IK	67.89	66.09	64.49
NaCl	75.1	74.7	74.4
KCl	83.6	82.3	81.2
K ₂ SO ₄	97	96.4	95.8

The tests are carried out for three temperature values 30 °C, 40 °C and 50 °C. The samples are weighed every 24 hours on a 0.01 g precision balance (Fig. 5).

Theoretical Method for Determining Desorption Isotherms

To model these isotherms, many empirical correlations exist in scientific literature. In order to better take into account, the influence of temperature on the hygroscopic equilibrium, and to be able to carry out interpolations, we use the Henderson an Oswin model [11]. Indeed, the choice of these models is justified by the fact that they have the advantage of describing all the sorption isotherms for a wider range of temperature and relative humidity of the environment surrounding the product. This is not the case with the Guggenheim, Anderson and Boer (G.A.B) model or the Brunauer, Emmet and Teller (B.E.T) model [12], which is only valid for low values of relative humidity RH . The correlation expressing the Henderson model are written as outline on Eq. (2) and Eq. (3)[13]:

$$w_{eq} = \left[- \left(\frac{1}{KT} \right) L_n(1 - H_r) \right]^{\left(\frac{1}{n} \right)} \quad (2)$$

$$w_{eq} = k \cdot \left(\frac{H_r}{1 - H_r} \right)^{(n)} \quad (3)$$

Where W_{eq} is the water content (kg water per kg dry matter),

H_r is the relative humidity and T is the ambient temperature.

The coefficients k and n are determined from the experimental data

The statistical parameters are defined as Eq. 4 and Eq. 5:

$$R^2 = 1 - \frac{\sum_{i=1}^N (w_{eq_{exp,i}} - w_{eq_{cal,i}})^2}{\sum_{i=1}^N (w_{eq_{exp,i}} - \overline{w_{eq_{cal,i}}})^2} \quad (4)$$

$$E(\%) = \frac{100}{N} \sum_{i=1}^N \frac{|w_{eq_{exp,i}} - w_{eq_{cal,i}}|}{w_{eq_{exp,i}}} \quad (5)$$

With, $w_{eq_{exp,i}}$: experimental equilibrium water content (kg/kg d.b),

$w_{eq_{cal,i}}$: predicted equilibrium water content (kg/kg d.b),

$\overline{w_{eq_{cal,i}}}$: predicted average water content,

N : Number of experimental points.

Water vapor permeability. Water vapor permeability is an important material property that characterizes the ability of the material to transport water vapor under a vapor pressure gradient once the steady state is reached. The test was carried out in accordance with ISO 12572 (NFENISO12572, 2001); the thickness sample (e) had to be sealed over a test cup containing a saline solution or silica gel to have a wet or dry atmosphere, respectively. The cups contained either a desiccant (silica gel) or a saline solution (barium chloride) which maintains the relative humidity of the atmosphere in the cups at 0-3% RH and 90% RH. The entire system is placed in a climate chamber controlled at temperature (20 °C) and humidity (RH 50%), so that the material will be between two environments with different partial vapor pressures; P_{v1} of the climate chamber and P_{v2} inside the cup. Due to the partial vapor pressure gradient between the inner part of the cup and the environmental chamber, a flow of water vapor causes the mass of the cup to vary (mass absorption for the "dry cup" test and mass loss for the "wet cup"). The device is weighed periodically and when the mass gain is constant. The mass rate (G) is calculated by linear regression of the mass kinetics (Eq. (6)), and the water vapor permeability is then deduced according to Eq. (7) [7,14]. This experiment allows the determination of the vapor flow through the sample.

$$G = \frac{\Delta m}{\Delta t} \quad (6)$$

$$\delta p = \frac{G.e}{A.(\Delta P_v)} \quad (7)$$

Where G: density (kg/s), Δm : mass change (kg), Δt : time (s), δp : water vapor permeability (kg/(ms Pa)), e: thickness of the sample (m), A: exposed surface area (m²), ΔP_v : vapor pressure difference (Pa). The vapor pressure is calculated from the temperature and relative humidity measured during the test period with the usual relationship Eq. (8) [7,14] :

$$P_v = \varphi. 100 \exp\left(18.986 - \frac{4052}{235.89 + T}\right) \quad (8)$$

Where φ : relative humidity, T: temperature (K)

The water vapor resistance factor is the ratio of the water vapor permeability of the air (δ_{air}) to the water vapor permeability of the material, according to Eq. (9)[10]:

$$\mu = \frac{\delta_{air}}{\delta_p} \quad (9)$$

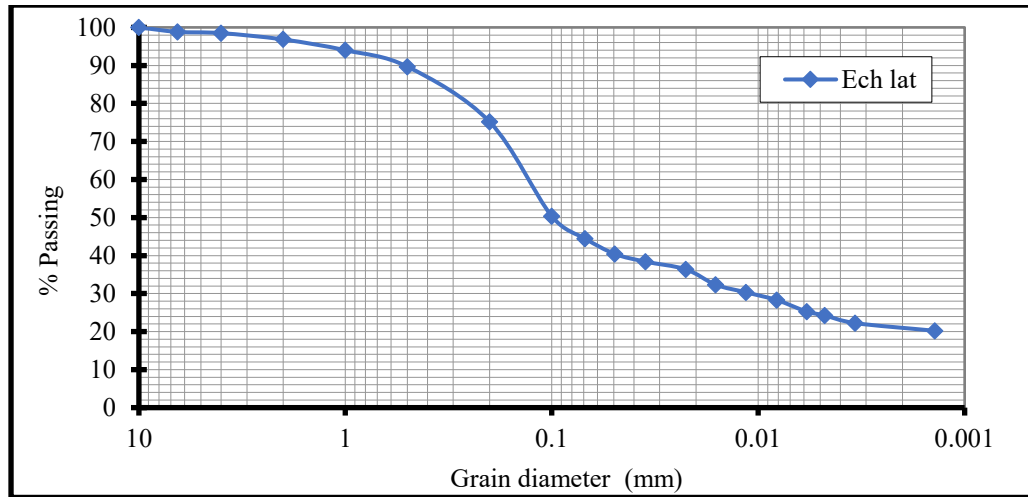
Where $\delta_{air} = 1.96 \times 10^{-10}$ (kg m⁻¹ s⁻¹ Pa⁻¹) is water vapor permeability of the air [7,15].

Results and Discussions

Particle size analysis. Firstly, a particle size analysis is carried out on the soil. The results obtained show that, whatever the test, the soil has the greatest sand and clay activity. The particle size analysis is carried out according to the standard (XP P94-041, 1995). The particle size analysis is the first test for the identification of the gauge [16,17]. The soil particle size curve is given in Fig. 7 Amongst the information obtained from a particle size curve, the maximum diameter (D_{max}), the 2 mm sieve and the fines content ($D < 80 \mu m$) are parameters of nature that allow classifying soils according to the standard (NF P11-300, 1992) provided in Table 2.

Table 2: Size distributions of soil Grain

Reference sample	% of gravels ($\Phi > 2$ mm)	% of sand ($2 > \Phi > 0.02$ mm)	% of silt ($0.02 > \Phi > 0.002$ mm)	% of clay ($\Phi < 0.002$ mm)
Echlat	3.2	60.4	15.2	21.2

**Fig. 7.** Grain size curve

Clays give the soil a water absorption capacity (called activity) which can lead to shrinkage/swelling phenomena and play an important role in the plasticity and cohesion of the soil. To evaluate this clay activity, two tests are used: the methylene blue test (NF P94-068, 1998) and the Atterberg limits (NF P94-051, 1993), presented in Table 3.

Table 3: Atterberg limits

Reference sample	Liquid limit	Plastic limit	Plasticity index
Laterite sample	34.0	16.4	17.6

The results show that the samples have a high plasticity index value which allows them to be classified as plastic soils. Furthermore, the plastic limit obtained for the different samples gives an approximate value for water needed during the shaping of the bricks (extrusion), without considering the additives. These tests make it possible to anticipate and save the amount of water needed in the production of bricks.

Sorption isotherms. The results of measuring the adsorption and desorption isotherms on the sample at different temperatures and fiber percentages are illustrated in Figs. 8 to 10.

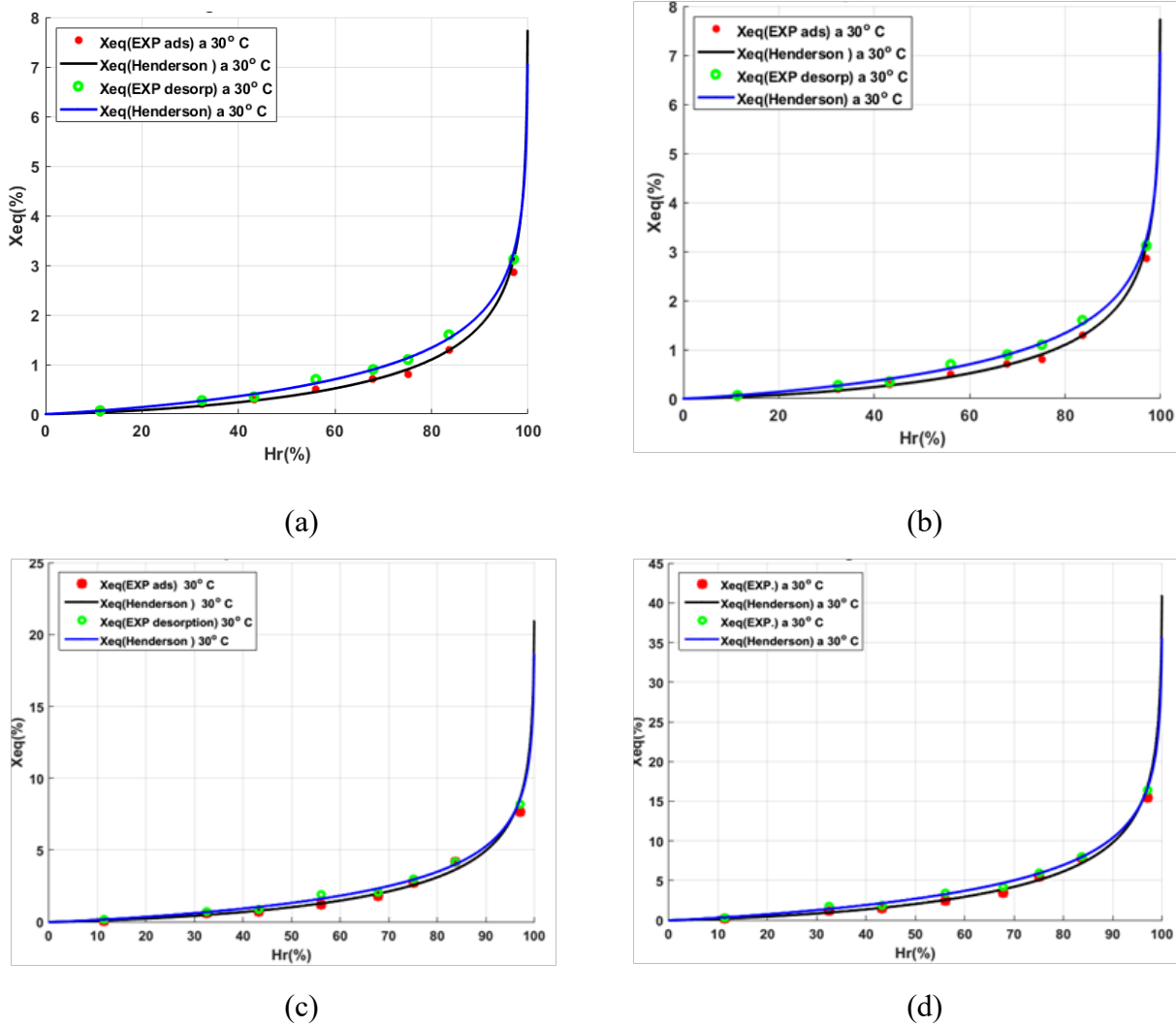


Fig.8. Adsorption / desorption isotherms at 30°C: (a) 0% of fiber (b) 5% of fiber (c) 10% of fiber (d) 15% of fiber

We obtain a non-linear function. For a range of relative humidity between 0 and 60%, the curve is quasi-linear and non-linear from 60%. According to the results presented, our material will have a moderate water retention capacity. According to the International Union of Pure and Applied Chemistry (IUPAC) classification [18,19], the isotherm of our material is type III. This form is frequently encountered in hygroscopic building materials. The quasi-linearity of the beginning of the curve can be interpreted as a weak interaction of the solid matrix with the gaseous molecules. By comparing our results with those obtained by Ahmad and Chen [20] it is a characteristic behavior of cellulosic and lignocellulosic materials, which highlight the strong capacity to moisture's capture and storage of straw materials

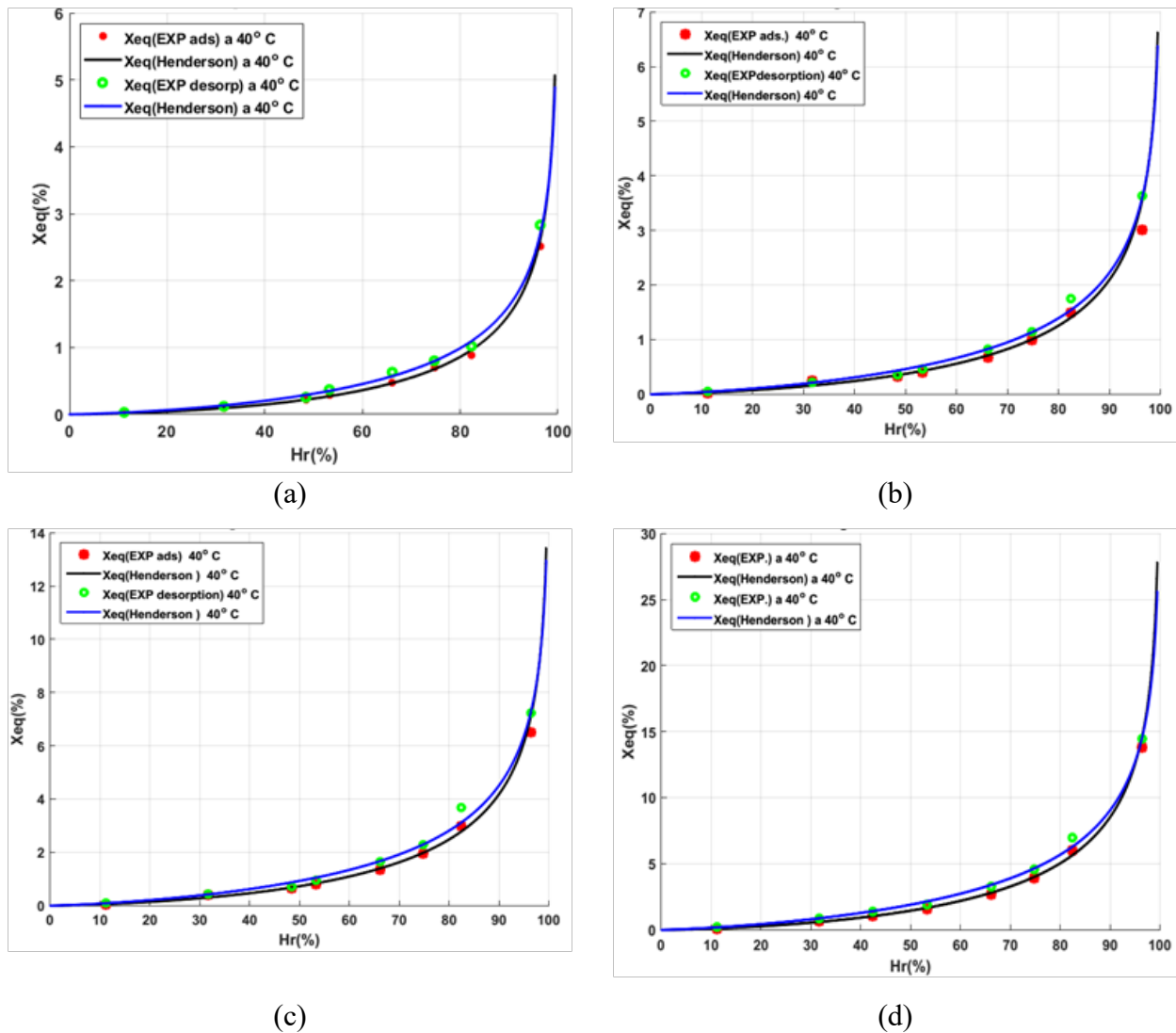


Fig.9. Adsorption / desorption isotherms at 40°C: (a) 0% of fiber (b) 5% of fiber (c) 10% of fiber (d) 15% of fiber

The experimental adsorption and desorption curves obtained in Fig. 8 show that, for a temperature of 40 °C, the equilibrium water content of the sample increases with increasing relative humidity of the environment in which it is placed. This result is in agreement with the behavior of other earth building materials [7,21]. The results also show that the equilibrium water content is between 0 and 15%. In contrast, similar results are observed in the majority of earth materials [11,22,23], compared to those obtained by [10,24,25]. There is an increase in the sorption capacity of the materials, with the amount of fibers incorporated, the presence of plant particles tends to show an improvement in the hygric performance of the material. The adsorption capacity of building materials is therefore directly related to the morphology and connectivity of their pores. Thus, composites with large open porosity show a more pronounced change in water content with relative humidity than others. In addition, small pore sizes are favorable for capillary condensation and concrete, with the largest number of small connected pores showing a higher adsorption capacity at very high humidity than other composites [10,26].

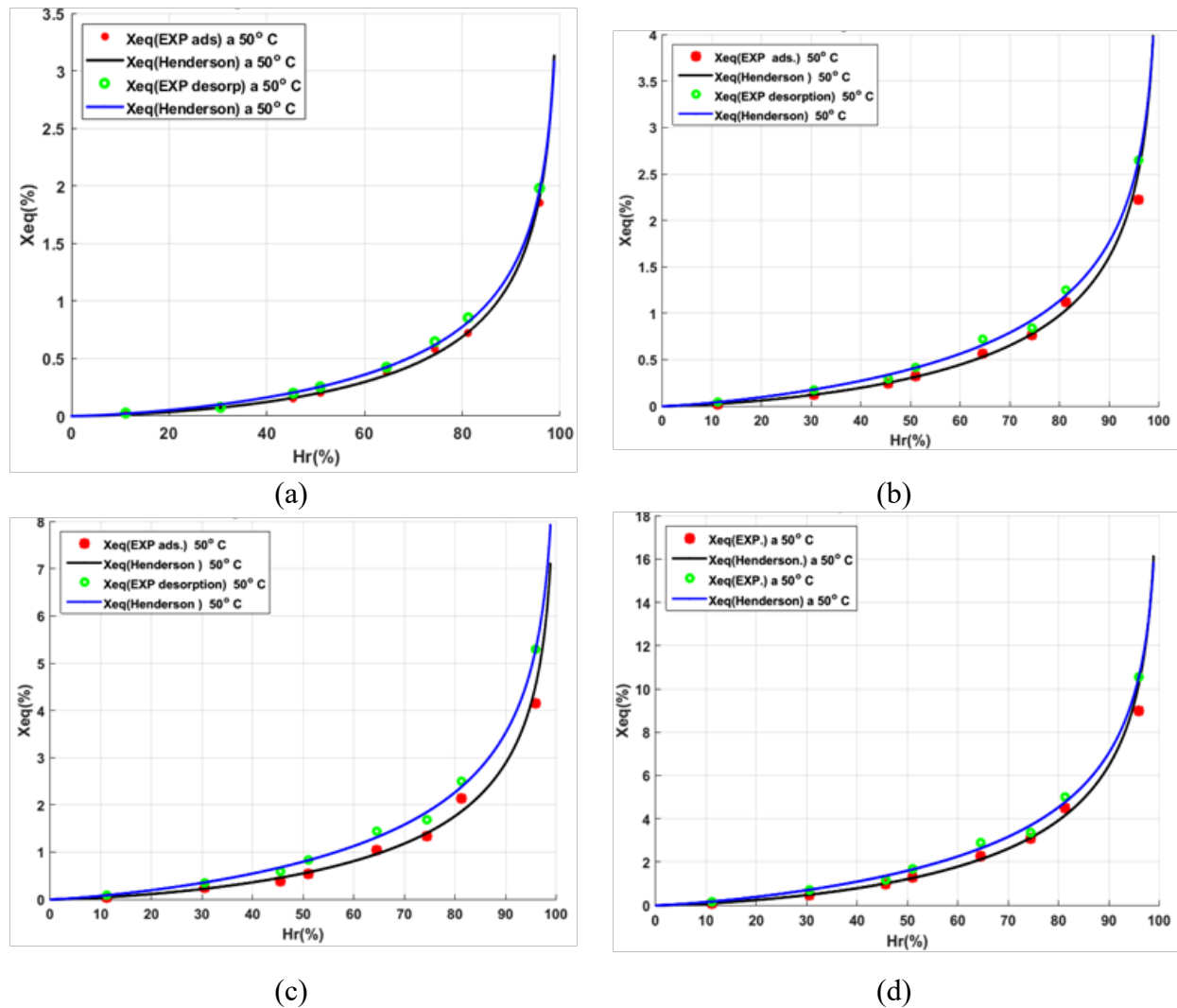


Fig.10. Adsorption / desorption isotherms at 50 °C: (a) 0% of fiber (b) 5% of fiber (c) 10% of fiber (d) 15% of fiber

The results show that the amount of water vapor absorbed increases as the relative humidity increases and that all samples have a high sorption capacity as the fiber percentage increases. It should be noted that the high fiber samples have a high adsorption capacity compared to the others. It should be noted that the effect of the fiber is more important than the compaction. Indeed, fibers affect the absorption rate and the sensitivity to moisture, as the addition of fibers generates voids, thus causing an increase in porosity. However, the water content is reached for samples with a fiber content of 0%, 5%, 10% and 15%, respectively, when the relative humidity increases from 33% to 97%, (2%, 2.75%, 5.20% and 11.4%). To this effect, the samples with high fiber content (10% and 15%) show a very high moisture absorption capacity, the effect of plant fibers on the absorption capacity of composites has been reported by many researchers [7,21,27]. Furthermore, the adsorption and desorption curves show little hysteresis. This reflects the fact that it is easier for water vapor to enter a porous network than to leave it. This occurs due to the influence of the electrostatic potential on the porous material inside the surfaces, which leads to a slight increase in water content. The hysteresis phenomenon can be associated with capillary condensations that take place in porous structures [11,15,28]. Indeed, water is condensed in the pores and thus becomes trapped, and capillary evaporation occurs for lower relative pressures at which water vapor should be released. The hysteresis gap (which is generally associated with capillary condensation in mesopores [11] is greatest between 33% and 85% RH for all temperatures. As usually observed for earth materials, this hysteresis remains low [11,29]. Compared with Fabri's results, sorption isotherms for biobased composites exhibit hysteresis that extends to the lowest hygrometry [30]. Our results show that, at the highest relative humidity (i.e. above 80 % RH), the water content increases more rapidly and even becomes asymptotic from 95 %

RH. In some cases, it reaches nearly 45% at 97% RH. The fixation of moisture by the material is no longer due to pure adsorption: capillary condensation appears. This phenomenon is favored in pores with smaller diameters and allows the capture and storage of a greater amount of moisture.

Fitting of sorption models. The average estimate of the deviations between the theoretical and experimental curves (E) and the correlation coefficient (R^2) are used to assess the accuracy of each model: those with low E and high R^2 indicate a good fit [31]. It should be mentioned that the accuracy of a model is acceptable for E values below 10% [32,33].

Table 4: Model constants from adsorption isotherms

T (°C)	% (fiber)	Adsorption							
		Model parameters							
		Henderson				Oswin			
		n	k	R^2	E (%)	n	K	R^2	E (%)
30 °C	15%	0.7552	0.0014	0.9848	6.096	1.0303	0.0287	0.9903	11.9925
	10%	0.7460	0.0024	0.9926	8.8105	1.0177	0.0023	0.9977	10.240
	5%	0.7430	0.0043	0.9984	5.9271	1.0136	0.0174	0.9934	12.21
	0%	0.7474	0.0056	0.9984	8.4735	1.2478	0.0233	0.9708	33.135
40 °C	15%	0.6805	0.0019	0.9870	8.256	0.9279	0.0074	0.9924	17.38
	10%	0.6727	0.0030	0.9844	8.560	0.9117	0.0088	0.9971	14.836
	5%	0.6728	0.0047	0.9822	12.68	0.9295	0.0165	0.9959	17.388
	0%	0.6519	0.0064	0.9995	4.212	1.0548	0.0201	0.9800	31.88
50 °C	15%	0.6992	0.0020	0.9857	2.74	0.9334	0.0018	0.9928	12.41
	10%	0.6976	0.0033	0.9859	2.73	0.9315	0.0090	0.9920	12.54
	5%	0.7021	0.0054	0.9856	2.358	0.9374	0.0145	0.9935	12.37
	0%	0.6682	0.0071	0.9993	5.89	1.0561	0.0169	0.9796	28.56

The reliability of the parameters is estimated from the correlation coefficient R^2 . These parameters are satisfactory when the absolute value of R^2 is between 0.87 and 1 [33]. In our study the R^2 values are between 0.982 and 0.998 for the adsorption isotherms and 0.996 and 0.997 for the desorption isotherms, as illustrated in Tables 4 and 5. The Henderson model is the best suited to describe the isotherms of the earth materials. This is because average estimates of the deviations between theoretical and modelled curves are lower than 10% as shown in Tables 4 and 5.

Water vapor permeability. Table 6 illustrates water vapor permeability and resistance factor. Water vapor permeability was measured using two methods, the wet cup, and the dry cup. Table 6 presents the results of the tests carried out. The results showed that those values obtained by the wet cup method were higher than those of the dry cup. This can be explained by the water vapor transport parameters measured in the wet cup configuration, when the material contains enough water (capillary zone area), the condensation-evaporation phenomenon can cause the acceleration of the water vapor movement through the material. The resistance factor is therefore reduced.

Table 5: Model constants from desorption isotherms.

T(°C)	% en fibre	Desorption							
		Model parameters							
		Henderson				Oswin			
		n	k	R^2	E (%)	n	k	R^2	E (%)
30°C	15%	0.8754	0.0010	0.9973	6.2151	1.1928	0.0461	0.9892	9.840
	10%	0.8615	0.0020	0.9919	8.556	1.1795	0.0065	0.9878	11.59
	5%	0.7433	0.0040	0.9984	5.927	1.1418	0.0127	0.9914	11.20
	0%	0.8758	0.0046	0.9982	5.468	1.4495	0.0187	0.9645	23.52
40°C	15%	0.6805	0.0019	0.9874	8.256	1.0612	0.0175	0.9962	10.11
	10%	0.7563	0.0026	0.9897	9.707	1.0164	0.0044	0.9988	5.91
	5%	0.7612	0.0045	0.9935	8.769	1.0219	0.0148	0.9987	6.021
	0%	0.7239	0.0058	0.9985	7.878	1.1639	0.0185	0.9835	23.36
50°C	15%	0.8111	0.0016	0.9927	6.656	1.0853	0.0087	0.9887	9.730
	10%	0.4781	0.0030	0.9685	85.20	0.8740	0.0096	0.9680	90.59
	5%	0.8088	0.0050	0.9928	6.57	1.0822	0.0128	0.9888	9.79
	0%	0.7335	0.0067	0.9996	7.99	1.1304	0.0158	0.9828	18.77

It is possible to compare these values with the results obtained by several researchers. However, our results are close to those obtained by [7,22,34–36]. The fiber-reinforced water vapor permeability is equal or superior to that of other building materials in both dry and wet cups. This performance is a good indicator of their use as a thermally efficient material. In addition, the water vapor permeability is found to be high for the fiber reinforced samples. This means that the fibers used have made the pore structure less tortuous (larger and more continuous pores). However, the samples without fibers became less permeable (μ high vapor resistance) where it seems that the absence of fibers leads to a decrease in porosity, which may result in the loss of some macropores.

Table 6: Water vapor permeability and water vapor resistance factor.

Soil sample	Dry cup		Wet cup	
	δ [kg/s.m.Pa) $\times 10^{-11}$]	μ	δ [kg/s.m.Pa) $\times 10^{-11}$]	μ
5%	1.22	16	6.53	3
10%	1.96	10	4.9	4
15%	2.46	8	3.92	5

Conclusion

Our work consisted in theoretical and experimental studies of the adsorption-desorption isotherms of the straw earth material. These sorption isotherms, often called sorption curves, reflect the hygroscopicity of the material. The experimental sorption/desorption curves were determined by the static gravimetric method for three temperatures (30, 40 and 50 °C). These curves showed that for a given water activity, the equilibrium water content W_{eq} increased inversely with temperature (i.e. decreased with increasing temperature, and vice versa). The adsorption/desorption curves did not overlap, highlighting the hysteresis phenomenon. The isotherm results also revealed that the incorporation of fibers was a determining factor for the storage of moisture and therefore for the water regulation of raw earth envelopes. Indeed, the samples with fiber incorporation had a higher water vapor absorption capacity than the simple ones, reaching up to 15%.

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Effect of Different C₃A Content on Rheological Parameters in Paste Mixtures

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Abstract. C₃A content of cement is of great importance in connection with the fresh and early age mechanical properties of cementitious systems. In this study, the effects of different C₃A content on the static and dynamic yield stress and viscosity values of paste mixtures were examined. Consequently, the use of polycarboxylate ether-based water reducing admixture (PCE) up to a certain dosage affected adversely the rheological characteristics of the mixtures. The dispersion effect, which increased with the increment of the PCE dosage, increased the hydration rate of C₃A by increment its contact with water by dispersing it. Therefore, dynamic yield stress and viscosity were adversely affected by the increment in PCE dosage in high C₃A-containing mixtures, while rheological parameters improved after a certain dosage in low C₃A ones.

Introduction

C₃A is the most reactive component in cement. Although its ratio is mostly low such as 5-10% of cement weight, it affects both the rheological characteristics and mechanical performance of cementitious systems at early ages [1] Ettringite is formed in consequence of the reaction of C₃A with water in the presence of gypsum. A high amount of ettringite is formed in cementitious mixtures containing high C₃A. The high surface area of ettringite leads to an increment in the surface area on which the PCE will be adsorbed. It is known that this situation causes an increase in the PCE requirement [2, 3]. In addition, the positive charged of C₃A and ettringite increases the adsorption of negatively charged PCE to C₃A and ettringite surface and reduces the effectiveness of PCE [4]. For these reasons, the optimum C₃A content is recommended to be 6-8% in the production of normal strength concrete. With this ratio, good early age strength can be obtained. The adversely effect of C₃A on workability should be considered, especially in the preparation of high-performance concretes having low w/c ratio [5]. Zingg et al. [6] investigated the dispersion ability and setting retardation effect of PCE on cement paste with different C₃A content. According to the results of the study, the PCE requirement increased with the increase in C₃A content. It was also claimed that PCE molecules with high charge density and long side chains can improve the workability performance of cementitious systems. In some studies, it was stated that PCE decelerates the dissolution rate of cement components [7], so hydration reactions are delayed [8].

It was understood that there is a lack of information in the literature related to the effect of PCE and C₃A compatibility on rheological parameters. In this study, the rheological properties of cements with different C₃A contents were investigated in the presence of PCE. For this purpose, paste mixtures having two different C₃A contents were prepared and the static yield stress (SYS) and dynamic yield stresses (DYS) and viscosities of the mixtures were obtained.

Materials and Method

Materials. In this study, two different CEMI 42.5R type Portland cements were used in accordance with EN 197-1 with C₃A content of 2.13% (C2) and 9.05% (C9). The properties of cements are shown in Table 1 and Table 2. Some characteristics of polycarboxylate ether-based water reducing admixture (PCE) used in the preparation of the mixtures are shown in Table 3.

Table 1. Physical, chemical and mechanical characteristics of cements (%)

Oxides (%)	C2	C9	Mechanical properties		C2	C9
SiO ₂	18.94	20.15	Compressive strength	2-day	25.8	25.8
Al ₂ O ₃	4.33	5.53		28-day	48.5	50.7
Fe ₂ O ₃	5.53	3.31				
CaO	61.67	62.68	Physical Properties			
MgO	1.55	1.69	Specific gravity		3.21	3.10
SO ₃	2.82	3.10	Specific surface area (cm ² /g)		3786	4259
Na ₂ O+0.658K ₂	0.68	0.64	Residual on 45µm sieve (%)		4.3	2.90
Cl-	0.03	0.05	Residual on 90µm sieve (%)		4.8	-
Loss on ignition	3.33	4.31				
Free CaO	0.75	0.70				

Table 2. Mineral composition of cements (%)

Type	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
C2	58.98	9.80	2.13	16.83
C9	48.42	21.25	9.05	10.07

Table 3. Some properties of water reducing admixture

Type	Solid content (%)	Density (g/cm ³)	pH value	Chloride content (%)	Alkaline content Na ₂ O (%)
Polycarboxylate ether-based	40.8	1.076	3.91	<0.1	<10

Method. In the preparation of paste mixtures, the w/c ratio was determined as 0.32, taking into account the flash set effect of C₃A. In order to determine the effect of different PCE dosage on rheological properties, paste mixtures containing PCE in 3 different dosages (0%, 0.10% and 0.15%) were prepared. 1000 gr cement and 320 gr water were mixed for 30 seconds at slow speed (62.5 rpm). Then, after the mixing, bowl was stripped, PCE was added and mixed at high speed (125 rpm) for 2 minutes.

Rheometer (MCR52, Anton Paar) with 8 mm diameter ball measuring system with a maximum shear stress of 4560 Pa was utilized to determine the rheological parameters of the mixes. In addition, the 4-period method in Figure 1 was applied as the deformation rate regime [2]. Flow curves were drawn using the raw data obtained. dynamic yield stress (DYS) and final viscosity were calculated by analyzing each drawn flow curve with the Herschel-Buckley model. Accordingly, the highest shear stress was obtained as the static yield stress (SYS) in the 1st period when the mixture was not subjected to any deformation. The value where the flow curve intersects the y-axis in the 4th period was recorded as DYS, while the point at which the viscosity value was fixed was determined as the final viscosity.

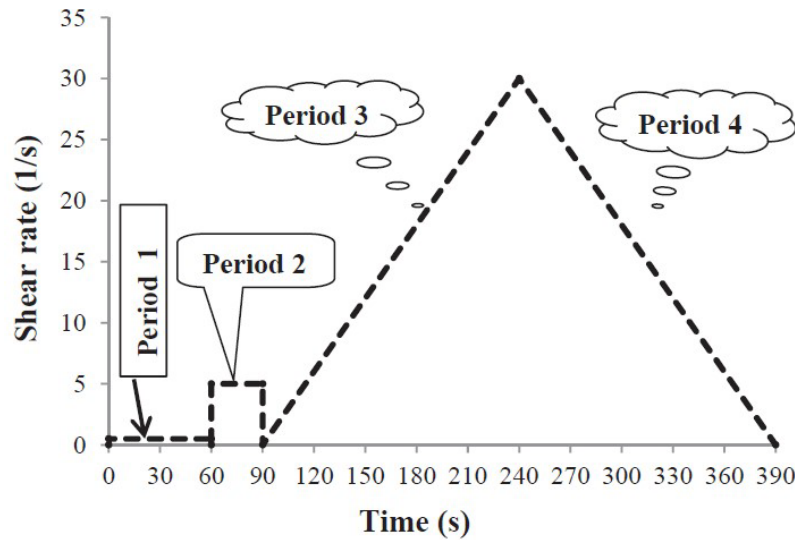


Fig. 1. The shear rate pattern used for rheological method

Results and Discussion

The results of rheological parameters (SYS, DYS, and final viscosity) in the presence of PCE for paste mixtures with different C_3A content are shown in Table 4.

Table 4. Rheological parameters of cement pastes

Cement	Dosage (%)	Static yield stress (Pa)	Dynamic yield stress (Pa)	Viscosity (Pa.s)
C2	0	4560	97.99	6.80
	0.10	129.14	108.35	10.65
	0.15	2.06	22.68	2.24
C9	0	4560	120.18	11.06
	0.10	4560	168.20	11.21
	0.15	2832.8	180.49	12.64

When Table 4 was analyzed, it was seen that the device reached the maximum shear stress capacity (4560 Pa) in the no-PCE containing C2 mixture. In addition, when 0.10% PCE was added to the mixture, a 97% decrease occurred in the SYS value, while an increase of 11% and 57% occurred in the DYS and viscosity values, respectively. It was thought that an increase in the investigated parameters occurred due to the decrease in free water in the mixture during up to the 4th period, when viscosity and DYS are determined due to hydration reactions. However, when PCE of 0.15% was added, a very serious decrease occurred in all the examined values. PCE addition of 0.15% dominated C_3A 's ability to adversely affect workability [9] resulting in the improvement of viscosity and rheological parameters [2]. However, the rheological results were different in C9 mixtures. It was observed that the C9 mixture containing no PCE reached the maximum shear stress value. In addition, when 0.10% PCE was added to the C9 mixture, it was detected that the maximum SYS value was reached due to the over stiff of the mixture, but the DYS and viscosity values increased by 40% and 1%, respectively. On the other hand, when 0.15% PCE was added to the mixture, it was established that the SYS value decreased by 38%, and the DYS value increased by 50% and 14%, unlike C2. Due to the dispersion effect that appeared with the addition of PCE to the mixture, the workability of the C9 mixture increased and there was a decrease in the SYS value. However, the rheological properties were severely affected due to the hydration reactions of C_3A and the adsorption of PCE to the C_3A and ettringite surface over time. When the results were evaluated, it was

determined that the long time elapsed until the 4th period in which the viscosity value was determined by DYS in the deformation rate regime used caused inconsistency between the SYS obtained from the 1st period and the viscosity and DYS values determined from the 4th period. In addition, due to the high adsorption affinity of the PCE [10], it was observed that problems such as the decrease in the effectiveness of the PCE occur depending on time during the measurement period. In addition, the use of 0.15% PCE caused the dispersion effect of PCE to be dominant in C2 cement, while water depletion was dominant in C9 cement due to the amount of C₃A and ettringite formation.

Conclusion

In this study, the effect of cements with different C₃A content on the rheological properties of paste mixtures in the presence of PCE were examined. Following results were obtained:

- The increment in cement C₃A amount adversely affected the rheological parameters of the mixtures.
- The dispersion effect of the PCE causes C₃A to come into contact with more water. However, while the increase in the dosage of PCE at low C₃A ratio positively affected the rheological parameters of the mixture, the rheological parameters were negatively affected at high C₃A content.
- In addition to the C₃A content, the dosage of the PCE should be taken into account in terms of cement admixture compatibility in the preparation of the mixtures.

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