



**PREPARATION AND STUDYING THE
MECHANICAL PROPERTIES OF POLYMER-
BASED NANO AND MICRO-COMPOSITES TO
ACHIEVE HIGH PERFORMANCE EFFICIENCY**

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ENGINEERING**

Ali Awad Abdulkadhim MUSLIMAWI

**Thesis Advisor
Prof. Dr. Hayrettin AHLATCI**

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Ali Awad Abdulkadhim MUSLIMAWI

**Thesis Advisors
Prof. Dr. Hayrettin AHLATCI**

**T.C.
Karabük Üniversitesi
Institute of Graduate Programs
Department of Metallurgical and Materials Engineering
Prepared as
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I certify that in my opinion the thesis submitted by Ali Awad Abdulkadhim MUSLIMAWI titled “PREPARATION AND STUDYING THE MECHANICAL PROPERTIES OF POLYMER-BASED NANO AND MICRO-COMPOSITES TO ACHIEVE HIGH PERFORMANCE EFFICIENCY” is fully adequate in scope and in quality as a thesis for the degree of Master of Science

Prof. Dr. Hayrettin AHLATCI
Thesis Advisor, Department of Metallurgical and Materials Engineering

This thesis is accepted by the examining committee with a unanimous vote in the Department of Metallurgical and Materials Engineering as a Master of Science thesis.
July 5, 2024

Examining Committee Members (Institutions) Signature

Chairman: Prof. Dr. Yavuz SUN (KBU)

Member : Prof. Dr. Hayrettin AHLATCI (KBU)

Member : Prof. Dr. Yunus TÜREN (NEU)

The degree of Master of Science by the thesis submitted is approved by the Administrative Board of the Institute of Graduate Programs, Karabuk University.

Assoc. Prof. Dr. Zeynep ÖZCAN
Director of the Institute of Graduate Programs

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Ali Awad Abdulkadhim MUSLIMAWI

ABSTRACT

Master Thesis

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Ali Awad Abdulkadhim MUSLIMAWI

Karabük University

Institute of Graduate Programs

The Department of Metallurgical and Materials Engineering

Thesis Advisor:

Prof. Dr. Hayrettin AHLATCI

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Polymer nanocomposites have emerged as a promising area of research, particularly for biomedical applications. This master's thesis focuses on exploring the potential of silicone rubber (SR) nanocomposites containing nano-zinc oxide (nano-ZnO) to improve mechanical properties and develop a suitable mixture for biomedical applications. Silicone rubber was chosen as the base material due to its flexibility and durability, while the addition of nano-ZnO was intended to improve crosslinking and mechanical performance. The addition of ZnO nanoparticles resulted in significant changes in the X-ray diffraction (XRD) patterns of the amorphous polymer, indicating increased crystallinity. However, the FTIR results showed no significant changes in the chemical structure of the silicone rubber, suggesting that the interactions between the nanoparticles and the polymer matrix are mainly physical in nature.

Morphological analysis revealed that the addition of 0.5 to 2 wt% N-ZnO improved homogeneity, reduced roughness, and improved mechanical properties. The addition of ZnO nanoparticles to the silicone rubber matrix effectively increased the density of the composite samples, although the influence on water absorption was less significant. Incorporating N-ZnO nanoparticles into the silicone rubber matrix can effectively improve the tensile strength, elongation at break, compressive strength and tear strength of the composites up to a certain concentration (1.5 wt% in this case). However, further increasing the nanoparticle loading resulted in agglomeration, which had a negative impact on the mechanical properties. The addition of N-ZnO nanoparticles also significantly improved the hardness of the composites, which is attributed to the strengthening mechanisms provided by the nanoparticles. The water absorption of the material was found to be controllable by adjusting the isocyanate to water ratio, with higher water contact and isocyanate ratio resulting in increased water absorption due to the foaming effect. In contrast, the incorporation of polyurethane (PU) into the silicone rubber-based interpolymer had a negative effect on tensile strength, elongation, tear strength, impact strength, and compressive strength, likely due to the formation of a more porous and less cohesive structure. as well as potential compatibility issues. However, the addition of PU led to a significant increase in the hardness and stiffness of the material. Importantly, the addition of NanoZnO to the silicone rubber significantly improved the antibacterial properties of the composite, with the most effective composition being the PU sample SR+1.5ZnO+30, which exhibited the strongest inhibition against both gram-positive and gram-negative bacteria. These results suggest the potential of the developed nanocomposite blend polymer for biomedical applications, where the combination of improved mechanical properties and enhanced antibacterial activity can be of great benefit.

Keywords : Nanocomposite, Blend Polymer, Silicon Rubber, Nano-Zno, Polyurethane, Mechanical Properties , Antibacterial Activity.

Science Code : 91524

ÖZET

Yüksek Lisans Tezi

POLİMER BAZLI NANO VE MİKRO-KOMPOZİTLERİN YÜKSEK PERFORMANS VERİMİ ELDE ETMEK İÇİN MEKANİK ÖZELLİKLERİNİN HAZIRLANMASI VE İNCELENMESİ

Ali Awad Abdulkadhim MUSLIMAWI

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Polimer nanokompozitler, özellikle biyomedikal uygulamalar için umut verici bir araştırma alanı olarak ortaya çıkmıştır. Bu yüksek lisans tezi, mekanik özellikleri iyileştirmek ve biyomedikal uygulamalar için uygun bir karışım geliştirmek amacıyla nano-çinko oksit (nano-ZnO) içeren silikon kauçuğu (SR) nanokompozitlerinin potansiyelini araştırmaya odaklanmaktadır. Silikon kauçuğu esnekliği ve dayanıklılığı nedeniyle temel malzeme olarak seçilmiş, nano-ZnO eklenmesi ise çapraz bağlanmayı ve mekanik performansı iyileştirmeyi amaçlamıştır. ZnO nanoparçacıklarının eklenmesi, amorf polimerin X-ışını kırınım (XRD) desenlerinde belirgin değişikliklere yol açarak kristalleşmenin arttığını göstermiştir. Ancak FTIR sonuçları, silikon kauçuğun kimyasal yapısında önemli değişiklikler olmadığını, nanoparçacıklar ve polimer matrisi arasındaki etkileşimlerin esas olarak fiziksel olduğunu göstermiştir.

Morfolojik analiz, %0,5 ila %2 N-ZnO eklenmesinin homojenliđi artırdıđını, pürüzlülüđü azalttıđını ve mekanik özellikleri iyileştirdiđini ortaya koymuştur. Silikon kauçuk matrisine ZnO nanoparçacıklarının eklenmesi, kompozit örneklerin yoğunluđunu etkili bir şekilde artırmıř, ancak su emilimi üzerindeki etkisi daha az belirgin olmuştur. N-ZnO nanoparçacıklarının silikon kauçuk matrisine dahil edilmesi, belirli bir konsantrasyona kadar (%1,5 ađırlık yüzdesi) kompozitlerin çekme dayanımını, kopma uzamasını, basma dayanımını ve yırtılma dayanımını etkili bir şekilde artırabilmektedir. Ancak nanoparçacık yükünün daha da artırılması, aglomerasyon oluřumuna ve mekanik özelliklerin olumsuz etkilenmesine neden olmuştur. N-ZnO nanoparçacıklarının eklenmesi ayrıca kompozitlerin sertliđini önemli ölçüde iyileştirmiş, bu da nanoparçacıkların sağladıđı güçlendirme mekanizmalarına atfedilmiştir. Malzemenin su emilimi, izosiyonat-su oranının ayarlanmasıyla kontrol edilebilir hale getirilmiş, daha yüksek su teması ve izosiyonat oranı, köpürme etkisine bađlı olarak artan su emilimi ile sonuçlanmıştır. Buna karřın, silikon kauçuk esaslı karıřıma poliüretan (PU) eklenmesi, daha gözenekli ve daha az yapıřkan bir yapının oluřumu ile uyumluluk sorunları nedeniyle, çekme dayanımı, uzama, yırtılma dayanımı, darbe dayanımı ve basma dayanımı gibi mekanik özellikleri olumsuz etkilemiştir. Bununla birlikte, PU eklenmesi malzemenin sertliđini ve rijitliđini önemli ölçüde artırmıştır.

Önemli bir husus, nano-ZnO eklenmesinin silikon kauçuđa antibakteriyel özelliklerini önemli ölçüde iyileştirmiş olmasıdır. En etkili bileřim olan SR+1,5ZnO+%30 PU, hem gram-pozitif hem de gram-negatif bakterilere karřı en güçlü inhibisyon etkisini göstermiştir. Bu bulgular, geliřtirilen nanokompozit karıřım polimerinin, geliřtirilmiş mekanik özellikler ve iyileştirilmiş antibakteriyel aktivite kombinasyonunun büyük fayda sağlayabileceđi biyomedikal uygulamalar için potansiyel taşıdıđını göstermektedir.

Anahtar Kelimeler : Nanokompozit, Karıřım Polimer, Silikon Kauçuk, Nano-ZnO, Poliüretan, Mekanik Özellikler, Antibakteriyel Aktivite.

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CONTENTS

	<u>Page</u>
APPROVAL.....	ii
ABSTRACT.....	vi
ÖZET.....	iv
ACKNOWLEDGMENT.....	ix
CONTENTS.....	x
LIST OF FIGURES.....	xiii
LIST OF TABLES.....	xiv
SYMBOLS AND ABBREVIATIONS INDEX.....	xv
PART 1.....	1
1.1. INTRODUCTION.....	1
1.2. MOTIVATION.....	5
PART 2.....	6
LITERATURE REVIEW.....	6
PART 3.....	9
THEORETICAL BACKGROUND.....	9
3.1. POLYMER MATERIAL.....	9
3.1.1. Thermoplastics.....	12
3.1.2. Thermosets.....	13
3.2. COMPOSITE MATERIALS.....	14
3.3. NANOCOMPOSITE MATERIAL.....	15
3.3.1. Advantages of Nanotechnology.....	17
3.3.2. Disadvantages of Nanotechnology.....	18
3.4. POLYMERIC NANOCOMPOSITES.....	18
3.5. AREAS OF USE OF POLYMERIC NANOCOMPOSITES.....	20
3.6. POLYMER BLEND.....	22

	<u>Page</u>
3.6.1. Polymer Blend Types	22
3.6.2. The Advantages of Blending	24
3.7. INTERPENETRATING POLYMERS NETWORKS (IPN)	25
3.8. SILICONE ELASTOMERS	27
3.8.1. Classification of Silicone	28
3.9. POLYURETHANE	29
3.10. ZINC OXIDE NANOPARTICALS (N-ZNO)	32
PART 4	37
MATERIALS AND METHOD	37
4.1. INTRODUCTION	37
4.2. MATERIALS	39
4.2.1. Silicon Rubber	39
4.2.2. Polyurethane	39
4.2.3. Reinforcement Materials	40
4.3. PREPARATION OF NANO COMPOSITE	40
4.4. POLYMERIC BLEND PREPARATION	41
4.5. CHARACTERIZATION OF THE NANOCOMPOSITE	41
4.5.1. Physical Inspections	41
4.5.2. X-Ray Diffraction Analysis	42
4.5.3. Fourier Transform Spectroscopy (Ftir)	43
4.5.4. Microstructure Analysis	43
4.5.5. Mechanical Analysis	43
4.5.6. Antibacterial Activity	47
PART 5	48
RESULT AND DISSCSUION	48
5.1. INTRODUCTION	48
5.2. XRD ANALYSIS	48
5.3. FTIR RESULT	49
5.4. MICROSTRUCTURE ANALYSIS	51
5.5. PHYSICAL PROPERTIES	52

	<u>Page</u>
5.6. MECHINCAL PROPERTIES.....	54
5.6.1. Tensile Strength And Elongation.....	54
5.6.2. Compression Strength.....	55
5.6.3. Tear Strength	56
5.6.4. Hardness	57
5.7. CHARACTERIZATION OF BLEND SR/PU NANOCOMPOSITE.....	59
5.7.1. Physical Properties.....	59
5.7.2. Tensile Strength, And Elongation.....	60
5.7.3. Tear Strength	61
5.7.4. Impact Strength.....	62
5.7.5. Compression Strength.....	63
5.7.6. Rebound Resilience	64
5.7.7. Hardness	65
5.8. ANTIBACTERIAL ANALYSIS	66
 PART 6.....	 69
CONCLUSIONS	69
 REFERENCES.....	 71
 RESUME.....	 82

LIST OF FIGURES

	<u>Page</u>
Figure 3.1. Vinyl chloride monomer forming polyvinyl chloride.....	10
Figure 3.2. Formation of polystyrene by the polymerization reaction of styrene monomer	11
Figure 3.3. Short representations of a polymer chain (polyethylene is taken as an example).....	11
Figure 3.4. Appropriate zigzag arrangement of carbon atoms in the regular tetrahedral geometry in the polyethylene molecule	12
Figure 3.5. Length scale in comparison to nanometers	16
Figure 3.6. Various uses of polymeric nanocomposites.....	21
Figure 3.7. Possible effect on the properties of polymer mixtures with the component concentration	24
Figure 3.8. Techniques for IPN synthesis. A, Sequential IPNs; B, simultaneous interpenetrating polymer networks	27
Figure 3.9. Schematic of polyurethane molecule	32
Figure 3.10 A schematic representation of ZnO crystal structures: Wurtzite and Zinc Sulfide	34
Figure 4.1. Experimental flow chart	38
Figure 4.2. Samples for Tensile strength, Elastic Modulus and Elongation test.....	44
Figure 4.3. Samples for Hardness test	44
Figure 4.4. Samples for Compression test.....	45
Figure 5.1. XRD of the nanocomposite of SR+ X ZnO.....	49
Figure 5.2. FTIR of the nanocomposite of SR+ X ZnO.	50
Figure 5.3. SEM & EDX of the nanocomposite of SR+ X ZnO.....	52
Figure 5.4. Density and water absorption of the nanocomposite of SR+ X ZnO.....	53
Figure 5.5. Tensile strength and elongation of the nanocomposite of SR+ X ZnO...	55
Figure 5.6. Compression strength of the nanocomposite of SR+ X ZnO.....	56
Figure 5.7. Tear strength of the nanocomposite of SR+ X ZnO	57
Figure 5.8. Hardness of the nanocomposite of SR+ X ZnO.....	58
Figure 5.9. Tensile strength and elongation of the nanocomposite of SR+ 1.5% ZnO +X PU.....	61

	<u>Page</u>
Figure 5.10. Tear strength of the nanocomposite of SR+ 1.5% ZnO +X PU.	62
Figure 5.11. Impact strength of the nanocomposite of SR+ 1.5% ZnO +X PU	63
Figure 5.12. Compression strength of the nanocomposite of SR+ 1.5% ZnO +X PU	64
Figure 5.13. Rebound Resilience of the nanocomposite of SR+ 1.5% ZnO +X PU.	65
Figure 5.14. Hardness of the nanocomposite of SR+ 1.5% ZnO +X PU.....	66
Figure 5.15. Antibacterial activity against Staphylococcus.	67
Figure 5.16. Antibacterial activity against S. aureus.	67

LIST OF TABLES

	<u>Page</u>
Table 4.1. Properties of Silicon Rubber.	39
Table 4.2. Properties of polyurethane components	40
Table 5.1. Effect of varying the amount of isocyanate and water contact on water absorption	60

SYMBOLS AND ABBREVIATIONS INDEX

SYMBOLS

- °C : Celsius degree
KJ/m² : force per unit area
MPa.S : millipascal-second
mg : milligram

ABBREVIATIONS

- SR : Silicon rubber
n-ZnO : Zinc oxide nanoparticles
JCPDS : Joint Committee for Powder Diffraction Standards
PU : polyurethane
IZ : Inhibition zone
PDMS : Poly-di-methyl-siloxane
SEM : Scanning Electron Microscopy

PART 1

INTRODUCTION

1.1 INTRODUCTION

Nanotechnology is one of the most investigated and studied areas today, being developed in basically all technical areas, such as materials, biomedical, electronics, among many others. For research to encompass nanotechnology, at least one of the components under study must have a dimension between 1 – 100 nm [1]. In the field of polymer science and technology, nanotechnology is present in biomaterials, pharmaceuticals, polymeric fuel cell catalysts, lithographic printing, nanocomposites and others [2]. Nanocomposites are materials designed to overcome the limitations of composites. They have superior properties compared to conventional composite materials. Depending on their matrix, they can be categorized as metal matrix nanocomposites, ceramic matrix nanocomposites, or polymer matrix nanocomposites. At the nanometer scale, interactions at the matrix-reinforcement interface tend to increase, leading to an improvement in material properties [3].

The emergence of polymer nanocomposites occurred in the late 1980s when Toyota produced a thermoplastic nanocomposite made of polyamide 6 and organophilic clays. This material had better mechanical, physical and thermal properties. From then on, other companies became interested in developing novel nanocomposites [4]. Another important factor in polymer nanocomposites is that excellent results can be achieved with low reinforcing filler contents (<5%). In recent years, interest in polymer matrix nanocomposites has increased significantly. Among the different types of polymer matrix nanocomposites, those reinforced with lamellar compounds are particularly interesting and have been extensively studied in recent years since they showed the best property gains and have the versatility to be modified by intercalation reactions [5].

General-purpose polymers such as polystyrene, polyethylene, polypropylene and other natural rubbers, which are often used in cost-effective applications, are characterized by easy processing and low mechanical demands. The production of nanocomposites from these polymers is a way to add value to these materials and improve their mechanical, thermal and physical properties [1]. Several experimental methods have been used in the synthesis of polymer nanocomposites, the most important of which are: in situ intercalative polymerization; storage of the polymer from the solution; direct mixing of polymer and particles; Sol-gel process [3] .

The development of composite materials has expanded significantly through advances in traditional materials and the emergence of new materials such as polymers. One of the biggest advantages of polymer materials over inorganic materials such as metals or ceramics is their low density. Typically, the replacement of inorganic materials with polymers occurs for economic and environmental reasons. Polymer composites were developed to improve the poor mechanical and thermal properties of polymers compared to other materials such as metals. However, to achieve better performance, a higher concentration of filler began to be used, which resulted in an increase in the density of the composite [6]. In recent years, improving the properties of composite materials has become increasingly limited, as properties are often achieved at the expense of others. For example, in some cases stiffness is replaced by toughness or toughness is achieved at the expense of transparency [7].

Thus, in the 1980s, attention began to turn to a new category of composite materials. In 1985, a polymer/clay nanocomposite was developed in Toyota's research and development laboratories. Since then, the new concept of “polymeric nanocomposites” has emerged, expanding the study of polymer science in terms of fabrication, structure and interfaces and enabling new applications in various industry segments. Cars equipped with nanocomposite parts appeared on the market in 1989, just four years after their discovery. Since then, several researches on nanocomposites have been carried out worldwide, both in industrial and academic fields [8]. Research on nanocomposites is very broad, covering areas such as electronics, computing, data storage, communications, aerospace and sports materials, medicine, oil and gas.

The transition from microparticles to nanoparticles led to significant changes in the physical properties of materials. The use of nanoparticles as fillers is interesting because they have different properties than chemically analogous materials, but have larger dimensions. Charges with nanometric dimensions have a large specific area. As a result, they distribute more easily in the polymer matrix and, depending on the homogeneity of the material, produce nanocomposites with better physical properties. Higher mechanical resistance, reduced permeability to liquids and gases, flame retardancy, increased thermal stability, and improved optical, magnetic, and electrical qualities are some of these qualities[9].

Calcium carbonate, talc, glass fibers, and other inorganic fillers have all been used to successfully reinforce polymers. A composite usually contains a high percentage of filler—between 30 and 50 percent (w/w). Failures or fractures are frequently the result of macroscopic defects caused by regions of high or low volume load fraction. These conventional fillers are usually swapped out for organophilic clays in a 3:1 ratio. For instance, 15–50% of a filler like talc can be substituted with 5% of an organophilic clay[8]. Thus, the synthesis of polymer nanocomposites frequently permits a trade-off between low cost (as a result of using less filler) and high performance (as a result of the components working together harmoniously).

Generally, the kind of polymer and clay, the synthesis technique, and the reaction circumstances can result in the formation of two distinct nanocomposite structures. In the intercalated structure, the ordered structure is preserved by inserting one or two polymer chains in between the clay's interlayer spaces. The clay layers are evenly distributed throughout the polymer matrix in the exfoliated structure[10]. The degree to which the clay layers are dispersed throughout the polymer matrix typically determines how much the properties are improved. Because of this uniform clay distribution in the polymer and the wide interface between the two, exfoliated nanocomposites are becoming more and more interesting.

In situ integration of fillers has been a thoroughly studied technique for the synthesis of polymer composites and nanocomposites, owing to the growing interest in optimizing the properties of polymer materials. But since so few studies have

examined this effect, little is known about how fillers affect the course of the reaction and the quality of the final polymer. To find out if the presence of fillers affects the polymerization process, the primary goal of this work is to examine how filler addition affects the molecular weights, polymer composition, conversion morphology, and in situ polymerization kinetics. Due to this, the uniqueness of this work lies in the thorough investigation of how different fillers' in situ incorporation affects the kinetics of polymerization in the process of creating polymer composites and nanocomposites.

Various polymerization techniques, fillers and polymer matrices were used. Polystyrene (PS) and poly (ethylene terephthalate-co-propylene terephthalate) (PEPT) polymer matrices were synthesized in the Modeling, Simulation and Process Control Laboratory of the Chemical Engineering Program at COPPE (LMSCP/PEQ/COPPE) and a modified MMT as filler was sodium MMT (MMT-Na⁺), barium sulfate (BaSO₄), zirconium dioxide (ZrO₂) and hydroxyapatite (HAp) added.

The unique properties of silicone rubber combine organic and inorganic properties. Because the siloxane bond (Si-O) of silicone rubber has a higher energy bond (106–0 kcal/mol) than the C-C bond (84–9 kcal/mol), silicone rubber has better chemical stability, heat resistance and electrical conductivity. Prolonged exposure to the elements, including water and UV radiation, has no effect on the physical properties of silicone rubber. High biocompatibility, durability, temperature resistance, non-adhesive properties, non-toxicity, chemical resistance and good resistance to sunlight, ozone and oxygen are just some of the many properties of silicone rubber [11].

Zinc oxide nanoparticles are often used due to their special properties. Initially, it was added to rubber to improve durability, toughness, aging resistance and other properties [1]. Zinc oxide nanoparticles have strong UV absorption and have excellent antibacterial, non-toxic and antimicrobial properties. Generally, zinc is found in body tissues, including muscles, brain, skin, bones, etc. Nano-ZnO is commonly added in the food industry as an additive. Furthermore, the Food and Drug Administration (FDA) classifies ZnO as "GRAS" (Generally Recognized as Safe)[12]. Currently, zinc oxide nanoparticles are used in many medical applications due to these special

properties such as drug delivery, anticancer, wound healing, antibacterial effect and anti-inflammatory effect [13, 14].

1.2 MOTIVATION

Polymer nanocomposites represent a burgeoning field of study with numerous potential uses, including the biomedical domain. This master's thesis aims to investigate how adding nano-zinc oxide (nano-ZnO) to silicon rubber nanocomposites can enhance their mechanical characteristics and create a combination that can be used in biomedical applications. For nanocomposites, silicone rubber makes an excellent base material because of its strength and flexibility. It has been demonstrated that adding nano-ZnO enhances cross-linking with the rubber matrix, leading to better mechanical qualities like increased toughness and tensile strength. The objective of the proposed research is to determine the ideal composition and processing conditions for silicon rubber nanocomposite by methodically examining the effects of various ZnO loading levels and dispersion techniques on the mechanical properties of the material. This knowledge will enable the development of a high-performance nanocomposite material that can be tailored for various applications, particularly in the field of biomedical applications. In addition, after determining the optimal nanocomposite formulation, the research will explore the potential to develop a blended polymer based on the best ratio of ZnO to silicone rubber. This blended polymer can be further investigated for its suitability for biomedical applications such as biodegradable implants, dental implants, socket linings, and wound healing. , where the combination of improved mechanical properties and biocompatibility can be extremely beneficial.

PART 2

LITERATURE REVIEW

Synthetic rubber composed of silicon-oxygen chains with organic side groups is called silicon rubber, or polysiloxane. It has a stellar reputation for electrical insulation, superior thermal stability, and resistance to oxidation, ozone, and weather. Unfortunately, its limited applications are caused by its poor mechanical properties, such as low tensile strength and elastic modulus. Nano composites have been created by combining different fillers, including metal oxides, silica, and carbon black, with silicon rubber to get around these restrictions. Because of its special qualities, which include high chemical stability, non-toxicity, and superior electrical and optical properties, zinc oxide (ZnO) has drawn the most attention among these fillers. A variety of techniques, such as mechanical mixing, in situ polymerization, and sol-gel processing, can be used to create silicon rubber/ZnO nano composites. Although mechanical mixing is a straightforward and affordable technique, the silicon rubber matrix's dispersion of ZnO particles is frequently compromised.

Noor H. Aysa et al., in 2015, demonstrated the use of alum, a potassium-aluminum sulfate salt (K_2SO_4), in 2015. $Al_2(SO_4)_3 \cdot 12H_2O$, a dual-purpose filler that helps achieve a more sterilized product and facilitates the creation of closed cell composites. There are different amounts of alum added to silicone rubber (0, 1, 2, 3, 4, and 5% percent). The mechanical properties of alum powder decrease as the alum percentage increases. The strengthening effect of the alum powder is minimal. The addition of alum lowers all mechanical parameters (tensile strength, tear resistance, modulus, compression, hardness, elongation, and specific gravity) because it creates holes in the material and weakens the cohesiveness of the recipe components[15].

Noor H. Aysa et al., in 2015, revealed in 2015 the creation of an antibacterial prosthetic liner utilizing zinc oxide nanoparticles mediated by artificial limbs, along with the investigation of mechanical properties and antibacterial efficacy. Tensile strength, tear resistance, elongation, modulus, hardness, compression, and specific gravity all decreased with an increase in the concentration of both kinds of ZnO nanoparticles (modified and unmodified). When compared to composites with unmodified ZnO nanoparticles, those with modified ZnO nanoparticles exhibit superior mechanical properties[16].

Sihama Issa Salih et al., in 2018, presented materials that could be used to replace lost maxillofacial facial components resulting from illness or trauma were presented. The best materials in this field are regarded to be silicone rubbers. Therefore, the aim of this study is to examine the impact of adding PMMA material to silicone rubber at different loading levels (5 percent, 10 percent, 15 percent, and 20 percent) on the mechanical properties of SiR/PMMA blends. The findings showed that 10% of PMMA should have the ideal proportion of flawless qualities. This suggests that the sample may work well as a material for maxillofacial prosthetic applications [17].

Salih (2019) has produced a new polymer blend composite for maxillofacial prosthesis application and studied the effect of addition of nano powder material on the properties of polymer blends, which prepared in different loading levels (5%, 10%, 15% and 20%) of poly methyl methacrylate to silicone rubber. Mechanical, physical and antibacterial tests were done, the results showed that best composite sample ((SiR: 5% PMMA): 0.2% Pomegranate peels powder) having the highest values of the mechanical properties, while the antibacterial efficiency of blend (SiR/PMMA) increased with adding 5%PMMA to blend compared with pure silicone rubber [18].

Saud et al., in 2019 The SR/HA/ZnO bio composite is a promising material for maxillofacial prosthetics and jawbone reconstruction. The bio composite was developed by incorporating hydroxyapatite (HA) synthesized using the sol-gel technique into a silicone rubber (SR) matrix. Nano ZnO particles were also added, with their surface modified for uniform distribution and reduced agglomeration. The addition of HA and ZnO significantly improved the bio composite's mechanical

properties, making it suitable for prosthetic applications. Furthermore, the SR/HA/ZnO bio composite exhibited excellent biocompatibility and demonstrated antimicrobial activity. The modified ZnO nanoparticles acted as an effective antimicrobial agent, reducing the risk of infection. The bio composite showed promise for inhibiting bacterial growth, the SR/HA/ZnO bio composite holds great potential for maxillofacial prosthetics and jawbone reconstruction. Its synthesis and combination of materials result in enhanced mechanical properties and antimicrobial activity [1]. Ahmed K. and Zohar J., in 2022, presented Silicone rubber liners that are recommended for usage because they can absorb moisture, distribute tension, and are anti-bacterial. Crosslink density is significantly influenced by temperature and curing time. The findings demonstrate that the cross-link density directly influences the percentage of elongation, tensile strength, modulus of elasticity, water absorption, and cure time (15 min.). yields optimal outcomes. By using it, the patient's prosthesis becomes more acceptable and comfortable. The effect of cure time on physical attributes was investigated in this research [19]. A recent study has made significant progress in this field by improving the silicone rubber socket liner used in lower extremity prostheses to enhance its physical and mechanical properties by incorporating hydroxyapatite (HA) and zinc oxide (ZnO) nanoparticles. The study also explores the impact of adding chlorophyll on water absorption. Different concentrations of HA and ZnO nanoparticles were added to a silicone rubber composite. Chlorophyll was included in varying proportions. The nanocomposite showed improved mechanical properties, with 1.5% ZnO and 0.5% HA nanoparticles yielding the most significant enhancements. The addition of 10% chlorophyll increased water absorption. The nanocomposite exhibited good antibacterial activity against *Staphylococcus aureus*. By incorporating HA and ZnO nanoparticles, the study successfully improved the silicone rubber socket liner for lower extremity prostheses. The addition of chlorophyll influenced water absorption. The nanocomposite demonstrated enhanced mechanical properties and significant antibacterial activity. This research offers potential for developing more comfortable and functional prosthetic socket liners. Further research and testing are necessary for real-world applications [20].

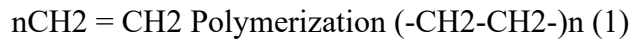
PART 3

THEORETICAL BACKGROUND

3.1 POLYMER MATERIAL

Long chain structures formed by small molecule structures called monomers coming together are called polymers, and this process is called polymerization. For a substance to be considered a polymer, hundreds of monomers must combine to form a large molecule. Polymer (macromolecule) appears as a large molecule consisting of repeated simple and small units. These simple and small chemical units that are repeated within polymer molecules are called "repeating units (mers)", and the organic substances with small molecules that are initially used to obtain polymers are called "monomers". If the units of the macromolecule are the same, this type of polymer is called "homopolymer". If it consists of the combination of two or more monomers, it is referred to as "copolymer" [21].

The main groups that make up polymers are in different numbers depending on the polymer type. Apart from this, these groups form a linear, branched or cross-linked structure. The number of groups in molecules is called the degree of polymerization. The molecular mass of the plastic material is calculated by multiplying the group molecular mass and the degree of polymerization. In most polymers, the molecular mass is generally between 10,000-100,000. All polymers have starting monomers. The monomers that make up polymers undergo various structural changes during their transition to the main group. The substances obtained because of polymerization have their natural color. Apart from this, they are marketed as tablets, films, sheets, blocks, profiles or shaped in different shapes for their ease of use and purpose [22].



Equation 1 above shows that polyethylene containing up to (n) monomers is obtained by polymerization of ethylene monomers. Polymers are divided into two groups: artificial and natural polymers. Polymers used in industrial practice generally appear as artificial polymers. When we look at the structure of polymers, we see that they have three different structures: homopolymer, which is formed by the repetition of a single monomer, copolymer, which is formed by the polymerization of two different monomers, and thermopolymer, which is formed by three different chemical repetitions. When we look at the areas where polymers are used, they are divided into three as fibers, coatings and adhesives, and physically they are divided into three as amorphous, crystalline and partially crystalline. The most commonly used classification of polymers is the classification made according to the processing method. Accordingly, polymers are divided into two as thermoplastic and thermoset [23].

Polymer is a large molecule composed of many monomers linked together by covalent bonds. The word polymer comes from the words -poly-, meaning many, and -meros-, meaning particle, small piece. All reactions that lead to the formation of polymers from monomers are called polymerization reactions or polymerization reactions [24].

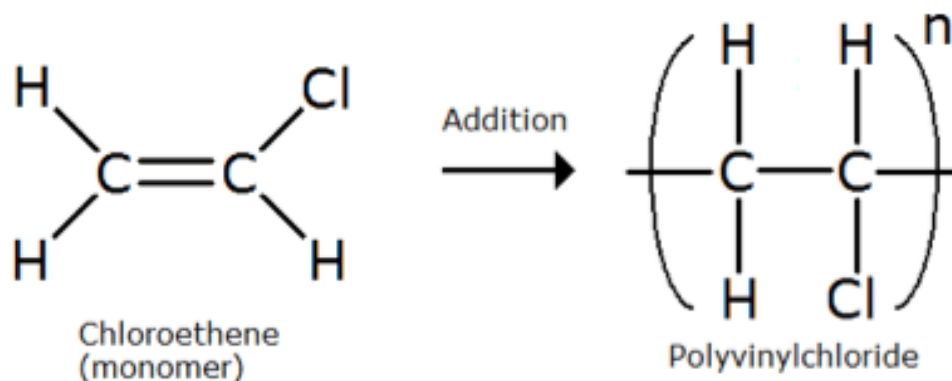


Figure 3.1. Vinyl chloride monomer forming polyvinyl chloride [25].



Figure 3.2. Formation of polystyrene by the polymerization reaction of styrene monomer [26].

Polymer molecules can be compared to a chain, and monomer molecules can be compared to the rings that make up that chain. Therefore, the term “polymer chain” is often used instead of the term “polymer molecule”. Polymer molecules can also be called macromolecules because of their size [22]. Polymer chains can be represented using different formats and software. For example, below are some representations of polyethylene (Figure 3.3.).

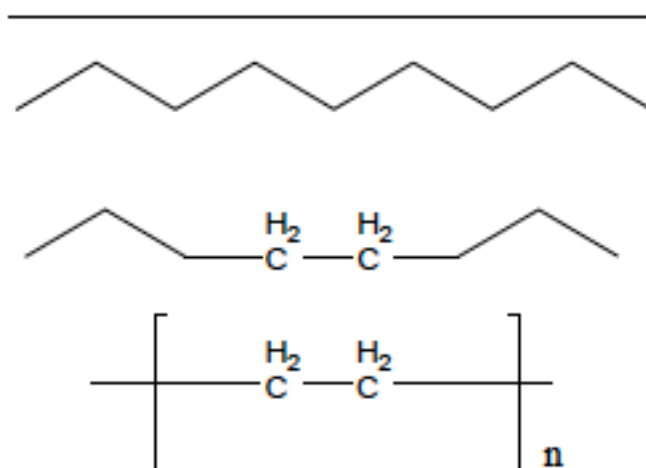
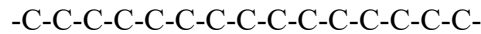


Figure 3.3. Short representations of a polymer chain (polyethylene is taken as an example)[27].

Carbon atoms on polyethylene chains,



They are not arranged in a straight line but are arranged in a tetrahedral geometry according to sp^3 hybridization, forming a zigzag-like structure. Each carbon atom undergoes sp^3 hybridization.

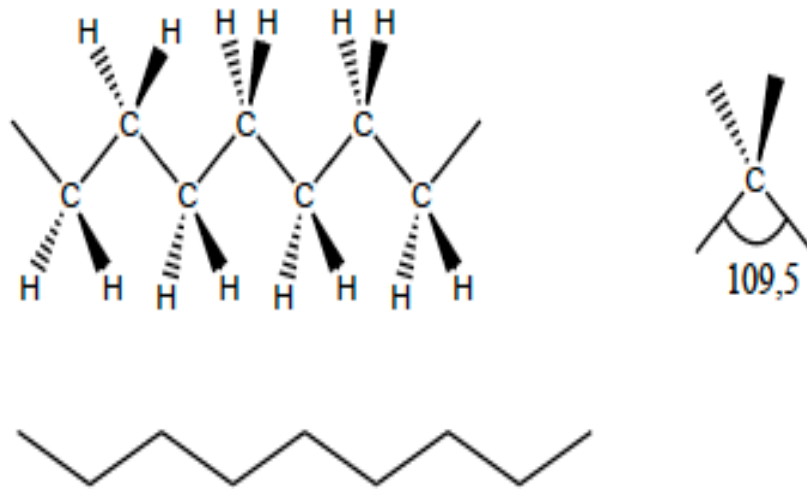


Figure 3.4. Appropriate zigzag arrangement of carbon atoms in the regular tetrahedral geometry in the polyethylene molecule [28].

3.1.1. Thermoplastics

Thermoplastic materials are materials that soften and become fluid when heated and solidify when cooled. Repeating this process does not cause thermoplastics to lose their properties. Therefore, thermoplastics can be reprocessed. Although their thermal conductivity is lower than metals, their thermal expansion coefficient is five times higher than metals. Their electrical insulation is extremely good, their impact resistance is high, their strength in terms of hardness and rigidity is low, they are flexible, and they are difficult to process at room temperature [29].

Thermoplastics are difficult to process because they have high fluidity at processing temperatures. The high shear stresses needed to ensure the flow of thermoplastics

cause the fibers to be damaged, causing the length of the fibers to decrease by 10-100 times. For this reason, one of the main goals in the production of new thermoplastic materials and processes is to reduce viscous effects in the fluid. Thermoplastic materials can melt and solidify with repeated heating and cooling without significant changes in their mechanical and optical properties. They are very common in industrial production and are used in high quantities in the production of mixed and bulky parts. Viscosity values of materials vary depending on the distribution of molecular weight, chain structure and average molecular weight. Although viscosity has an important place especially in the process of thermoplastics, it is stated that it is more suitable for processes such as extrusion because the flow behavior of materials at high viscosity values is more difficult, while polymers with high flow behavior at low viscosity[30].

values are easier to use in molding and shaping methods in terms of processability. While thermoplastic materials are defined by the chemical monomer units that form their chain structures, structural systems in which the monomers in the polymer structure are well dispersed and there is no crystallization are defined as amorphous polymers, and when crystallized structures begin to form, they are defined as semi-crystalline structures [31].

3.1.2 Thermosets

Polymers that harden permanently above a critical temperature and soften when heated again are “thermoset” polymers. Thermoset polymers or thermosets are polymers that can be permanently set, cured or hardened. The hardening process usually occurs rapidly at room temperature, under heat or ultraviolet (UV) and causes irreversible cross-linking of the polymer [32].

Thermosets have covalent bonds that connect the polymer chains in three dimensions, and these bonds prevent the chains from passing through each other, providing a higher modulus and flexibility resistance. Thermosets generally have a more brittle structure than thermoplastics and have cross-linked or networked internal structures with covalent bonds with all molecules. Once shaped, it cannot be melted and remolded

again, whereas thermoplastics can melt/soften when heated and can be shaped again and again [32].

The reason for this is that the long molecular chains of thermosets are connected to each other by cross-links and when heat is applied again, they lose their ability to slide on each other. Thermoset materials generally take their final form as composite materials under the influence of heat and pressure. The areas of use of thermoset resins can be listed as indoor furniture, marine vessels, various structural elements in the construction industry, and the automotive industry [23].

3.2 COMPOSITE MATERIALS

Most of the composite materials developed to date have been specifically manufactured with the aim of improving properties and performance at high temperatures as well as physical (toughness) and durability, such as: Strength, [the composite materials have a certain property due to the nature of the base material or the type of compound used [33] .Therefore, composite materials can be classified according to the type of base material or the type of compound used. Rubber composites with various types of rubber have covered a wide field of research and research because rubber has good properties and can improve various types of rubber. Filament rubber is used to form rubber (fiber) and fiber (particle) composite materials using reinforcement methods such as particles that improve the dynamics of the materials.

Composites in general can be defined as materials resulting from the process of physical union of two or more materials that differ in shape or composition depending on their state. One of them does not interact chemically with the other, but they combine physically to form a new substance that differs in its properties from the properties of the individual substance included in its composition , where the Material represents a separate phase and as composite materials is divided into two basic phases, namely[22]:

- i. Matrix Material Phase
- ii. Reinforcement Material Phase

Which substance is mixed with it also depends on the mixing ratio, the type of interaction between the two substances and the formation conditions to which the final compound is subject. The material blended together may be a polymer of another type, a ceramic, or a metal. For this reason, mixing the polymer with other materials results in a wide range of compositions of the material in combination with the base material or the new material (continuous phase). . The continuous phase is called the hardener or filler (distribution phase), while the distributed phase is called (matrix). There are three properties that determine the properties of the composite material, namely the filler (reinforcement or filler), (interaction) and the interaction that occurs between them (matrix) and the base material (filler) [34].

The polymer comprises fillers like carbon black and is a base material. Elastomer, thermoplastic, and thermoset materials can all be used as the base material. These materials are thought to be the best since their production process is fluid and they have excellent mechanical qualities in relation to their density[35].

Composites made of polymers are among the most widely used materials. Since these materials are lightweight and can be used for a wide range of purposes, including the production of molds and aircraft parts, interest in them has grown dramatically in recent years. The excellent durability allowed for the production of materials that were both inexpensive and energy efficient. Because of this, reinforced resins are now widely acknowledged as a cutting-edge industrial material that provide a variety of substitutes for conventional materials and their alloys in a wide range of applications. Nevertheless, because polymers lack strength and durability and have a low density, additional ingredients are added to homogenous polymers to give them new and altered properties. This process creates composite polymers[35].

3.3 NANOCOMPOSITE MATERIAL

The prefix “Nano” comes from the Greek word “nanos” and means “dwarf”. In terms of size, one nanometer (nm) corresponds to one billionth of a meter (10^{-9} m). The thickness of human hair is about 80,000 nm and that of red blood cells is about 7,000 nm. When expressed in nanometer, atomic or molecular size; It is as long as 6 carbon

atoms or 10 water molecules side by side. Atoms are smaller than 1 nm [36]. Figure 3.5 shows the nanometer scale compared to various organic structures and synthesized substances.

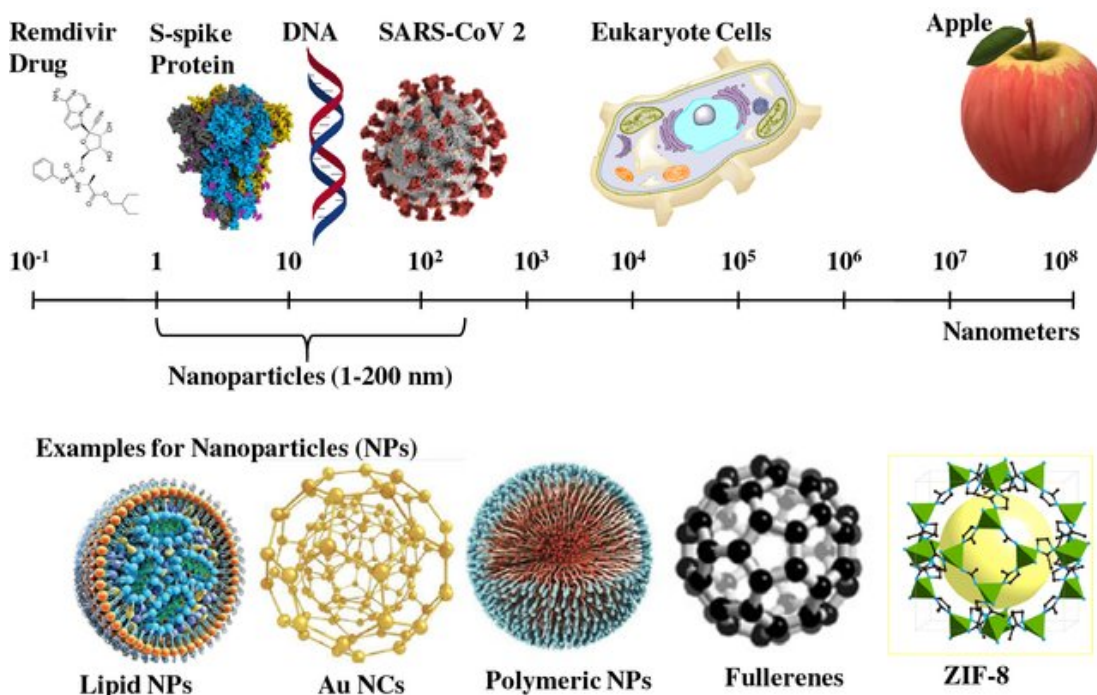


Figure 3.5. Length scale in comparison to nanometers [37] .

Richard Feynmann, a Nobel Prize-winning physicist, was the first to mention nanotechnology in his speech titled "There's plenty of room at the bottom" (1959). He mentioned that nanotechnology conceptually covers many different areas (1959). In the same speech, Feynmann said that the 24 volumes of Basic Britannica could actually be written on the head of a pin and that great things could be done with very small particles. The term "Nanotechnology" was not used until the 1970s, but it began to be used in 1974 when Norio Taniguchi from the University of Tokyo defined material engineering at the nanometric scale. After this date, nanotechnology has progressed rapidly [38, 39].

Nano literally means one billionth of any physical size. Nanostructures correspond to systems with a length of 10–100 atoms (10^{-9} meters). Different properties can be observed in the physical behavior of systems in these dimensions compared to normal

systems. These differences, known as nanoscience and nanotechnology, have determined the civil-military science and technology strategies of countries around the world for about ten years [40].

As materials shrink to the nanoscale, their properties drastically change compared to when they are at a larger scale. This shift gives rise to unique phenomena and novel properties that can be highly beneficial for various applications.[41]. For instance, the conduction properties—mass, momentum, and energy—are now discrete rather than continuous. Similarly, behaviors related to optics, electronics, magnetism, and chemistry are characterized as quantum as opposed to classical. It is now possible to create new technological devices and materials at the nanoscale by processing matter at the nanometer level and exploiting the different properties that result. Using scanning tunneling and atomic force microscopes, for example, it is possible to separate atoms from each other and arrange them in the desired shape by transferring them to the surface [42]. All of these developments ushered in a scientific and technological revolution that paralleled the Industrial Revolution that changed the world in the 19th century. In this way, by playing with atoms and molecules, transistors and electronic devices made of single molecules have been created and are being further developed with the active work of many groups around the world. All of these studies and processes are brought together at a common interface between electronics, chemistry, physics, materials science, space and even health sciences.

3.3.1 Advantages of Nanotechnology

The importance of nanotechnology arises from the fact that it allows the achievement of structures with advanced and/or completely new physical, chemical and biological properties, working at the level of atoms and molecules (on a scale of 1 to 100 nanometers (nm))[43]. Technically, it is based on traditional models and theories that rely on assumptions based on sizes larger than 100 nm. When critical lengths fall below 100 nm, conventional theories and models are often insufficient to explain the resulting features. This is where nanotechnology comes into play. The desire to develop more durable, higher quality, more durable and cheaper, lighter and smaller devices can be seen in many business areas. This tendency, which can be called

miniaturization, forms the basis of many engineering studies. In practice, miniaturization manifests itself in less material in production, less energy, cheaper and easier transport, more functions and user-friendliness. Since the second half of the 20th century, tolerances have been continuously improved in many industries and an understanding of the highest quality has been developed. Parts that we can call microtechnological products are widely used in areas such as automobiles, electronics and communications. Today, the use of smaller technologies than microtechnology, or nanotechnology, is becoming increasingly widespread [44].

3.3.2 Disadvantages of Nanotechnology

In self-repeating production mechanisms such as nanotechnology, the smallest units must be developed in such a way that repetition in the natural and uncontrolled environment is not possible [45]. For this mechanism to work, energy must be supplied from outside. If controlled molecules are possible, nanotechnology can theoretically be improved enormously every day. But it takes a very long time for the individual atoms to line up together. Therefore, different production mechanisms are required. Of course, this production must be feasible. It can list the main disadvantages of research and production on this scale below [22]: .

- i. Adhesion at the atomic scale[46]
- ii. Friction and wear
- iii. Thermal vibrations
- iv. Rigidity of the device
- v. Position finding and control mechanisms
- vi. Quantum effect

3.4 POLYMERIC NANOCOMPOSITES

Various modification methods are applied to improve these defects of conductive polymers that do not have good physical, chemical, mechanical, thermal, processability and solubility properties or to obtain new conductive polymer systems. These processes are usually carried out chemically or electrochemically and occur by mixing a conductive polymer with an insulating matrix or another conductive polymer.

Three types of structures are encountered in such syntheses. Composite structures are generally used for systems that are made by mixing two or more different materials or combining them in a specific order. In composite formation, two polymer matrices are diffused into each other to form a mixture. The composite manufacturing method generally involves suspending or dissolving a polymer and polymerizing another monomer on this system to obtain a composite. The main purpose of producing conductive composites using an insulating polymer matrix is to create composites that have the mechanical properties of the insulating polymer matrix and conductivity close to those of conductive polymers. If layer-by-layer colonization occurs between two polymer layers without the formation of a chemical bond, the resulting double-layer system is referred to as a blend. Generally, blends are formed by mechanically suspending or mixing two or more polymers in a solvent [47].

In the copolymer structure, there are more than one monomer with different chemical structures in the same chain. When a covalent bond is formed between the layers of the double polymer layer, we can say that the newly formed structure is a conductive copolymer structure. There are three types of copolymerization mechanisms: random, sequential and block copolymerization, depending on the arrangement of monomer molecules in the copolymer chain [48].

Composites are usually reinforced with fibers and particles depending on the reinforcing element used. In fiber-reinforced polymer composite structures, polymer matrices can be reinforced with fibers of different shapes. In the case of particle-reinforced composite materials, the matrix material contains particles made of one or more different materials. These particles can be made of metallic or non-metallic materials. The resulting composite materials are called polymeric nanocomposites. Polymeric nanocomposite materials form the most recently developed group of composite materials. Nanocomposites exhibit significant enhancements in their physical and mechanical properties, even at low clay densities, due to the filler particles' nanometric dimensions which result in a high area-to-volume ratio allowing for a larger interaction area between the phases [1, 22, 49]. The development, production, determination of material properties and application of such composite materials with nanoscale reinforcing particles have recently become a very important

research area. Research studies, particularly on the development of nanocomposites from industrial thermoplastic and thermoset polymers, continue to increase rapidly. One of the important advantages of nanocomposites is that nano-sized inorganic additives increase thermal stability. In many applications it is desirable that the polymer material does not change significantly in size at different temperatures and during long-term use, i.e. is thermally stable. In comparison to conventional composite systems, nanocomposites have significantly better physical, mechanical, barrier, and thermal stability and non-flammability improvements[50] . Various methods are used to increase the thermal conductivity of polymers. One of them is the addition of particles or fibers with high thermal conductivity to polymers during production. Thanks to these particle additives, the thermal conductivity of the polymer increases.

Three methods are generally used to disperse nanoparticles within the polymer. These are:

- i. Direct mixing and blend preparation,
- ii. Creating a metal or metal oxide structure through hydrolysis or condensation reactions based on the molecular precursor,
- iii. It is in situ graft polymerization of macromolecule chains on nanoparticles.

In addition to the methods mentioned above, there are techniques for composite preparation that use systems or tools to produce materials for polymer matrix nanocomposite manufacturing. Most researchers tend to favor the combination of mixing, extrusion, and compression molding processes. The intended composite properties and production efficiency determine which of these approaches is preferred [51]. It is necessary for the particles to be uniformly distributed throughout the matrix to produce a polymer matrix nanocomposite sample with the appropriate characteristics

3.5 AREAS OF USE OF POLYMERIC NANOCOMPOSITES

Nowadays, the resources of natural materials are decreasing day by day. Polymers have a wide range of applications as an alternative to resource depletion. The reasons for their widespread use lie in their important advantages such as easy processability,

mechanical behavior, flexible structure and low density [52]. By producing various composite materials, their properties are improved and materials suitable for the desired area are produced. Polymer composites are materials that are corrosion-resistant, suitable for long-term use, easy to process, lightweight, can be formed into complex geometries, and have high load-bearing properties per unit mass [53]. Due to these superior properties, they are used in many areas. Various areas of application of polymer nanocomposites are shown in Figure 3.6.

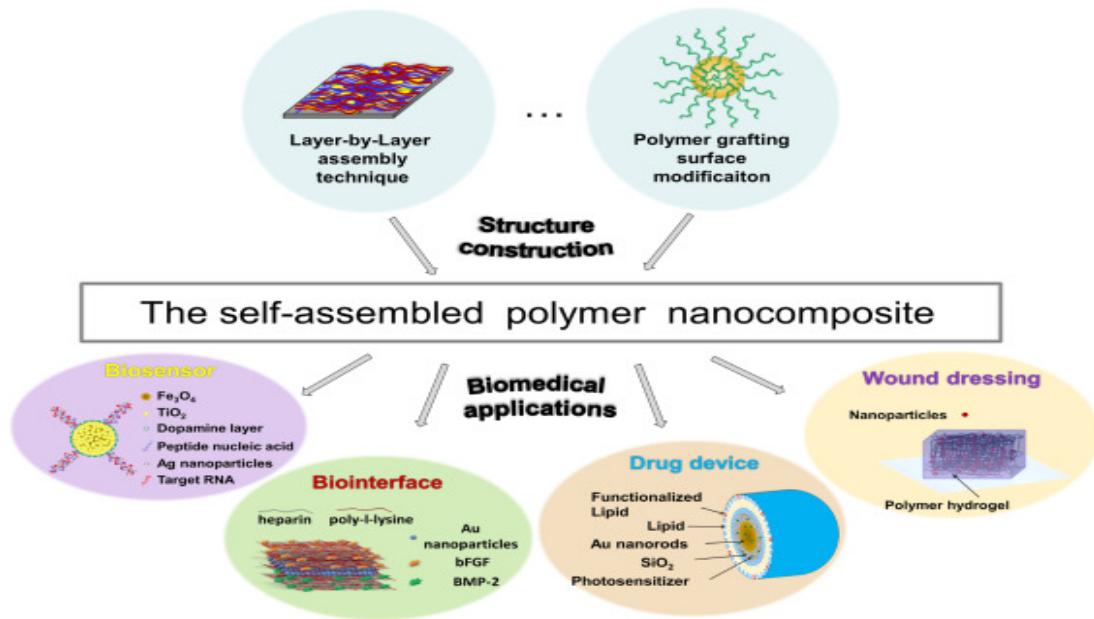


Figure 3.6. Various uses of polymeric nanocomposites [54].

Polymer composites are mainly used in electronic components, automotive and aircraft industries. Glass fiber reinforced polyester composites are most used in marine vehicles, and boat hulls are made from this composite.

As a result of numerous studies, polymer nanocomposites began to be used in automobiles. For example, polymers used in electronic components must have high thermal conductivity. Therefore, research into thermally conductive polymers is currently being carried out. In addition, properties such as impact resistance and good appearance are important in the parts used on the exterior surfaces of automobiles (e.g. the outer panels of the doors, the hood, the bumpers). Composites are materials that can meet these properties. Very low filler materials are 10 times lighter and 10 times

stronger than traditional talc-filled composites [55]. This important property makes these materials very suitable for automotive applications. Due to their high load capacity per unit mass and low weight, they are preferred for aviation and military purposes. The wings, fuselages and some parts of aircraft are made of polymers reinforced with aramid and carbon fibers.

The most used polymer matrix in aircraft are epoxies, and their composites can be made with carbon, which makes up to about 70% of the aircraft's weight. With new studies, polymeric nanocomposites are manufactured to improve the properties of supercapacitor electrodes such as charge/discharge, electrical conductivity, capacity and durability of materials [56]. Some researchers are also pursuing the use of polymer composites in the form of nanoparticles for biomedical applications and gene therapy [1, 20, 57].

3.6 POLYMER BLEND

A polymer blend, also called a polymer blend, is a class of materials in which one or more polymers are combined to form a new material with different physical properties. The properties of the alloy components and, in certain situations, the properties of the mixtures exceed those of the individual components when they combine in an advantageous manner. Polymer blend technology offers improved materials with all the required specific properties at the lowest possible cost, e.g. B. G. a mixture of properties such as solvent resistance, toughness and strength. Improved process capability, product uniformity, rapid recipe changes, plant flexibility and high productivity are additional benefits of mixing for the manufacturer [58].

3.6.1 Polymer Blend Types

Polymer blends can be divided into two categories from a thermodynamic perspective: miscible and immiscible. The basis of very few commercially important polymer blends is miscible and partially miscible (i.e., polymer pairs that are miscible within a certain concentration range). Producing a new polymer blend from immiscible resins requires a specific blend compatibility strategy to ensure optimal physical performance

and long-term stability. It is rare to combine two or more polymers and produce a blend with useful properties [59].

3.6.1.1 Miscible (Homogeneous) Polymer Blend

Miscible polymer blends have a single-phase structure and thermodynamically miscible systems with metastable properties among the constituent parts. The miscibility thermodynamic criteria that yield these kinds of polymer blends must be followed by the resulting miscible polymer blends [60].

3.6.1.2 Immiscible (Heterogeneous) Polymer Blend

Mixtures show more than two stages. Because the two components of an immiscible mixture are phase separated, they and their T_g separate. This results in the mixture of two amorphous polymers having two glass transition temperatures, which is an unusual property. To determine whether a mixture is miscible or immiscible, scientists commonly calculate its T_g. The mixture is immiscible if two T_gs are found. The mixture is likely miscible if only one T_g is observed. Compatible mixtures - mixtures that are miscible in some useful composition and temperature ranges but immiscible in others - are also called immiscible mixtures if the inhomogeneity created by the individual phases is small enough to be imperceptible when the Mixture is useful [60]. Immiscible and incompatible (bottom line), immiscible and compatible (top line), or miscible and incompatible (solid middle line) are the idealized expected property combinations resulting from the mixture of two polymers [61].

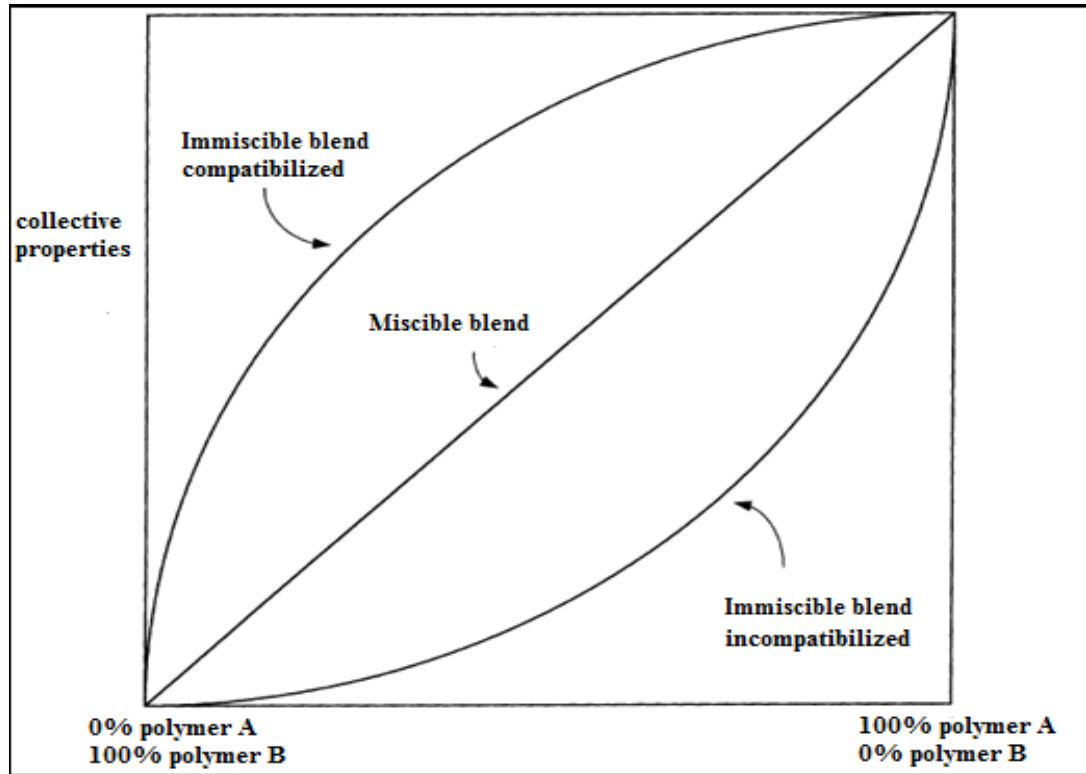


Figure 3.7. Possible effect on the properties of polymer mixtures with the component concentration [61].

3.6.2 The Advantages of Blending

Blending can improve the performance of resins or products by developing materials with all the required properties at the lowest possible cost. The performance of engineering resins is improved by the addition of lower cost polymers. Improvement of specific properties. Toughness of brittle polymers without the use of low molecular weight additives. Adding a stiffer, heat-resistant resin to the mix can increase modulus and dimensional stability. The addition of semi-crystalline polymer to an amorphous resin increases solvent and chemical resistance. Combining combustible and non-combustible polymers improves flame resistance. Polymers with -OH or -SH functionality in mixtures produce permanently antistatic mixtures (e.g. ethylene oxide-epichlorohydrin with ABS/PC mixture). Biodegradable materials made from biodegradable resin. Mixing enables the production of multi-layer integrated structures and enables the recycling of industrial and/or municipal plastic waste. Blending

technology allows the recovery of high molecular weights of partially degraded polymers, enabling the production of high-performance items from plastic waste[62].

Blending could improve workability. The high glass transition temperature (T_g) resin can be treated at temperatures well below the thermal degradation limit by incorporating a miscible resin with a lower glass transition temperature (T_g) (e.g. PS/PPE blends). The use of a low viscosity immiscible resin such as B. LCP/PEEK blends, reduce the pressure drop between nozzles or runners and thus increase productivity. Mixing with resins that, on their own, have high strain hardening (SH) (e.g. LDPE in a PO blend) or that produce long chain branches during reactive mixing (e.g. PS in a PO blend). to mixtures with a regulated SH level. These materials offer better performance in technologies that require a large extensional flow field, such as: B. Film blowing, blow moulding, wire coating and foaming. The use of elastomer particles increases the formation of gas bubbles, which stabilizes the foaming process, reduces the bubble size and lowers the final foam density. The addition of a biodegradable resin to an engineering or specialty resin allows the formation of a controllable amount of foam gas during the later processing stages, especially when Injection moulding. The molecular weight distribution is expanded by mixing different grades of the same resin. This makes processing easier and more stable (as well as better mechanical performance). Product uniformity (and therefore plant efficiency) is improved by mixing (and therefore plant efficiency). Mixing allows for quick recipe changes and increases system flexibility and performance [62].

3.7 INTERPENETRATING POLYMERS NETWORKS (IPN)

IPNs are defined as a combination of two or more polymers in network form that are synthesized in juxtaposition. Thus, there is some type of "interpenetration.". Many IPNs exhibit dual phase continuity, which means that two or more polymers in the system form phases that are continuous on a macroscopic scale.

A composition created by combining two or more polymers is called a multicomponent polymer material. A polymer blend can be made in several ways by combining two different types of polymer molecules, for example in an extruder. Graft or block copolymers are formed when chains are linked together. Graft copolymers

are formed when a chain is bonded between part of the backbone of polymer I and the end of polymer II; Block copolymers are formed when chains are connected end to end. Other types of copolymers include AB-crosslinked copolymers, in which a single network is formed from two polymers, as well as IPNs and semi-IPNs (SIPNs)[63].

IPNs are in many ways most like block copolymers. The length of the block controls the domain size in block copolymer systems. Accordingly, the degree of cross-linking or the chain length between the cross-links is an essential factor in determining the domain size of IPNs. In many circumstances, small domains consist of either short blocks or short chain segments between networks. However, there are some significant differences. Because they promote better miscibility between the polymer components, short block lengths are important. In the case of IPNs, there is increasing evidence that in systems in which the linear polymer components are miscible, crosslinks reduce the miscibility of the system compared to the corresponding mixture[63].

There are numerous methods for creating IPNs. IPN or sequential polymer network I is created. As shown in Figure 3.8A, monomer II, cross-linker, and activator are swollen in network I and polymerized in situ. Numerous potential materials are contained in the sequential IPNs, in which the synthesis of one network after another occurs. Simultaneous Interpenetrating Network (SIN): The activators and crosslinkers of both networks are combined with the monomers or prepolymers. The reactions occur simultaneously but do not interfere with each other. Chain and step polymerization kinetics serve as examples; see Figure 3.8B. Latex IPN: The IPNs are made from latex, often with a core and shell structure. One way to vary this is to combine two different latices and create a film that crosslinks the two polymers. This variation is in some cases referred to as an interpenetrating elastomer network (IEN). Materials classified as gradient IPNs exhibit macroscopic variation in their overall composition or cross-linking density from one location to another. For example, one surface of a film might have network I predominate, the other surface network II*, and the interior would have a gradient composition. Thermoplastic IPN materials are a cross between IPNs and polymer blends; They have physical networks as opposed to chemical ones. Therefore, these materials behave like IPNs when used at room

temperature and flow at higher temperatures, like thermoplastic elastomers. Ionic groups, semi crystallinity, and block copolymer morphologies are examples of crosslinking types. Semi-IPN: Polymers that are branched or linear and/or cross-linked together form semi-IPN compositions (SIPN)[63].

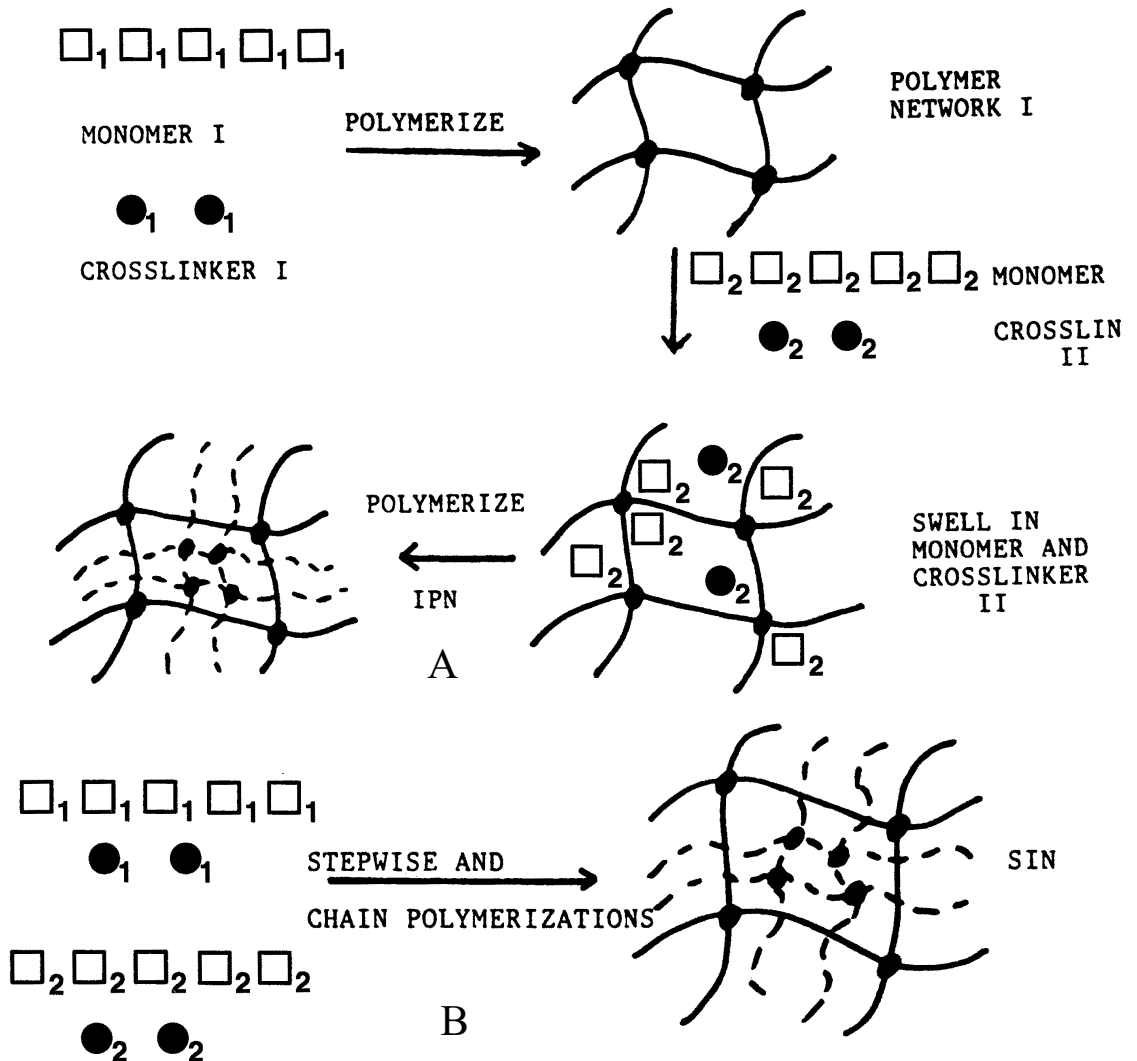


Figure 3.8 Techniques for IPN synthesis. A, Sequential IPNs; B, simultaneous interpenetrating polymer networks [63].

3.8 SILICONE ELASTOMERS

Polydimethylsiloxane is the collective name for the inorganic and organic substances that make up silicone. Although silicone elastomers were first developed in 1946, they

have only recently been used to make jaw and facial prostheses. In 1960, Barnhart first used silicone for an extraoral prosthesis. It consists of alternating chains of oxygen and sodium, which can be modified by cross-linking the molecular chains or by introducing various organic side groups to the silicon atoms. Their properties range from liquids to elastomers to rigid plastics. Once cured sufficiently, they can resist the absorption of organic materials that promote bacterial growth. This means that they are comparatively safe compared to other materials, have sufficient hygiene quality and are easy to clean (Mohammad et al. 2010). According to Montgomery[64], silicones are probably the most commonly used materials for facial restorations today.

3.8.1 Classification of Silicone

3.8.1.1 According to application

Depending on the application, there are four types of silicones [65]:

- i. Implant quality: This material must meet or exceed the requirements of the Food and Drug Administration (FDA). The cytotoxicity of the materials used in breast implantation has been the subject of medical and legal investigations. This type of silicone undergoes more rigorous testing.
- ii. Medical grade: This material is mainly found in facial prostheses and is used externally. The cytotoxicity of this material has been tested in some studies, but none of these studies have found negative side effects.
- iii. Clean: This material is suitable for use with food covers and packaging.
- iv. Industrial grade: The majority of uses for this material are in the industrial domain.

3.8.1.2 According to Vulcanization

Depending on the vulcanization process, there are two types of silicone:

- i. HTV (High temperature vulcanization)

Silicones The filler is available in a one- or two-component version. It typically has an opaque, white color and a very viscous, putty-like consistency. A

polydimethylvinylsiloxane copolymer with vinyl side chains and a catalyst (vulcanizing agent), which is either dichlorobenzoyl peroxide or a salt of chloroplatinic acid (platinum salt), are the components of heat-vulcanized silicones[65]. By changing the ratio of matrix to filler particles, the desired mechanical and physical properties can be improved. Although the addition of silica fillers strengthens the prosthesis, it can also reduce its translucency. Metal molds are processed under pressure at temperatures between 180 °C and 220 °C for about 30 minutes [66]. HTV silicones are physically superior to RTV silicones, particularly in terms of tear resistance. They also have higher tensile strength, superior thermal, color and chemical stability (making them biologically inert) and high percentage elongation. Disadvantages include lack of technique sensitivity, low edge strength, lower elasticity, poor opacity, opaque and lifeless appearance, and lack of technique[66].

ii. RTV (Room temperature vulcanization)

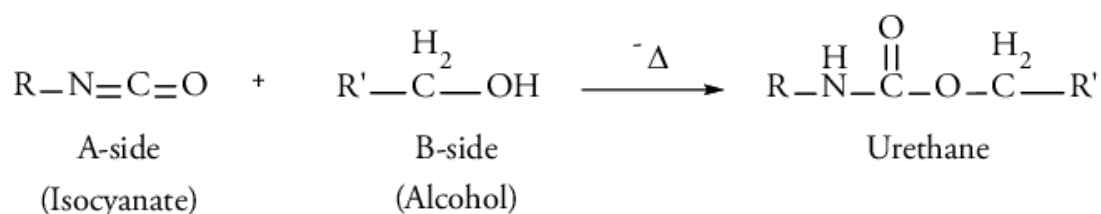
RTV silicones are viscous polymers that are inert and color stable. They consist of diatomaceous earth as a filler and two main components: ortho-alkyl silicate, a cross-linking agent, and tin octate, a catalyst. Because these materials are translucent, they can be combined with appropriate earth pigments to better match the patient's natural skin tone while ensuring greater color stability. The material is easy to process and is biologically inert [66].

3.9 POLYURETHANES

As one of the most important classes of industrial polymers, polyurethane has the fastest growing market in the world. This is because a variety of polyurethanes with desired properties can be produced by modifying the initial chemical composition. With a market valuation of over \$65 billion, the global polyurethane market is expected to grow at a compound annual growth rate of 31.2 percent through 2027 [67]. Polyurethanes, developed by Dr. Otto Bayer and partners, are an extremely versatile group of polymers used in various applications such as insulators, foams, elastomers, synthetic skins, coatings and adhesives. They are characterized by a urethane bond and can be easily synthesized through an addition reaction between alcohol and an

isocyanate. The synthesis of polyurethanes can be carried out at room temperature and under mild conditions, which is why they have been widely used on the market since their industrial production in the 1950s.

As can be seen from the following reaction, the PU compounds are typically thermoset polymers that are formed by an addition reaction between a di- or triisocyanate and a multifunctional alcohol (polyol) and produce a reticular urethane structure [68, 69].



Methyl diphenyl isocyanate (MDI) and toluene diisocyanate (TDI) are two examples of aromatic derivatives of isocyanates that are categorized based on their chain structure. To adapt the product properties to the intended use, PUs are synthesized with a range of additives, including catalysts, surfactants, antioxidants, pigments and fillers, in addition to polyol and isocyanate [70].

The structure of polyols (soft segments) or isocyanates (rigid segments) can be easily modified using various chemical techniques, giving polyurethanes a variety of properties. One way to produce an elastic polyurethane is to use a polyol with a linear structure, high molecular weight and minimal functionality. Meanwhile, polyols with low molecular weight, higher crosslinking functionality and aromatic groups in their structure can be used to produce a rigid polyurethane. Typically, the hard segment consists of a diisocyanate and a chain extender, while the soft segment consists of polyester polyol or polyether. While the hard segment provides additional strength and rigidity through physical networking points, the soft segment provides elasticity. Water-dispersible polyurethanes for coating applications are prepared by balancing hydrophilicity and hydrophobicity in the chemical structure [67].

Energy consumption drops by 75-95% when polyurethane foams are used as thermal insulators in housing, which has a long-term positive impact on the economy and the environment. Their high electrical resistance allows the use of dielectrics and electrical

insulation in electronic devices. Due to their high mechanical strength and low weight, polyurethanes are critical to the automotive industry's efforts to improve efficiency through reduced fuel consumption, increased safety and improved driving comfort. The furniture and automotive industries use flexible foams for a variety of purposes, including mattresses, sofas and seat cushions. In addition, flexible polyurethanes are used in the shoe industry as shoe cushioners and in the packaging industry to prevent transport damage. Their chemical inertness and environmental stability make them ideal for use in adhesives and anti-corrosion coatings. The latter has attracted considerable attention because corrosion is a major problem affecting many nations, causing an average loss of 3 percent of gross domestic product. Due to their large surface area, flexibility and chemical stability, polyurethanes have the potential to be used in a variety of novel applications in areas such as biomedicine and tissue engineering. They can be used as materials to support fluid transport in the body, for example in artificial veins or pacemaker components, or as synthetic scaffolds for cell culture [67].

Polyurethanes have a huge market and a variety of uses, but some problems, such as their high flammability, limit their use in useful applications and require further research. Additionally, most chemicals used to produce polyurethanes come from petroleum-based resources, and concerns about the toxicity and sustainability of polyurethanes are growing. It is also important to pay attention to the instability and degradation of polyurethane in outdoor applications [67].

In terms of mechanical properties, polyurethane elastomers perform better than silicone elastomers, especially about tear and abrasion resistance as well as resistance to flexural fatigue. Scientists working with synthetic polymers can adapt the structures of these elastomers to specific needs thanks to their chemical composition. Polyurethanes have good tissue and blood compatibility as well as good resistance to mechanical degradation [71]. The main ingredients used in the synthesis and formulation of polyurethanes, including additives, blowing agents, polyols, isocyanates, catalysts and surfactants. Foams are created in the production of polyurethanes by adding blowing agents, such as water. In addition, they play a crucial role in regulating the morphology and structure of cells through the formation of

bubbles within polyurethanes during the foaming process [72]. The reason for the improvement in dispersion is surfactants.

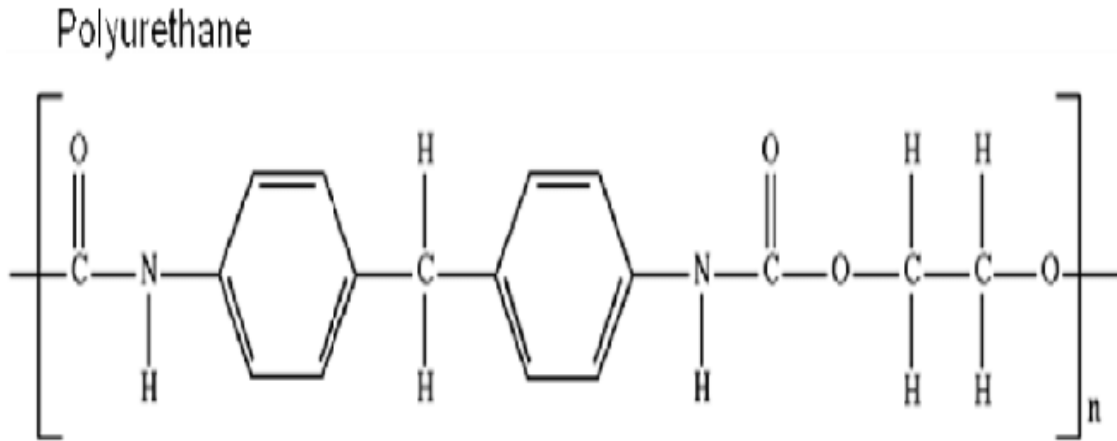


Figure 3.9 Schematic of polyurethane molecule [73]

3.10 ZINC OXIDE NANOPARTICLES (N-ZNO)

Zinc (Zn) and its oxide (ZnO) have special properties that make them one of the most promising metallic nanomaterials. An essential step in the creation of zinc oxide nanoparticles is the easy oxidation of zinc, a highly active element and strong reducing agent. Zinc is an essential trace element in human physiology that is present in all tissues, mainly in the skin, muscles, and bones, as well as in different cell components.

It is an essential component that serves both structural and catalytic functions in the structure and operation of many macromolecules and enzymes. Excessive free zinc ions have been linked to neuronal damage despite their relative non-toxicity and lack of redox activity. Therefore, binding zinc cations with bioactive ligands is necessary to reduce cytotoxic effects [74].

Functional materials such as sensors, solar cells, transparent electrodes, catalysts, piezoelectric nano generators, and optoelectronic devices are all made of zinc oxide (ZnO). With its large exciton binding energy, specific optical performance, good biocompatibility, high electron mobility, and low cost, zinc oxide (ZnO) is a promising

semiconductor oxide. Over the past 20 years, ZnO has gained attention due to these benefits [75].

The crystallinity, size, shape, and composition of ZnO nanoparticles all play a major role in determining their intrinsic qualities. Zinc oxide has high chemical stability, high photostability, and high electrochemical coupling coefficient in addition to these well-known characteristics [76]. Numerous studies have been conducted on the photoluminescent quality of bulk or nanostructured zinc oxide particles, revealing a variety of optical characteristics depending on morphology.

Under visible light stimulation, ZnO-based nanocomposites show antibacterial activity against both Gram-positive and Gram-negative bacteria [76]. The release of Zn²⁺ ions from ZnO nanoparticles, the third most produced metal oxide nanoparticle, in acidic aqueous solutions may upset the balance of zinc within cells. These nanoparticles are small enough to be easily absorbed by cells, and when ZnO nanoparticles dissolve further within the cell, intracellular Zn²⁺ levels rise to supraphysiological levels, which can be harmful[77].

Many techniques have been used to lessen the toxic effects of ZnO nanoparticles because of their well-established toxic nature. The physical, chemical, and biological properties of nanoparticles can be tailored to improve desired properties and remove deficiencies through a commonly used technique called surface modification.

ZnO nanoparticles' internal characteristics have been changed rather than their toxicity being decreased in the majority of surface modification work. By doping and capping, ZnO nanoparticle toxicity has been lessened in a few instances, though. The toxicity of ZnO nanoparticles should be significantly decreased for biological applications, such as antimicrobial agents present in food or food-related products, thanks to this surface modification[77].

Both consumers and business professionals may experience serious health problems because of being exposed to nanomaterials like zinc oxide nanoparticles (ZnO NPs). Therefore, it is essential to carry out additional research to investigate any possible

harmful effects. A thorough understanding of the detrimental effects of ZnO NPs is essential for ensuring their safety, particularly in biomedical and personal care applications.

The toxicity of ZnO NPs has been investigated extensively using a wide range of organisms, including cyanobacteria, bacteria, algae, crustaceans, fish, nematodes, plants, and mammalian cells. These studies demonstrated that ZnO NPs can accumulate inside cells and cause mechanical harm. Inflammation, genotoxicity, oxidative stress, cytotoxicity, and genomic instability are examples of possible toxicity mechanisms [78]. ZnO possesses multiple stable crystal structures, including hexagonal wurtzite and cubic zinc blende (Figure 1.2)[79].

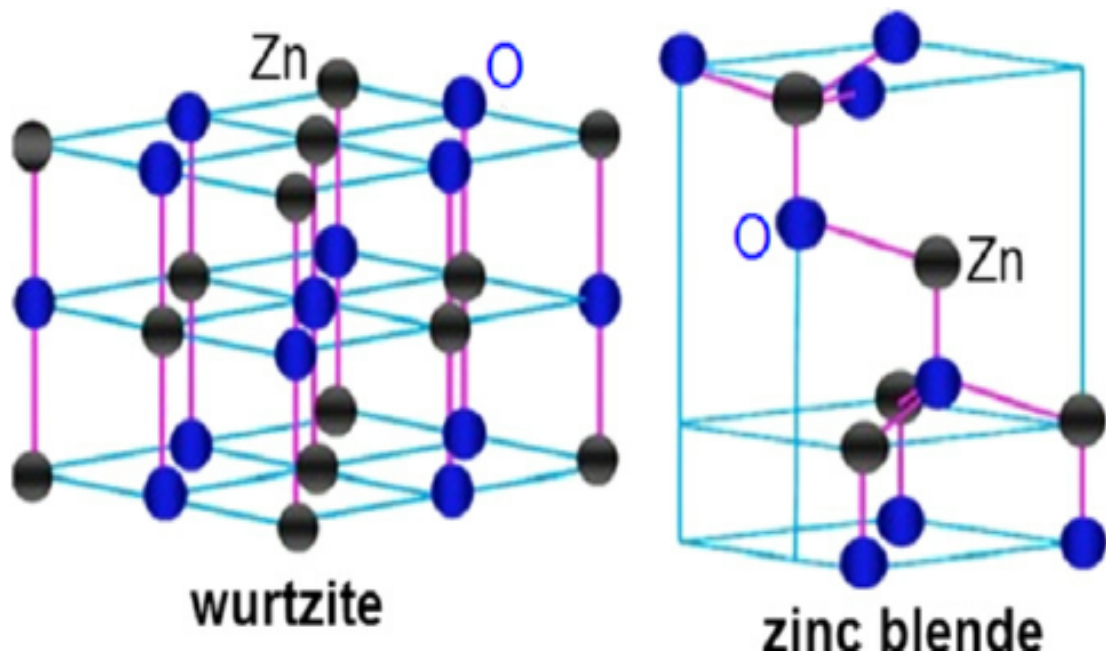


Figure 3.10 A schematic representation of ZnO crystal structures: Wurtzite and Zinc Sulfide[79].

ZnO NPs are extensively produced and commonly found in commercial products like cosmetics and sunscreens [80]. Zinc Oxide (ZnO) is an essential inorganic UV filter that is commonly found in sunscreens. Because of their exceptional sub-400 nm UV attenuation capabilities, ZnO NPs are among the most widely used engineering

nanomaterials and are perfect for use in sunscreens and other personal care products[81].

Zinc oxide nanoparticles are commonly used in personal care products like cosmetics and sunscreens because they can absorb UV rays while still allowing visible light to pass through. However, when these particles exceed 100 nm in size, they lose this beneficial property. Recent research has shown that larger ZnO nanoparticles can be harmful to various biological organisms, including skin cells, blood vessel cells, certain bacteria, fish, and mice.

To address this toxicity, scientists have suggested making changes to the nanoparticles, such as adding surface coatings, introducing dopants, or altering their size and shape. However, evaluating the toxicity of all these modifications is time-consuming and costly. Therefore, developing computational models to predict nanoparticle toxicity quickly is crucial. These models could help determine which changes have the most impact on reducing toxicity, guiding the design of safer nanoparticles[82].

For the quantitative assessment of trait-dependent cellular damage that forecasts unfavorable outcomes in vivo, selecting appropriate cellular response endpoints is essential. ZnO nanoparticles can cause two types of cell damage: internal toxicity, which is the result of particles absorbed by endolytic processes, and external toxicity, which is the result of cell damage brought on by zinc ions in the environment because of the dissolution of nanoparticles. The lysosome's acidic environment can trigger the release of ions from metal or metal oxide nanoparticles when they enter a cell, interfering with regular biological processes by producing reactive oxygen species (ROS).

Because ZnO nanoparticles dissolve quickly in lysosomes, they also raise intracellular Zn²⁺ concentrations, which can damage transcription factors and enzymes dependent on zinc as well as cause cell death. This is in addition to the generation of ROS. Measurement of the oxidative stress response in cells can be done most accurately and sensitively in vitro using the antioxidant response element (ARE) reporter.

The principle of Nuclear Factor-E2-Related Factor (NRF2) regulating mRNA transcription serves as its foundation. Luminase assays are quick, extremely sensitive, and have a broad dynamic range for identifying ROS-induced reporter signals. Aside from apoptosis (programmed cell death), which is brought on by intracellular processes, membrane damage is another unfavorable outcome that can result from direct contact with ZnO nanoparticles or zinc ions. This will cause cell necrosis[82].

PART 4

METHODOLOGY AND EXPERIMENT

4.1 INTRODUCTION

This chapter covers all important details of the methodology used in this study, from material selection and specification to sample preparation. Additionally, this chapter describes all tests performed on all prepared samples.

In this work, there are two basic parts that were followed in the preparation of nanocomposite polymers. The first is the part of biomaterials, where nano powder materials (ZnO) are used as a reinforced material to obtain polymeric nanocomposite materials, which are used to improve some required properties of the composite materials. The second part is to add polyurethane in different concentrations to improve the properties of the silicone rubber nanocomposite specially with porosity side. All information is shown in Figure 4.1.

Many tests were used to characterize the nanocomposite polymer and tertiary blends, e.g. B. XRD, FTIR, SEM and comparing the differences between them. For each mechanical test, three samples of the same sample were averaged. Test the prepared tertiary mixture for zone of inhibition with two species of bacteria, E. coli and S.aureus, which are gram-negative and gram-positive, respectively.

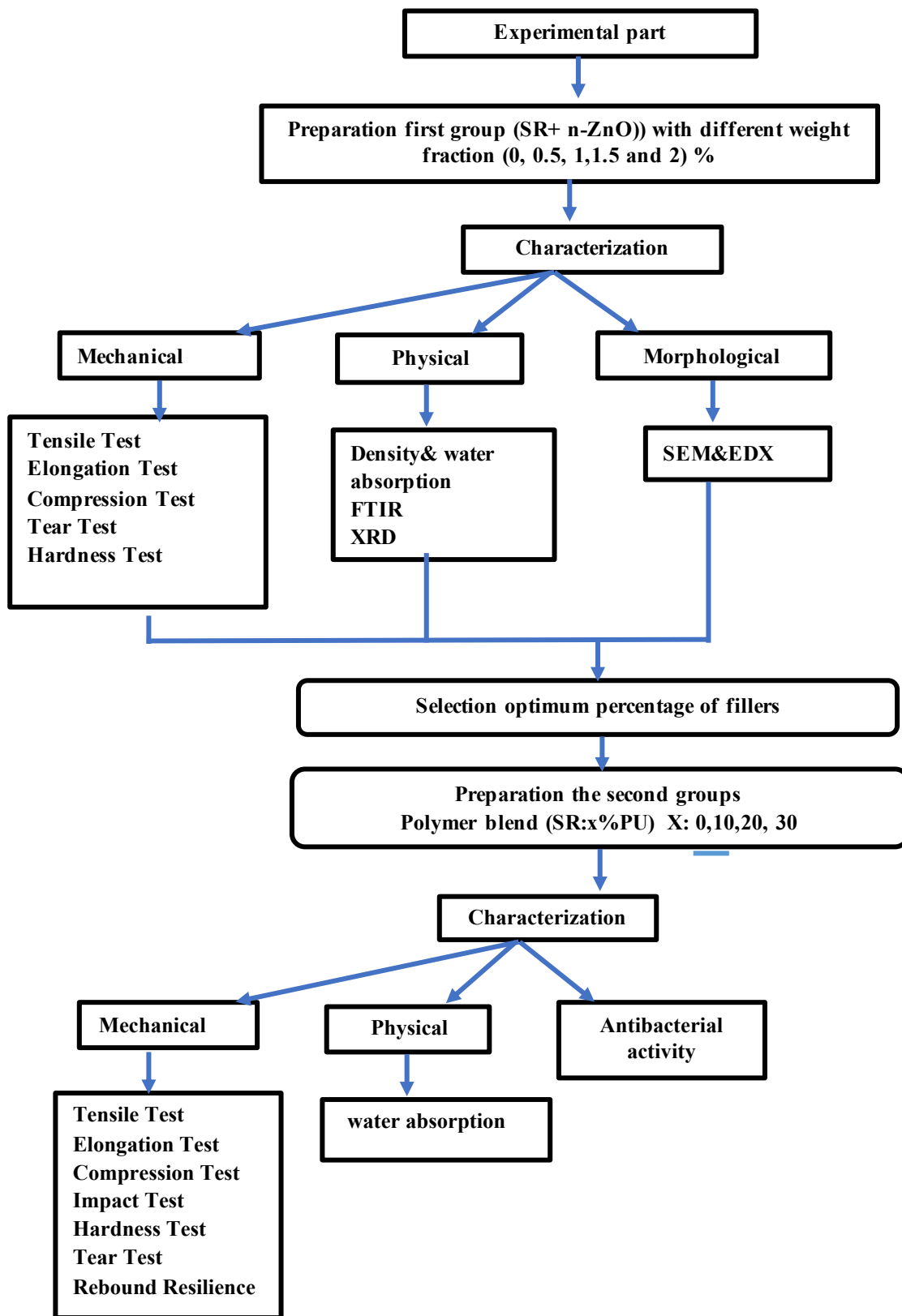


Figure 4.1 Experimental flow chart

4.2 MATERIALS

4.2.1 Silicon Rubber

Silicone rubber, denoted as SR, is a platinum-cured elastomer procured from Dongguan Guochuang Silicone Co. LTD, China (Product Code: G-815). This elastomer finds extensive applications in the medical field and food industry. The preparation process involves the amalgamation of two liquid components: the silicone rubber and a catalyst, in a specific ratio of 100:2. This silicone rubber variant possesses the ability to cure at ambient temperature or can be hardened through the application of heat. The mechanical and physical attributes of SR are detailed in Table 4.1, as provided by the manufacturer.

Table 4.1 Properties of Silicon Rubber [20].

Property	Value
Color	White.
Mixing ratio (%)	2-3
Pot life (mines, at 25°C)	30-40
Viscosity (MPa.s)	27000+5000/-8000
Curing time (hrs., at 25°C)	4-5
Hardness (Shore A)	30±2
Tensile strength (MPa)	4.3+1/-0.5
Tear strength (KN/m)	26+5/-2
Shrinkage rate (%)	≤0.3%
Elongation (%)	≥400

4.2.2. Polyurethane

This material was supplied by Henkel Polybit Industries (VAE). Polyfoam I-20 is a two-component product consisting of polyol as a resin and MDI (isocyanate) as a hardener. Cream time: 22-24 seconds, gel time: 115-140 seconds. The properties of the PU components are listed in Table 4.2.

Table 4.2 Properties of polyurethane components[83]

Type of Component	Color	Viscosity at 20°C (cps)	Specific gravity At 20°C
MDI	dark brown	150 - 200	1.24
Polyol	brown to yellow	450	1.16

4.2.3 Reinforcement Materials

Zinc oxide was used as nanoparticles as a reinforcing material in the current work. ZnO was added to the polymer matrix material to prepare biocomposite material. According to the manufacturer, ZnO nanopowder with a purity of 99.5% is supplied by Nanografi Nanotechnology Company. The average particle size of ZnO nanoparticles is (30–50 nm).

4.3. PREPARATION OF NANO COMPOSITE

Pure samples (matrix) were prepared by combining two parts of silicone rubber in a ratio of 100:1.5 based on laboratory studies, where Part A is the base material and Part B is the catalyst material. The formulation includes silicone rubber as a matrix and zinc oxide nanoparticles as a bifunctional agent that provides reinforcing and antibacterial properties. The best result was provided by nanopowders in the concentrations shown in Figure 4.1. It was used to prepare the nanocomposites. To produce silicone rubber nanocomposite material for prosthetic liner supports, many mechanical tests are required, Tensile strength, tear strength, impact strength and hardness, physical tests, including temperature and water intake, are necessary. Proper formulation for these applications requires improving these parts by preparing reinforcing materials such as ZnO and mixing these reinforcements in different ratios with the formulation to provide a laboratory sample of various formulations for mechanical testing using ASTM standard molds.

4.4 POLYMERIC BLEND PREPARATION

Binary polymer blend specimens were synthesized by integrating silicone rubber with a silicone rubber composite (SR: x% PU) at various concentrations (0%, 10%, 20%, and 30%). The initial step involved blending liquid Part A silicone rubber with Part A polyurethane for a duration of three minutes. This was followed by the addition of Part B silicone rubber hardener to the blend, which was then stirred for an additional four minutes. Subsequently, Part B liquid polyurethane hardener (isocyanate) was incorporated into the blend and mixed thoroughly for three minutes. The optimal proportion of ZnO nanoparticles was then added. The resulting nanocomposite was placed in a vacuum apparatus for fifteen minutes to eliminate any air bubbles. After the degassing process, the blend was transferred into a pre-greased mold. The final product was allowed to cure at ambient conditions for a period of twenty-four hours.

4.5 CHARACTERIZATION OF THE NANOCOMPOSITE

4.5.1 Physical Inspections

4.5.1.1 Density Test

The density analysis is performed in accordance with the ASTM standard (D-792). The weights of the samples are determined using the Archimedes method with a precision balance, specifically the PS 360/C/1 device[84]. This test can accommodate samples of any size, provided that the volume is not less than 1 cm³. It is essential that the surfaces and edges of the samples are smooth and devoid of contaminants such as oil, grease, or other foreign substances. The samples under test must be weighed in air and then submerged in distilled water. The density can be calculated using the following equations

$$\text{Specific Gravity (S.G)} = \frac{WD}{WD - W_i} + 0.02 \quad (4.1)$$

Where:

WD: Represents the dry weight of the sample (in milligrams).

W_i: Denotes the weight of the sample when immersed and suspended in water (in milligrams).

0.02: Is indicative of the essentially embedded wire's mass

The specific gravity can be converted to density (g/cm³) by multiplying the specific gravity by the density of purified water (g/cm³), which equals (0.9975), as shown in the following equation.

$$\text{Density} = (\text{Specific gravity}) * (0.9975) \quad (4.2)$$

4.5.1.2 Water Absorption

According to ASTM 570-98 [85], water absorption is used to measure the amount of water absorbed under certain conditions. This measurement serves as a reference point for evaluating the effects of water exposure on the liner properties. Various factors, including plastic type, additives, and exposure temperature and duration, influence the water absorption process. To evaluate the samples' water absorption capacity—a crucial component in the production of liner sockets—they were submerged in room temperature water for a full day. To demonstrate the impact of varying isocyanate ratios on water absorption capacity, (3,6, and 9) drops of water were added to the polyurethane hardener for the blend samples of SR with PU. The mixture was then rapidly shaken for 20-40 seconds, and the best drops additive were added. The water absorption percentage in the sample is determined by calculating the change in weight using the equation:

$$\text{water absorption} = \left(\frac{W_2 - W_1}{W_1} \right) \times 100\% \quad (4.3)$$

Where W₁ is the initial weight of the specimen, W₂ is the weight of the specimen after water immersion [86].

4.5.2 X-Ray Diffraction Analysis

The XRD analysis, employed to characterize the SR+n-ZnO nanocomposite, was conducted using the RIGAKU XRD D/MAX/2200/PC automatic powder diffractometer. Diffractograms were obtained using a CuK α beam with a wavelength

of 1.54056 Å, a scanning angle (2θ) ranging from 10-60°, and a scanning speed of 2°/min. The X-ray was operated at a voltage of 40 kV and a current of 30 mA.

4.5.3 Fourier Transform Spectroscopy (FTIR)

The FTIR analysis was performed using a Shimadzu 1800 FTIR spectrometer, manufactured in Japan. This instrument is equipped with a DTGS detector that operates at room temperature, a medium IR source with a range of (4000 to 400) cm^{-1} , and a KBr beamsplitter. The FTIR analysis was conducted on spectra obtained from polymer composites reinforced with nanoparticles at various concentrations.

4.5.4 Microstructure Analysis

Scanning Electron Microscopes (SEM) are sophisticated instruments that utilize beams of high-energy electrons to scrutinize objects at incredibly minute scales, capturing images of structures as small as 10 nanometers. The technique of scanning electron microscopy provides a unique blend of high-resolution imaging capabilities. To ensure optimal electrical conductivity, composite materials were subjected to gold sputtering. This examination can yield insights into both the topography, which characterizes the surface attributes of an object and identifies the fracture process, and the morphology, which pertains to the size and form of the particles within the object.

4.5.5. Mechanical Analysis

4.5.5.1 Tensile Strength, Elastic Modulus and Elongation

A mold, with dimensions of 150 mm in length, 150 mm in width, and 3 mm in thickness, was utilized for the preparation of samples for tensile, elastic modulus, and elongation tests. The mold was lubricated prior to the introduction of the suitable quantity of the mixture. After a day of rest, the mixture in the mold was manually compressed using a dumbbell-shaped tool, as depicted in Figure 4.5, to perform a tensile test on the resultant samples. The tests for tensile strength and percentage elongation were conducted in accordance with the ASTM-D412 standards [87].

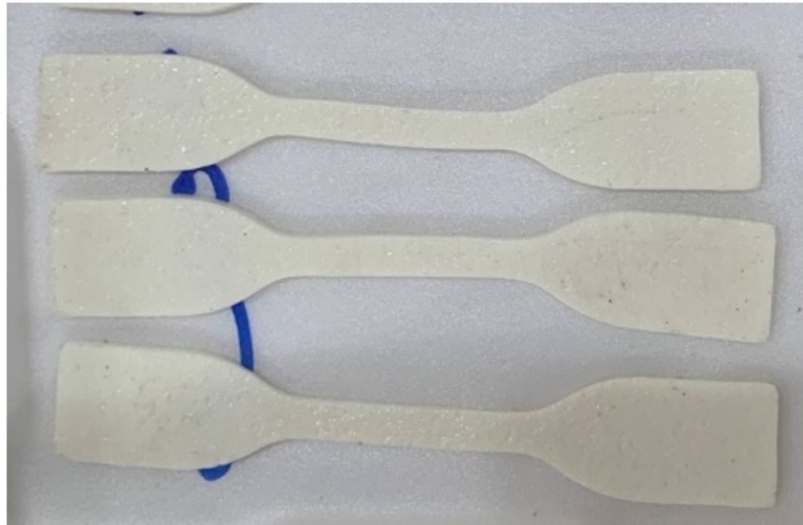


Figure 4.2. Samples for Tensile strength, Elastic Modulus and Elongation test.

4.5.5.2 Hardness Samples

Figure (4.3) illustrates the cylindrical shape of the mold used to create these samples, which has a diameter of 30 mm and a thickness of 4 mm. Test samples were prepared in compliance with ASTM D2240 for Shore A Durometer hardness testing. With the Shore device, a needle is attached perpendicular to the sample. To obtain correct readings, the surface of the sample must be smooth and clean, and the minimum thickness of the sample is 4 mm, the position where the test is performed. The distance to the edge is at least 12 mm. Each sample was tested five times simultaneously at different positions of each sample, and the final hardness is the average of these samples.

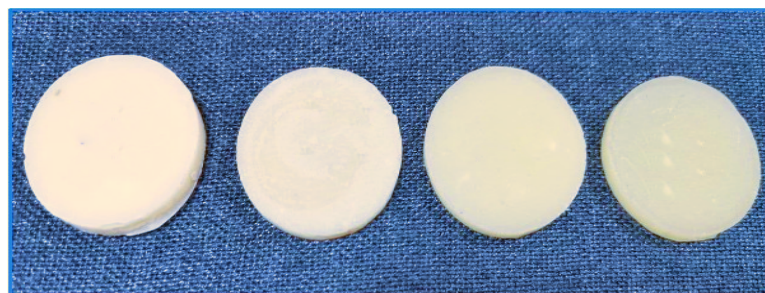


Figure 4.3. Samples for Hardness test.

4.5.5.3 Compression Test

The compression analysis was performed in accordance with ASTM D695 standards, utilizing an identical tensile apparatus. The process involved a steady strain rate of 1 mm/min, with the compressive force being progressively increased until the specimen exhibited deformation, as referenced in[88]. Figure 4.4 illustrates the apparatus employed for the compression test, along with a standard specimen used for such testing in this investigation. This test was conducted on three specimens, and the presented data is an average derived from these tested samples

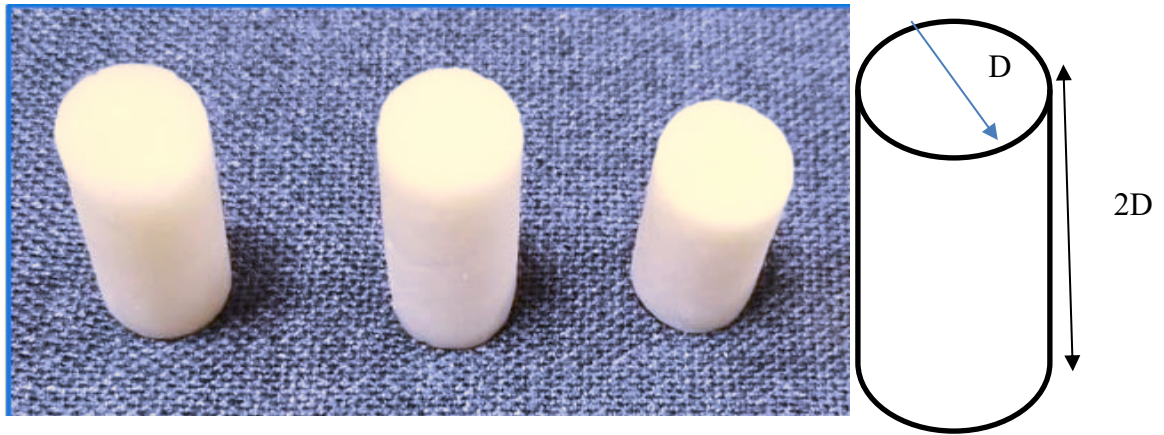


Figure 4.4. Samples for Compression test.

4.5.5.4 Preparation for Tear Specimens

Samples for tensile strength testing were fabricated by placing the formulation into a mold with dimensions of (150 x 150 x 3) mm. The procedure for preparing tear test samples mirrors that of the tensile test samples. The tear strength test is conducted using the Monsanto T10 tensometer at a velocity of 500 mm/min, in accordance with the ASTM D624-07 standard[1]. The tear strength is computed using the equation:

$$Tear = \frac{F}{D} \quad (4.4)$$

Here, the tensile strength (T) of a sample is quantified in N/mm, the force (F) necessary to fracture the sample is measured in N, and the thickness of the sample (D) is gauged in mm.

4.5.5.5 Resilience Test

Rebound elasticity, expressed as a percentage, refers to the proportion of an object's post-impact energy to its pre-impact energy. The test specimen undergoes only half a deformation cycle in these testing methodologies. A rubber sample is loaded by an indenter that falls freely. This demonstrates the capacity of a vulcanized rubber to absorb and rebound impact energy, a characteristic that is influenced by the rubber type, vulcanization conditions, curing components, operating temperature, and filler quantities. This property is crucial for predicting vibration damping in specific applications [20].

4.5.5.6. Impact Test

As one of the most significant mechanical tests, it determines the amount of energy needed to fracture a sample taken straight out of the device. An impact test using dimensions of 55 x 10 x 4 mm was conducted in compliance with ISO Standard 179 [89]. By placing the sample horizontally and applying the Charpy method, the pendulum was raised to its maximum height and securely fixed at the point where its potential energy would have been converted to kinetic energy. Although impact strength and fracture toughness are computed, the device measured the absorbed energy of fracture. The following equation can be used to determine impact strength.:

$$G_c = U_c / A \quad (4.5)$$

Where

G_c : The impact strength (KJ/m²).

U_c : The needed energy for fracture the sample (J).

A : - the cross-section area of the specimen (m²).

Impact resistance depends on the type of material, the type of load applied, the process conditions, the shape, and dimensions of the sample.

4.5.6. Antibacterial Activity

The antibacterial properties of the specimens were evaluated using the agar well diffusion technique. Muller-Hinton agar plates were prepared and inoculated with bacterial strains, *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*), which were uniformly distributed across the medium's surface with a sterile swab. The inhibition zone was determined by placing pristine polymer and polymer-nanocomposite samples on the plates. These plates were then incubated at 37 °C. After 24 hours of incubation, the inhibition zones were observed, and the diameters of these zones were measured and documented in millimeters.

PART 5

RESULTS AND DISCUSSION

5.1 INTRODUCTION

In this chapter, the practical results obtained in the laboratory of the materials are compared in this part, whether these tests apply to pure materials of nanocomposite silicone rubber with ZnO, and the tertiary mixture prepared, and the products of these materials were compared. Also, the changes in physical (hardness, tensile strength, elastic modulus, elongation, rebound, specific gravity and water absorption), characterization (XRD, FTIR and SEM) and biological properties of nanocomposite silicone rubber with ZnO and tertiary mixture were observed by agar well diffusion against evaluated the gram-positive bacterium *Staphylococcus aureus* and the gram-negative *Pseudomonas* bacterium, and determined biofilm formation for the same type of bacteria using the microtitration plate method.

5.2 XRD ANALYSIS

X-ray diffraction (XRD) has played an important role in analyzing and understanding the structures of solids since the beginning of the 20th century. The bonding principles and the guidelines for distinguishing between short-range and long-range order in crystalline assemblies and nanocrystalline substances were largely derived from XRD studies. This technique remains a valuable tool for obtaining structural information because it can reveal details about the arrangement of atoms in a material.

Amorphous polymers exhibit distinct XRD patterns compared to their crystalline counterparts, as shown in Figure 1 with 0.5 wt% ZnO. The XRD pattern of an amorphous polymer does not have sharp, high-intensity peaks, while amorphous polymer nanocomposites have sharp and intense peaks. This is due to the development of crystallinity in the amorphous polymer upon introduction of reinforcing materials. The XRD patterns of the SR/ZnO nanocomposites are shown in Figure 1. The diffraction peaks at $2\theta = 14.2^\circ, 28.6^\circ, 31.8^\circ, 34.4^\circ, 36.3^\circ, 47.6^\circ, 56.6^\circ, 62.9^\circ, 68.1^\circ$ and 69.1° correspond to the planes (100), (002), (101), (102), (110), (200), (211), (202), (112) and (300) of the hexagonal wurtzite ZnO Structure (JCPDS #36-1451). The diffraction peaks of SR appeared at $2\theta = 13.9^\circ$ and 21.6° , which can be assigned to the (100) and (110) planes of the orthorhombic structure of SR (JCPDS No. 29-0525). No other diffraction peaks were observed, indicating that the ZnO nanoparticles were well dispersed in the SR matrix. The intensity of ZnO diffraction peaks increased with increasing ZnO content, indicating an increase in the crystallinity of the ZnO nanoparticles[1].

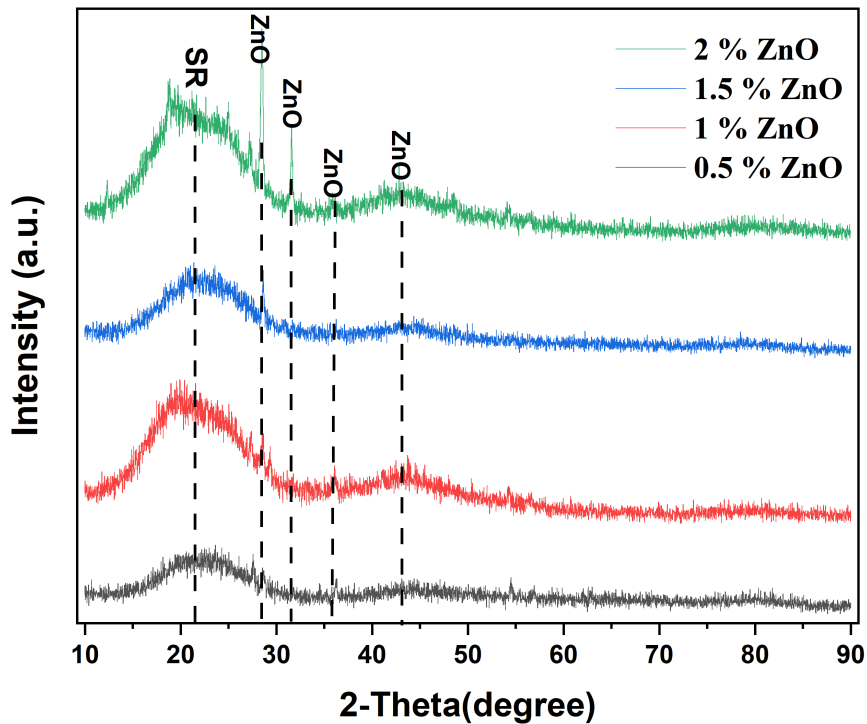


Figure 5.1 XRD of the nanocomposite of SR+ X ZnO.

5.3 FTIR RESULTS

The Fourier Transform Infrared (FTIR) spectroscopy results for the SR+X ZnO nanocomposite are depicted in Figure 5.2. The infrared spectrum of the unadulterated SR and the molecular structure of silicone rubber is represented as $[-CH_2-CH=CH_3-(CH_2)-]_n$.

Upon analyzing the FTIR spectra of silicone rubber integrated with varying concentrations of nano-ZnO, it is observed that the incorporation of nano-ZnO does not induce any significant alterations in the chemical structure of the silicone rubber. The spectral peaks observed at 1007 and 1090 cm^{-1} can be attributed to the stretching vibrations of the Si-O-Si bonds. Similarly, the peaks at 1260 and 1410 cm^{-1} are indicative of the CH₃-Si stretching vibrations. The peak at 3440 cm^{-1} is a result of these vibrations in conjunction with the O-H stretching vibrations [1, 17].

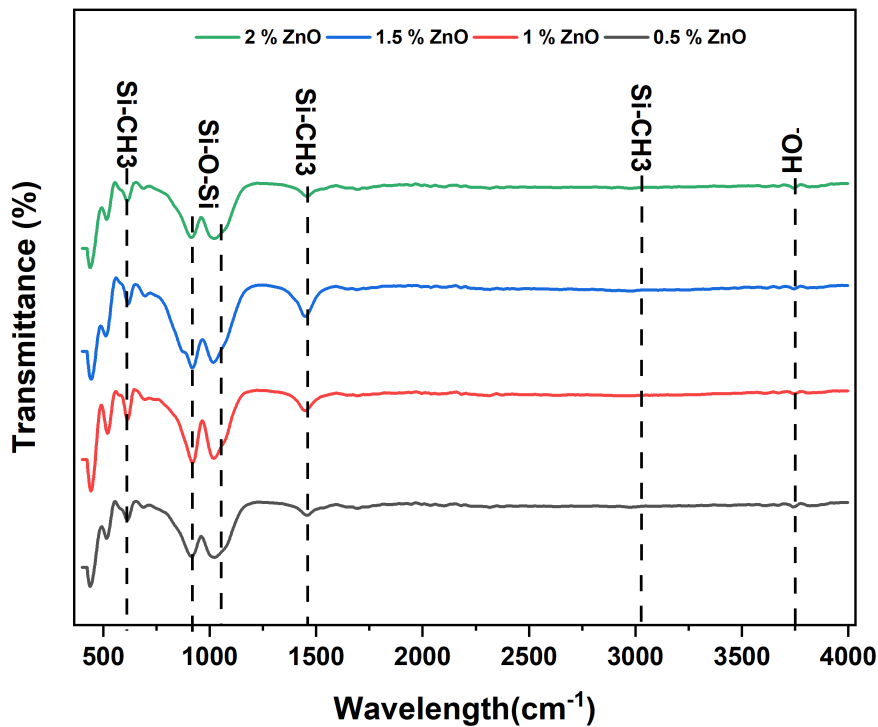


Figure 5.2 FTIR of the nanocomposite of SR+ X ZnO.

The FTIR spectra of all samples, irrespective of the nano-ZnO concentration, exhibit these peaks. This indicates that the integration of nano-ZnO does not lead to substantial modifications in the silicone rubber's chemical structure. Furthermore, it is noteworthy

that the enhancement with N-ZnO did not result in the emergence of any new peaks, nor did it cause any shifts in the existing peaks. This implies that the interactions between the assembled components are purely physical in nature. Such interactions serve as a reliable indicator of the homogeneity state between these components and confirm the absence of any residual monomers or by-products. The latter could potentially induce toxic, allergic, and anti-inflammatory responses in the human body. Therefore, their absence is a positive sign [1, 90].

5.4. MICROSTRUCTURE ANALYSIS

Figure 5.3 shows the effects of N-ZnO on the morphologies of the silicone rubber at 5K magnification. The structural morphology of nanocomposite materials is influenced by few limitations, such as the type of filler, particle shape, particle size, filler selection, segment proportions, softening viscosities of segments and manufacturing conditions [91].

By adding 0.5 to 2% by weight of N-ZnO. % ratios, the homogeneity is increased, the roughness is reduced and the new additional material N-ZnO appears clearly. These nearly smooth surfaces indicate good compatibility between the bone cement components, good dispersion of N-ZnO in the silicone rubber matrix and a high degree of bonding, which predicts high mechanical properties and high resistance to the occurrence of defects. It is also clear from the figures that most of the N-ZnO is embedded in the polymer and constitutes an essential component of the silicone rubber structure, resulting in better interfacial adhesion between its components.

By incorporating the nanoparticles, the crosslinking density of the SR/ZnO nanocomposite is increased. On the other hand, excessive crosslinking density may ultimately cause the strength of mechanical properties to decrease. To achieve better mechanical properties, the filler content of the nanoparticles must be optimized. Compared to other SR/ZnO nanocomposites, the SR/ZnO nanocomposites have better elongation at break and tensile strength. This is explained by the higher cross-linking density and the improved interfacial contact between the silicone rubber matrix and the nanoparticle surface.

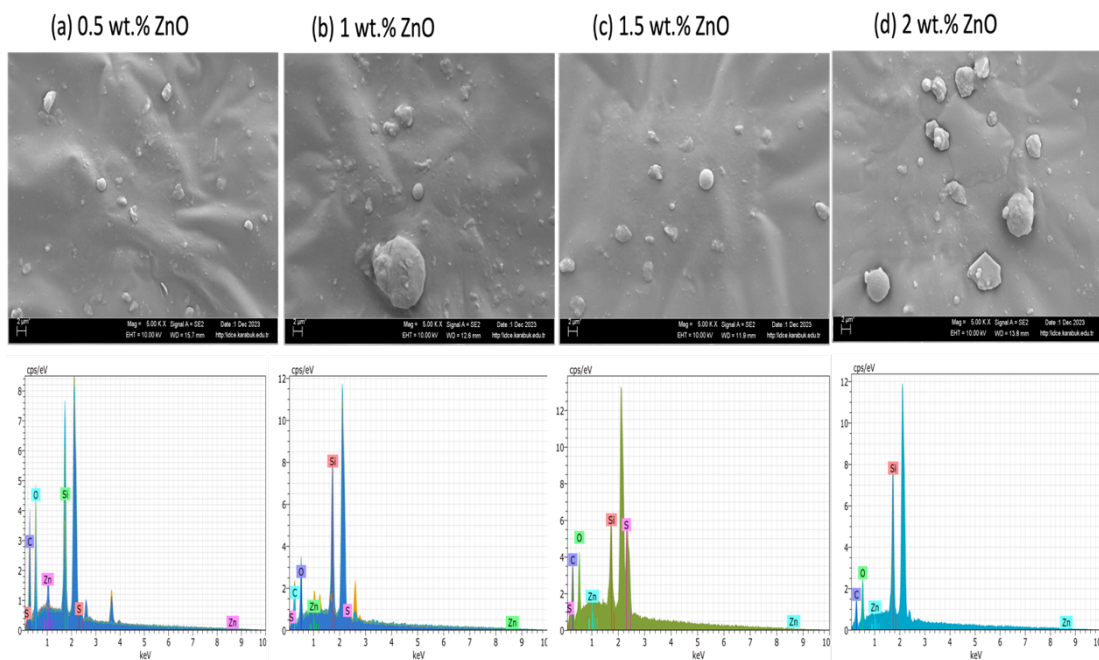


Figure 5.3 SEM & EDX of the nanocomposite of SR+ X ZnO.

5.5 PHYSICAL PROPERTIES

Figure 5.4 shows the relationship between the addition of ZnO nanoparticles in silicone rubber and the density and water absorption of the samples. The density values increase with increasing volume fraction of both types of particles. This is because these particles have a high-density value compared to the silicone rubber matrix.

Additionally, these particles are said to shrink or fill the voids and spaces within the silicone rubber matrix, as demonstrated by SEM testing. The result results in denser composite samples with the same volume. It can also be seen in this figure that the increase in the addition of N-ZnO particles has a noticeable impact on the density of composite samples, more so than pure silicone rubber, which is due to the higher density of N-ZnO particles compared to Silicon is attributed to rubber [92].

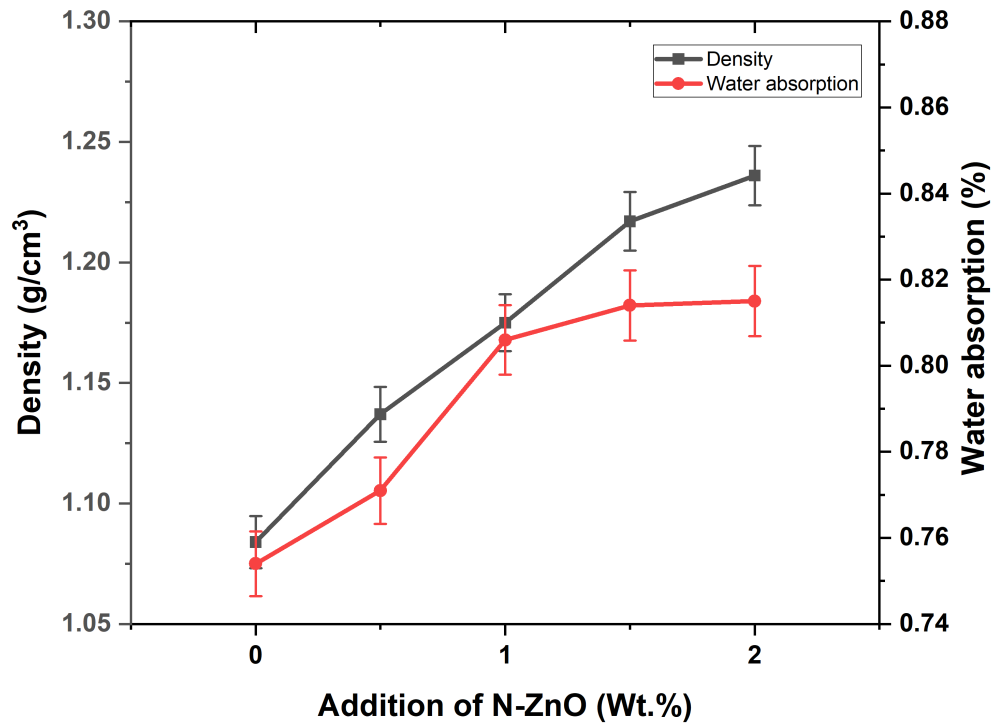


Figure 5.4 Density and water absorption of the nanocomposite of SR+ X ZnO.

Multiple factors influence the degree of water absorption in the composite material: the size, shape, and distribution of nanoparticles within the silicone rubber matrix, as well as the quantity of nanoparticles added. Water absorption rate can generally be increased with increase the nanoparticle concentrations, smaller particle sizes, and more homogeneous dispersion.

The incorporation of ZnO nanoparticles into the silicone rubber showed an ineffective increase in water absorption. This implies that the incorporation of a ZnO nanoparticle can improve the properties of the silicon rubber composite as it is considered as a reinforcing material[93]. ZnO nanoparticles are naturally hydrophilic, meaning they can absorb water molecules from the environment. When incorporated into a hydrophobic material such as silicone rubber, the ZnO nanoparticles can create microscopic channels for water molecules to penetrate the material, resulting in increased water absorption[94].

5.6 MECHANICAL PROPERTIES

5.6.1 Tensile Strength and Elongation

Tensile tests are primarily carried out to study the mechanical properties of silicone rubber composites. The adhesion bond (bond strength) between matrix and reinforced material as well as the properties of matrix and reinforced material determine the mechanical behavior of these samples. The elongation and tensile strength of N-ZnO reinforced silicone rubber in different weight ratios (0, 0.5, 1, 1.5 and 2 wt%). Figure 5.5 shows the percentages. The results indicate a general increase in elongation and some variations in tensile strength. It is observed that the tensile strength values increase with increasing weight fraction of N-ZnO and reach their maximum value of 2.834 MPa with the addition of 1.5 wt% N-ZnO. It is reduced due to the agglomeration state and represents the critical fracture volume of the filler component. The onset of the NP agglomeration tendency causes the tensile strength to decrease beyond this ratio. Because of this behavior, only small tensile stresses are required. This has the potential to weaken the overall physical interactions between the nanoparticles and the silicone rubber matrix [95].

In general, the elongation increases with increasing N-ZnO; at 1.5% by weight, it reached its maximum value of 537.154 %. Percentage of total. This discovery provides further evidence that the 1wt. The ideal ratio for reinforcement is represented by the percentage ratio, and when this ratio is exceeded, the negative effects of agglomeration occur. N-ZnO aids in polymerization, increasing the overall cross-linking density of the polymer and giving it more strength and stiffness. This is one of the reinforcement mechanisms. In addition, it increases tensile strength by preventing the polydimethylsiloxane chains from breaking. N-ZnO produces a stiffer structure and improved tensile strength by increasing the contact area between elastomer chains [16, 96].

The agglomerated morphology is the result of the filler-filler interaction at high N-ZnO particle loading. Particle agglomeration reduces the contact area between the particles and the polymer matrix by reducing the aspect ratio of N-ZnO. Furthermore,

the agglomerated N-ZnO in the composites could serve as stress concentration sites. As a result, particles separate and detach from the polymer matrix when subjected to tensile mode deformation[97] . This explains the decrease in percent elongation, tensile strength, and tear strength at a ZnO concentration of 2 wt.%.

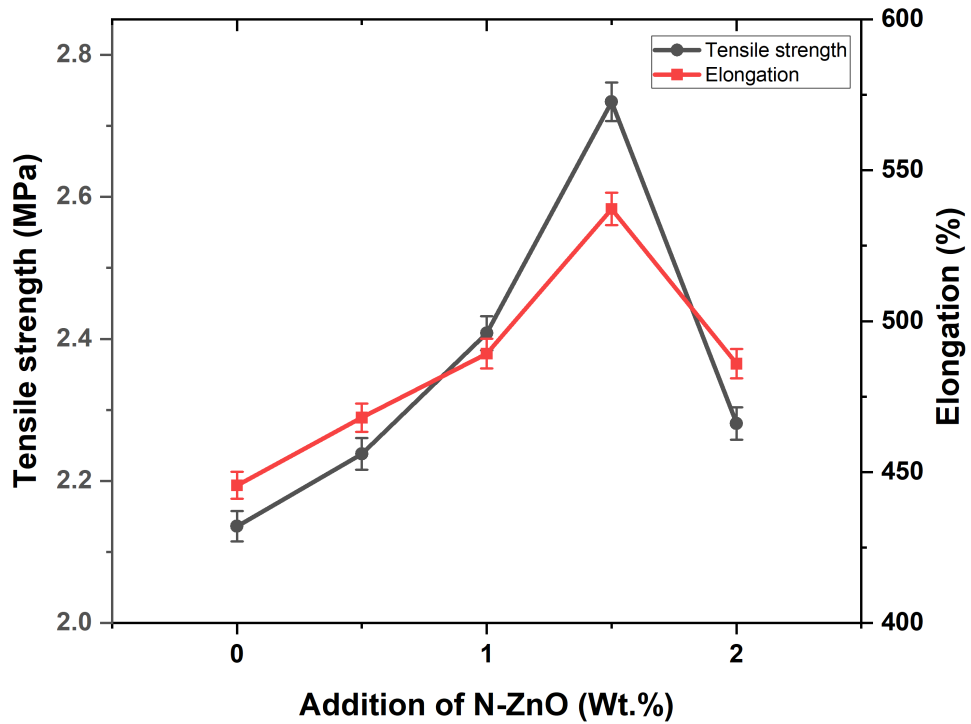


Figure 5.5 Tensile strength and elongation of the nanocomposite of SR+ X ZnO.

5.6.2 Compression Strength

Figure 5.6 delineates the correlation between the weight fraction of N-ZnO in silicone rubber and the compressive strength of the samples. An upward trend in compressive strength is observed with an increase in the modified N-ZnO content, peaking at a value of 17.148 MPa at 1.5 wt%.

This implies that the silicone rubber polymer matrix achieves its maximum strength at 1.5 wt% N-ZnO, owing to the highest density of physical interactions among the composite components. This substantial enhancement necessitates the refinement and modification of the inert surfaces of the N-ZnO particles. The treatment with silane

coupling agents facilitates the creation of new active sites on their surfaces [98]. The escalation in compressive strength can be attributed to the robust interaction and high adhesive force between the polymer components and the nanoparticle reinforcement materials. This interaction results in a decrease in the free volume within the molecular structure of the polymer composite materials, thereby reducing the molecular movement of the prepared composite samples. Consequently, the polymer chains stiffen by inhibiting crack propagation, thereby exhibiting compressive resistance under a vertically applied load [98].

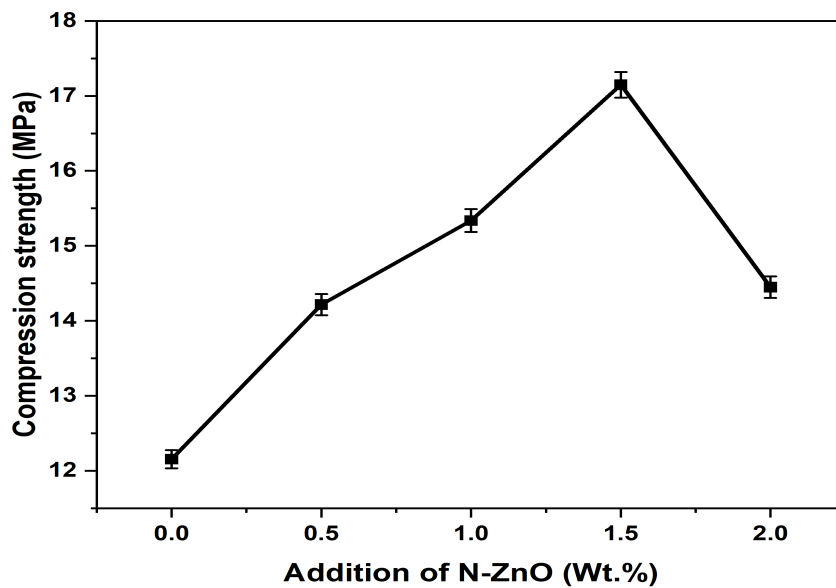


Figure 5.6 Compression strength of the nanocomposite of SR+ X ZnO.

5.6.3 Tear Strength

Figure 5.7 shows the tear strength test results for silicone rubber with different N-ZnO ratios (0.5, 1, 1.5, and 2 Wt.%). Compared to silicone rubber (7,541), there was a significant increase in the tear strength result of 1 point 5 Wt.% n-ZnO (8.634 N/mm). The tear strength test results showed that the tear strength increased with increasing amount of nano-ZnO.

Notably, the groups receiving 5 percent and 3 percent ZnO showed a highly significant increase in tensile strength compared to the silicone rubber. The action of nanoparticles

in the continuous phase of the silicone elastomer, which promotes the formation of cross-linked structures of the silicone material as well as an increase in cross-sectional area and force, leads to an increase in the tensile strength of nanoparticles. ZnO after addition. Consequently, fillers containing nano-ZnO nanoparticles in silicone elastomers are associated with material reinforcement [99]. The increase in tear strength can be explained by the stress energy that propagates through the polymer in and around the resulting cracks. As the crack propagates through nanofillers, the energy is released within the polymer matrix, increasing the crack and requiring greater force and tension to completely rupture the polymer matrix [100]. The tensile strength result of this study is consistent with Han et al. and Nobrega [101, 102], found that the addition of nanoscale ZnO oxide increased tensile strength.

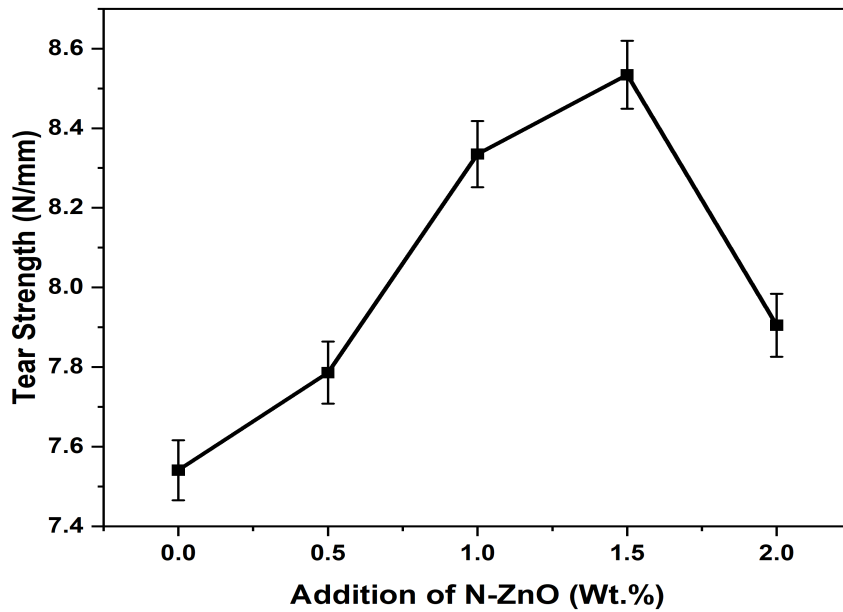


Figure 5.7 Tear strength of the nanocomposite of SR+ X ZnO.

5.6.4 Hardness

The resistance of a material to plastic deformation is quantified by its hardness. This hardness is determined using the indentation load, which provides a measure of the material's softness [103]. Hardness, akin to tensile and tear strength, is a crucial property as it dictates the material's flexibility. Ideally, the material should be as flexible as the region surrounding the defect site [104].

Figure 5.8 presents sample results from the Shore A hardness test. There is a direct and proportional increase in the hardness value as the filler concentration rises. This phenomenon can be attributed to the role of ZnO filler in aiding polymerization and the ZnO nanoparticles in fortifying the formulation, thereby making it resistant to external forces[16] . The resultant higher silicone polymerization and increased hardness are likely outcomes [101].

The influence of nanoparticles on the elastic modulus of the silicone elastomer, coupled with their predominant location on the material's surface, corroborates the findings of a prior study by Xia et al.[105] This is another factor contributing to the higher Shore A hardness of the nano-ZnO silicone elastomer compared to the pure silicone elastomer. Meththananda [106]found correlation between the Shore A hardness and the elastic modulus of the silicone elastomer. Moreover, the dispersion of nanoparticles within the silicone elastomer enhances the cross-linking density, leading to a subsequent increase in the material's hardness.

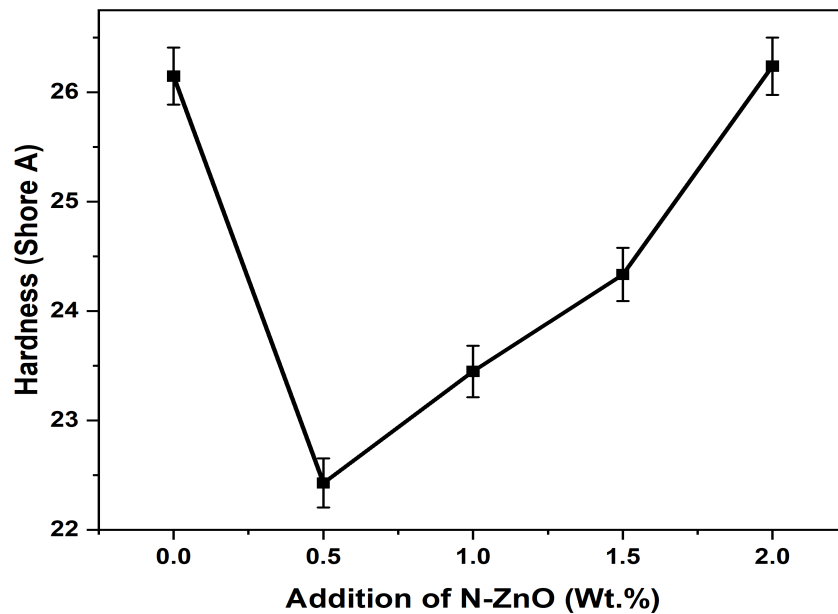


Figure 5.8 Hardness of the nanocomposite of SR+ X ZnO.

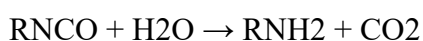
According to these results, 1.5 wt% N-ZnO was selected to prepare a mixture of silicone rubber and PU composite.

5.7. CHARACTERIZATION OF BLEND SR/PU NANOCOMPOSITE

5.7.1 Physical Properties

Table 5.1 shows the effect of varying the amount of isocyanate and water contact on water absorption. The water contact is measured in drops, the isocyanate ratio in ml and the water absorption in percent. The results show that as the number of water drops increases, the percentage of water absorption also increases. With 3 drops of water and an isocyanate ratio of 2 ml, the water absorption is $2.914 \pm 0.14\%$. However, when the number of drops is increased to 9 while maintaining the isocyanate ratio at 2 mL, the water absorption increases to $8.742 \pm 0.43\%$. Furthermore, the results show that increasing the isocyanate ratio also leads to higher water absorption. For example, increasing the isocyanate content from 2 ml to 4 ml with 6 drops of water results in a higher water absorption percentage. The isocyanate group is known to be very reactive and its reaction with water can result in the formation of carbon dioxide, which is commonly used as a blowing agent in the production of polyurethane foams. This reaction can also be used to modify isocyanates and produce biurets[107].

The overall reaction can be summarized as follows:



As for the effect on water absorption, the reaction between isocyanate and water directly contributes to the formation of foam and the formation of carbon dioxide. The carbon dioxide acts as a blowing agent and creates porosity and bubbles in the polymer matrix. This foaming process can affect the final structure and properties of the material, including its water absorption properties. By controlling the isocyanate-water ratio and the reaction conditions, it is possible to individually adapt the foaming process and thus the water absorption properties of the resulting polyurethane material. The best sample is the second one which contained isocyanate (2 ml) and the absorbency of the mixture was about 5.824% after 60 minutes, resulting in good water absorption and good mechanical properties[108].

Table 5.1 Effect of varying the amount of isocyanate and water contact on water absorption.

Water contact (drop)	Isocyanate ratio (ml)	Water absorption %
3	2	2.914 ± 0.14
	4	2.142 ± 0.10
6	2	5.824 ± 0.29
	4	4.285 ± 0.21
9	2	8.742 ± 0.43
	4	6.428 ± 0.32

5.7.2 Tensile Strength, and Elongation

Figure 5.9 clearly shows that the addition of PU to the silicone rubber-based blend polymer results in a reduction in both the tensile strength and elongation of the material. This indicates that the PU phase, when added to the silicone rubber, creates a more porous and less cohesive structure, which affects the mechanical properties of the mixture. As the PU concentration increases, the tensile strength of the material decreases. It starts at around 2.8 MPa at 0% PU and drops to around 1.1 MPa at 30% PU addition. The elongation starts at about 550% at 0% PU and gradually decreases to about 270% at 30% PU addition.

The reduction in tensile strength and elongation is likely due to the formation of pores or voids within the material structure, as mentioned in the previous discussion. These porous structures act as stress concentrators, making the material more susceptible to failure under tensile and deformation forces. Furthermore, the compatibility and interfacial adhesion between the silicone rubber and PU phases can also play a role in the degradation of these mechanical properties. If the two phases do not interact well, this can limit the material's ability to effectively transfer and distribute the applied stresses, leading to the observed decrease in tensile strength and elongation[83].

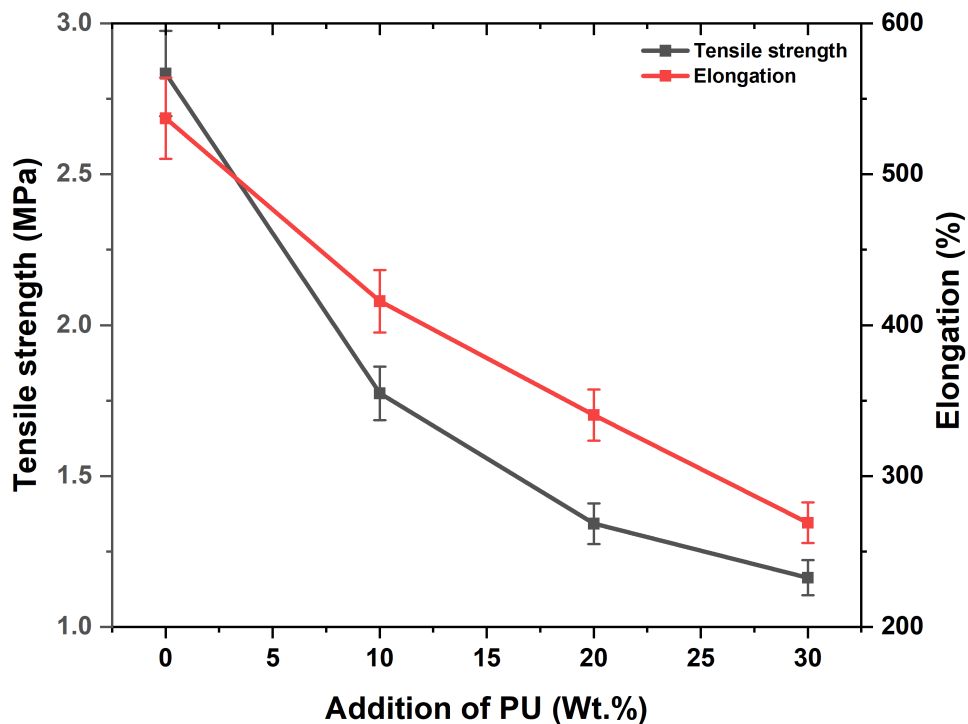


Figure 5.9 Tensile strength and elongation of the nanocomposite of SR+ 1.5% ZnO +X PU.

5.7.3 Tear Strength

Figure 5.10 illustrates a decline in the tear strength of the samples with an increase in polyurethane content. It's important to note that the ratios exhibit some relative inconsistencies, often attributed to the presence of impurities or bubbles in certain samples. A gradual decrease is generally observed, which is particularly evident in the final sample where the polyurethane proportion escalates to 30%. This reduction is a consequence of the chain restriction within the mixture, which hinders the smooth movement of the chains as aromatic rings of the polyurethane. Due to the chemical structure of polyurethane, they contain hard segments that hinder the movement of the silicone chains and limit their movement, which favors the crack growth process and the resulting gaps cause a type of crack[83].

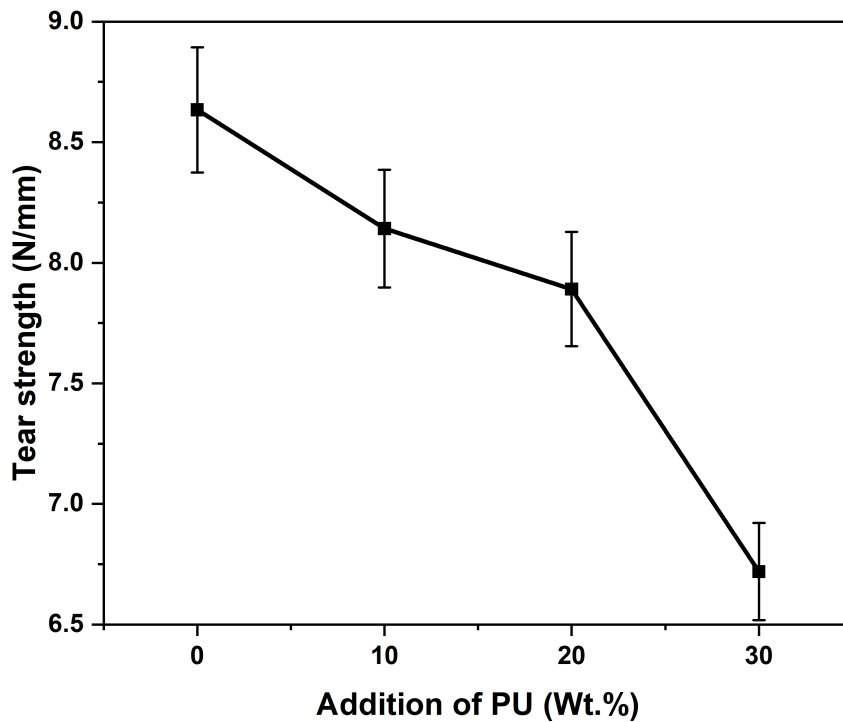


Figure 5.10 Tear strength of the nanocomposite of SR+ 1.5% ZnO +X PU.

5.7.4 Impact Strength

Impact strength refers to a material's capacity to withstand fracture when subjected to an impact load or a load applied at a high speed. This property is often a key specification for technical materials. Unlike other mechanical tests, the impact test involves subjecting the sample to swift loading, leading to tangible alterations in the material's responses. The absorption energy of polymer materials is directly linked to their impact resistance. This characteristic is crucial for applications such as bone cement, where the energy return determines its effectiveness[109].

Figure 5.11 shows the relationship between the addition of polyurethane (PU) in weight percent and the impact strength of the mixed polymer. The initial impact strength of the polymer is approximately 13.5 kJ/m². As PU addition increases, the impact strength of the polymer decreases. This indicates that adding more PU to the silicone rubber reduces the impact resistance of the blended material. As PU addition

increases from 0% to around 10%, the impact strength drops sharply from around 13.5 kJ/m² to around 12.2 kJ/m². After 10% PU addition, the impact strength continues to decrease, albeit more slowly, reaching around 11.8 kJ/m² with 20% PU addition.

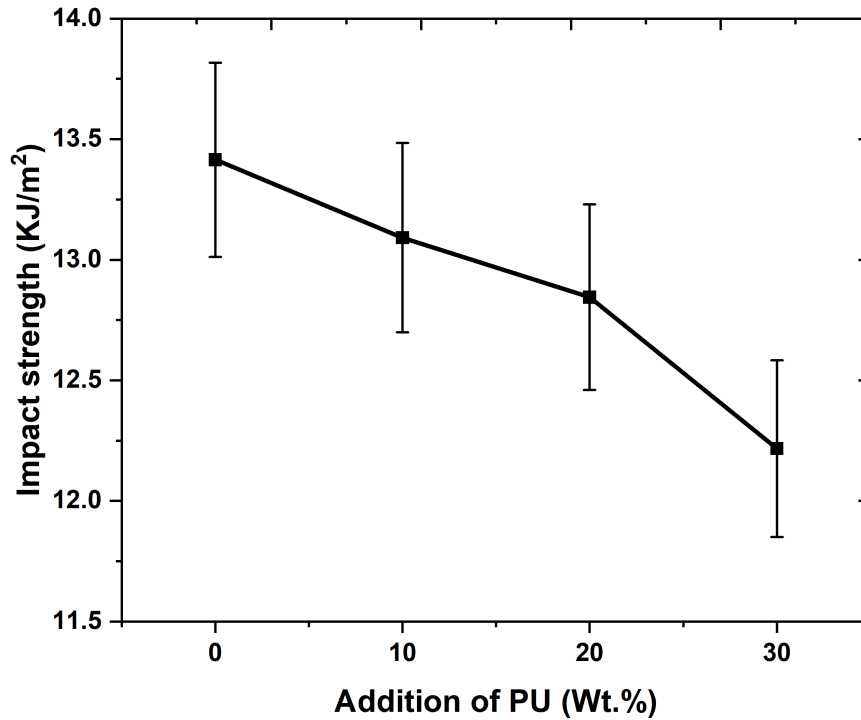


Figure 5.11 Impact strength of the nanocomposite of SR+ 1.5% ZnO +X PU.

5.7.5 Compression Strength

The compressive strength for polymer mixtures (SR+1.5ZnO): From the figure the compressive strength decreases with increasing weight ratio of the PU content in the mixture and reaches the lowest value (12.47 MPa) at a PU content of 30%. The polymer blends of SR/PU samples have lower compressive strength compared to the nanocomposite (SR=1.5N-ZnO). In general, silicone rubber and polyurethane have different physical and chemical properties, silicone rubber may not be distributed evenly of the silicone rubber matrix. Polyurethane could act as a plasticizer in the silicone rubber matrix. Plasticizers are additives that increase the flexibility of a material and lower its glass transition temperature (T_g), making the material more

flexible and less resistant to compressive forces the chains for SR as a matrix material and PU as a second material[110].

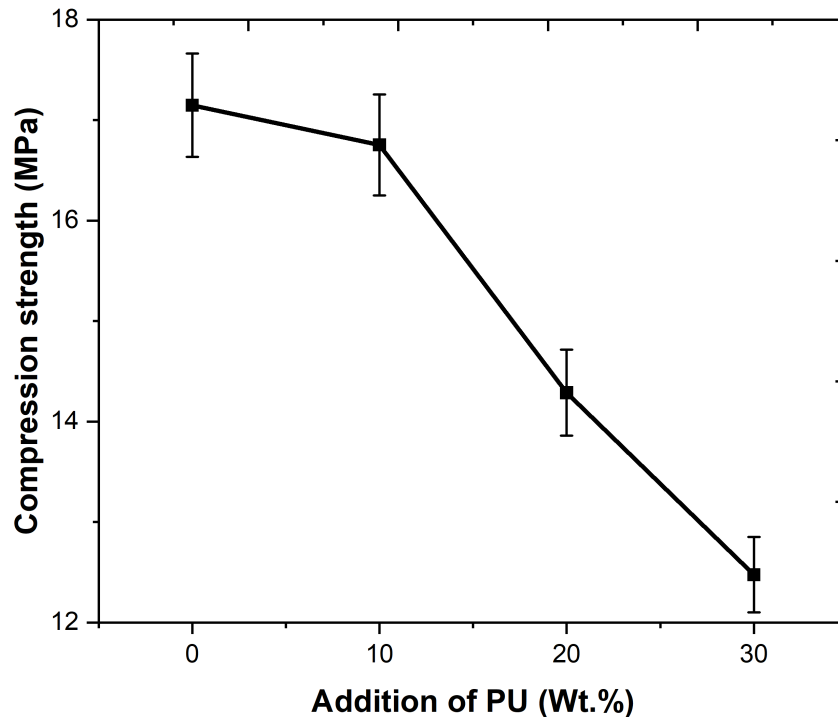


Figure 5.12 Compression strength of the nanocomposite of SR+ 1.5% ZnO +X PU.

5.7.6 Rebound Resilience

The rebound elasticity, which measures the elastic recovery of the material, decreases the more PU is incorporated into the silicone rubber. The results shown in Figure 5.13 indicate that the damping ability of the material increased as the proportion of polyurethane in the IPN increased, which is due to the presence of pores in the structure that contribute to damping. The porous structure created by adding more polyurethane appears to be the reason for the improved cushioning performance of the IPN material. The pores likely help dissipate energy and dampen vibrations more effectively compared to a denser, non-porous structure. The PU disrupts the continuous, elastic silicone rubber network, making the blended polymer less able to store and release energy. The sharp initial decrease in elasticity from 13.5% to 12.2% with only 10% PU addition indicates that PU has a significant influence on the elastic properties even

at low concentrations. The increased polyurethane content appears to cause more discontinuities and voids throughout the polymer network, resulting in a porous morphology that has a positive effect on the material's damping properties. This suggests that the composition and microstructure of the IPN can be tailored by adjusting the polyurethane content to optimize the damping properties for specific applications[83].

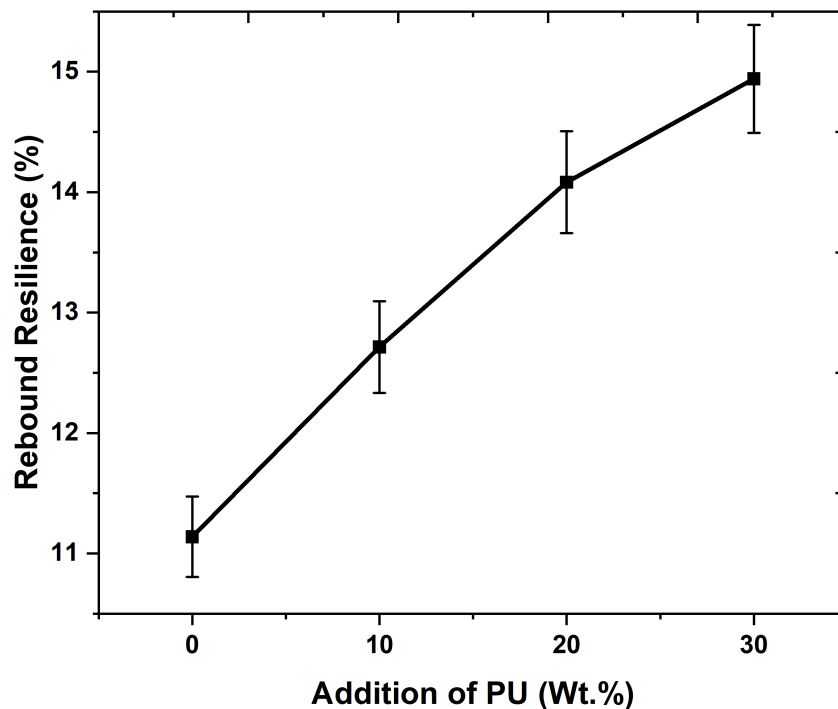


Figure 5.13 Rebound Resilience of the nanocomposite of SR+ 1.5% ZnO +X PU.

5.7.7 Hardness

Figure 5.14 shows an increase in the hardness rate as the proportion of polyurethane foam in the samples increases. The initial hardness of the polymer mixture is around 23.5 Shore A. As the amount of PU added increases, the hardness of the mixture increases steadily. As the PU content increases from 0% to 10%, the hardness gradually increases from 23.5 Shore A to around 26 Shore A. A further increase in the PU content beyond 10% leads to a faster increase in hardness, reaching approximately 30 Shore A with 30% PU addition. This indicates that the incorporation of higher

amounts of polyurethane into the silicone rubber results in a significant increase the hardness or stiffness of the mixed polymer. The addition of the harder PU component appears to progressively strengthen the overall material, making it less flexible and more resistant to indentations[83].

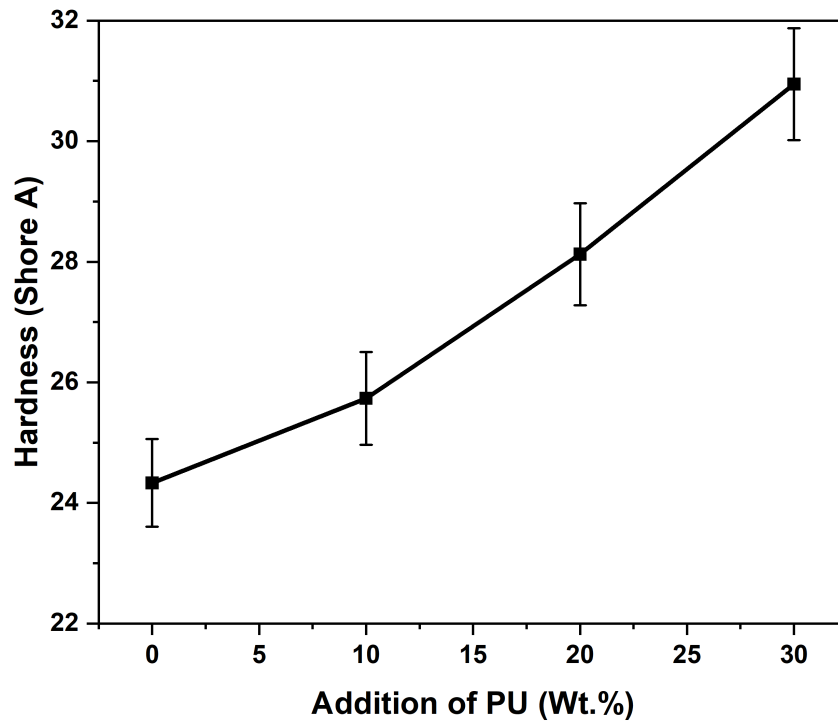


Figure 5.14 Hardness of the nanocomposite of SR+ 1.5% ZnO +X PU.

5.8 ANTIBACTERIAL ANALYSIS

Figures 5.15 and 4.16 represent the antibacterial activities of SiR, SR+1.5Zno and SR+1.5Zno+30%P at different time points (0, 1, 6, 12, 24) hours against *Staphylococcus aureus* and *E. Coli* that are gram positive or gram negative. Biological activity depends on the diameter of the zone of inhibition created around each disc. Based on the figures, excellent antibacterial activity can be demonstrated, and a large and clear inhibition zone can be demonstrated. This behavior can be explained by the chemical structure of the material used and leads to good inhibition behavior.

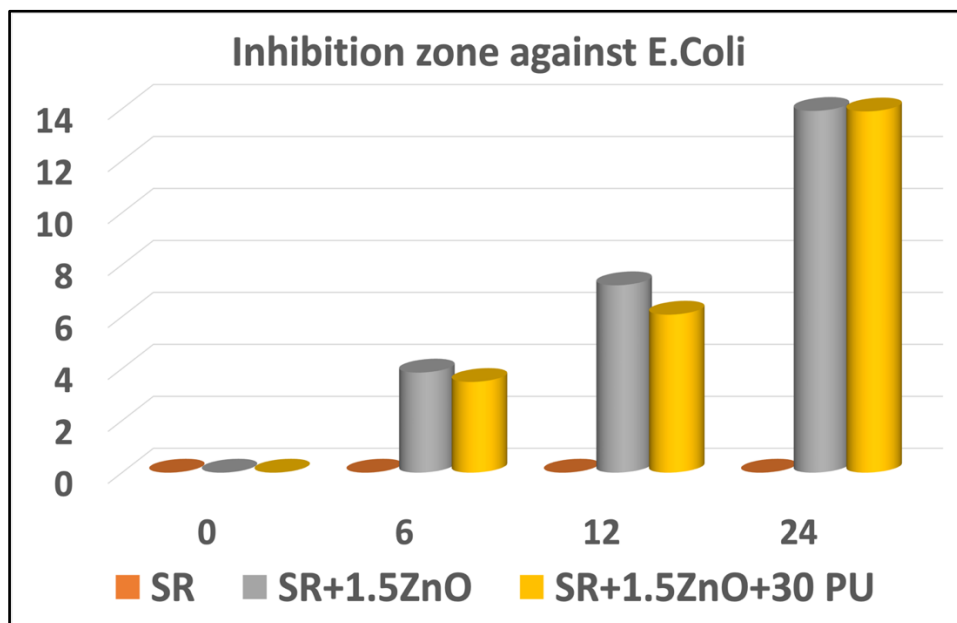


Figure 5.15 Antibacterial activity against Staphylococcus

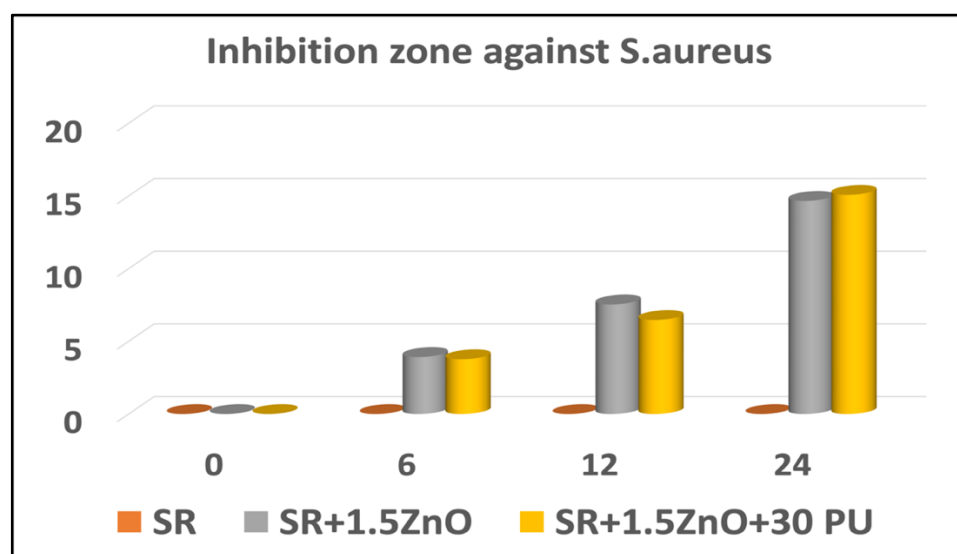


Figure 5.16 Antibacterial activity against S. aureus

The inhibition efficiency (IE) was calculated according to the following equation[83].

$$IE = \frac{I \text{ Zone at high concentration} - I \text{ Zone at low concentration}}{I \text{ Zone at low concentration}} * 100\% \dots \dots \dots (5.1)$$

The zone of inhibition for the silicone rubber (SR) alone starts at 0 and gradually increases to about 6mm within 24 hours. This suggests that although the pure silicone rubber has some inherent antibacterial properties against *S. aureus*, these are relatively limited. By adding 1.5% by weight of NanoZnO to the silicone rubber (SR+1.5ZnO), the antibacterial activity is significantly improved. The zone of inhibition starts at about 3 mm and reaches over 10 mm after 24 hours.

The nanoZnO particles likely offer enhanced antimicrobial effects. The most effective composition is silicone rubber with 1.5 wt.% NanoZnO and 30 wt.% polyurethane (SR+1.5ZnO+30 PU). This sample shows the largest zones of inhibition, starting at around 4 mm and reaching almost 18 mm after 24 hours. The antibacterial activity of zinc oxide nanoparticles (ZnO NPs) against *Staphylococcus aureus* has been the subject of several studies. The antibacterial activities of the three silicone rubber compositions against *E. coli* are compared at different time intervals. The simple silicone rubber (SR) shows limited antibacterial activity with a small zone of inhibition that increases slightly with time. The addition of 1.5 wt% nanoZnO (SR+1.5ZnO) significantly increases the antibacterial activity, with a larger inhibition zone that increases more rapidly over time. The most effective composition is the silicone rubber with 1.5 wt% NanoZnO and 30 wt% polyurethane (SR+1.5ZnO+30 PU), which has the largest inhibition zone that increases rapidly over time, indicating the strongest antibacterial activity against *E. coli*. ZnO NPs were found to be effective against a variety of bacterial strains, including methicillin-resistant *S. aureus* (MRSA). The mechanism of action of ZnO NPs includes generation of reactive oxygen species (ROS), inhibition of bacterial enzymes, and destruction of bacterial cell membranes [1, 20, 83].

PART 6

CONCLUSIONS

In this work, the effect of preparing a nanocomposite blended polymer using nano-ZnO oxide and polyurethane was investigated. The results of the current study, which were based on the preparation of nanocomposite blends, are summarized below: .

- i. The addition of ZnO nanoparticles resulted in significant changes in the X-ray diffraction (XRD) patterns of the amorphous polymer, indicating increased crystallinity.
- ii. FTIR results showed no significant changes in the chemical structure of the silicone rubber, suggesting that the interactions between the nanoparticles and the polymer matrix are primarily physical.
- iii. Morphological analysis revealed that the addition of 0.5 to 2 wt% N-ZnO improved homogeneity, reduced roughness, and improved mechanical properties.
- iv. The addition of ZnO nanoparticles to the silicone rubber matrix effectively increased the density of the composite samples. However, the impact on water absorption was less significant because the hydrophilic nature of the ZnO nanoparticles opened avenues for water molecules to penetrate the hydrophobic silicone rubber.
- v. The addition of N-ZnO nanoparticles to the silicone rubber matrix can effectively enhance the tensile strength and elongation at break of the composites as well as the compressive and tear strength to a certain concentration (1.5 wt% in this case). However, further increasing the nanoparticle loading leads to agglomeration, which negatively impacts the mechanical properties by reducing the polymer-filler interfacial interactions

- vi. The addition of N-ZnO nanoparticles to the silicone rubber matrix significantly improves the hardness of the composites as measured by the Shore A hardness test. This increase in hardness is attributed to the strengthening mechanisms of the nanoparticles, including their role in the polymerization process, their influence on the elastic modulus, and the resulting increase in cross-link density within the silicone elastomer.
- vii. The water absorption of the material can be controlled by adjusting the isocyanate-water ratio. Increasing water contact and isocyanate ratio results in higher water absorption, which is due to the foaming effect caused by the reaction between isocyanate and water and the resulting formation of carbon dioxide.
- viii. The incorporation of PU into the silicone rubber-based mixed polymer has a negative effect on the tensile strength and elongation of the material. This is attributed to the formation of a more porous and less cohesive structure, as well as possible compatibility and adhesion problems between the silicone rubber and PU phases
- ix. The incorporation of PU into the silicone rubber-based blend polymer has a negative impact on mechanical properties, including tear resistance, impact resistance and compression resistance. The restriction of polymer chain movement, the incompatibility between the two phases and the possible plasticizing effect of PU contribute to the observed deterioration in the mechanical performance of the blended material.
- x. The addition of PU to the silicone rubber-based mixed polymer leads to a significant increase in the hardness or stiffness of the material. The progressive incorporation of the harder PU component into the mixture leads to a steady increase in Shore A hardness, with the most significant changes being observed at PU concentrations above 10%. This shows that the inclusion of PU can effectively improve the indentation strength and overall stiffness of the silicone rubber-based polymer blend.
- xi. By adding NanoZnO to the silicone rubber, the antibacterial properties of the composite are significantly improved, with the most effective composition being the PU sample SR+1.5ZnO+30, which has the strongest inhibition against both gram-positive and gram-negative bacteria.

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RESUME

Ali Awad abdukkadhim MUSLIMAWI is a material engineer who graduated from the Faculty of material Engineering, UNIVERSITY of Babylon - Iraq. He received His Bachelor's degree in 2020. He is currently studying for her master's degree at Karabük University in the field of Material Engineering.