



**PREPARATION OF THE LINING OF THE LIMBS  
FROM SILICONE RUBBER USING FOR  
ARTIFICIAL LIMBS**

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MASTER THESIS  
METALLURGICAL AND MATERIALS  
ENGINEERING**

**Husam Awaid ABED**

**Thesis Advisors  
Assist.Prof.Dr. Yasin AKGÜL  
Prof.Dr. Mohammed H. AL MAAMORI**

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**Assist.Prof.Dr. Yasin AKGÜL**

**Prof.Dr. Mohammed H. AL MAAMORI**

**T.C.**

**Karabük Üniversitesi**

**Institute of Graduate Programs**

**Department of Metallurgical and Materials Engineering**

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I certify that in my opinion the thesis submitted by Husam Awaid ABED titled “PREPARATION OF THE LINING OF THE LIMBS FROM SILICONE RUBBER USING FOR ARTIFICIAL LIMBS” is fully adequate in scope and in quality as a thesis for the degree of Master of Science

Assist. Prof. Dr. Yasin AKGÜL .....

Thesis Advisor, Department of Metallurgical and Materials Engineering

Prof. Dr. Mohammed H. AL MAAMORI .....

Co-Thesis Advisor, Department of Biomedical Engineering /Al-Mustaqbal university

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 24, 2023

Examining Committee Members (Institutions)

Signature

Chairman: Assoc.Prof. Dr. Yüksel AKINAY (YYU) .....

Member : Assist. Prof. Dr. Alper İNCESU (KBU) .....

Member : Assoc. Prof. Dr. Yasin AKGÜL (KBU) .....

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

Prof. Dr. Müslüm KUZU .....

Lisansüstü Eğitim Enstitüsü Müdürü

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Husam Awaid ABED



## **ABSTRACT**

**Master Thesis**

### **PREPARATION OF THE LINING OF THE LIMBS FROM SILICONE RUBBER USING FOR ARTIFICIAL LIMBS**

**Husam Awaid ABED**

**Karabük University**

**Institute of Graduate Programs**

**The Department of Metallurgical and Materials Engineering**

**Thesis Advisors:**

**Assist.Prof.Dr. Yasin AKGÜL**

**Prof. Dr. Mohammed H. AL MAAMORI**

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Lower extremity prostheses can be worn either above or through the knee or even below the knee. One of the most important parts of an above-the-knee amputation is the socket, which needs an inner liner to stabilize the socket containing the amputated portion, prevent direct friction between the socket and the skin, and discourage the growth of decay. It is important to improve the physical and mechanical properties of this liner. Silicone rubber elastomer is the most commonly used material for prosthesis wearers. The goal of this project is to develop a socket liner for amputees, as sweat from the prosthesis is a common complaint. The different concentrations of hydroxyapatite (HA) and zinc oxide (ZnO) nanoparticles, which influence the therapeutically important mechanical properties of the prosthesis lining made of silicone rubber, were examined.

Addition of chlorophyll in different proportions (10, 20 and 30%) to silicone rubber to influence its water absorption. Nano-ZnO was added at concentrations of 1.5%, 3% and 4.5% by weight to a silicone rubber composite with 10% chlorophyll, and the best percentage of zinc oxide addition was determined based on mechanical properties. Nano-HA was then added at concentrations of 0.5%, 1%, and 1.5% by weight to a composite blend of 10% chlorophyll + 1.5% ZnO silicone rubber. Water absorption was according to ASTM 570-98. Tensile strength and elongation tests were performed according to ASTM-D412. A tear strength test was performed according to ASTM D624-07. Shore A hardness testing was performed according to ASTM D2240. The resilience test was performed according to ASTM-D1054.

The dispersion of the nanoparticles was examined with the field emission scanning electron microscope (FESEM). In addition, antibacterial activities against *Staphylococcus aureus* microorganisms were measured by the agar well diffusion method.

FESEM showed agglomeration and dispersion of ZnO and HA nanoparticles with pores due to chlorophyll within the silicon matrix. The 10% chlorophyll showed a significant increase in water uptake, while the addition of 1.5% ZnO and 0.5% HA nanoparticles showed a highly significant increase in all mechanical properties tested. Hardness increased with increasing nanofiller concentration, with the increase being directly proportional. The antibacterial results showed that the nanocomposite compound (SR + 10% chlorophyll + 1.5N-ZnO + 0.5% N-HA) has good activity against the microorganism *Staphylococcus aureus* (inhibition zone of 20 mm).

**Key Word:** Socket liner Protheses, Biomaterial, Silicone rubber, Nanofiller  
Mechanical properties, Antibacterial.

**Science Code:** 91501

## **ÖZET**

**Yüksek Lisans Tezi**

### **YAPAY UZUVLAR İÇİN KULLANILAN SİLİKON KAÜÇUKTAN UZUVLARIN ASTARININ HAZIRLANMASI**

**Husam Awaid ABED**

**Karabük Üniversitesi**

**Fen Bilimleri Enstitüsü**

**Metalurji ve Malzeme Mühendisliği**

**Tez Danışmanları:**

**Dr. Öğr. Üyesi Yasin AKGÜL**

**Prof. Dr. Mohammed H. AL MAAMORI**

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Alt ekstremitte protezleri diz üstü veya diz boyunca, hatta diz altına giyilebilir. Diz üstü amputasyonun en önemli bileşenlerinden biri sokettir. Bu soket, kesilen kısım ile soketi stabilize etmek, soket ile cilt arasındaki doğrudan sürtünmeyi önlemek ve çürümenin büyümesini engellemek için bir iç astar içerir. Bu astarın fiziksel ve mekanik niteliklerini geliştirmek ise esastır. Silikon kauçuk elastomer, protez astar destekleri için en yaygın kullanılan malzemedir. Bu tezin amacı, protezden kaynaklanan yaygın terleme şikâyetlere yönelik, amputeler için bir soket astarı geliştirmektir. Değişen konsantrasyonlardaki hidroksiapatit (HA) ve çinko oksit (ZnO) nanoparçacıklarının silikon kauçuk protez astarın terapötik açıdan önemli mekanik özelliklerine etkisi araştırılmıştır.

Su emilimini arttırmak için silikon kauçuğa farklı oranlarda (% 10, 20 ve 30) klorofil eklenmiştir. Ardından, nano-ZnO, %10 klorofil içeren silikon kauçuktan kompozite ağırlıkça %1,5, %3 ve %4,5 oranlarda ilave edilmiştir ve mekanik özelliklere dayalı olarak çinko oksit ilavesinin en iyi yüzdesi belirlenmiştir. Daha sonra %10 klorofil + %1.5 ZnO içeren silikon kauçuk matrisli kompozit bileşiğe ağırlıkça %0.5, %1 ve %1.5 konsantrasyonlarında Nano-HA ilave edilmiştir. Su emme testi ASTM 570-98'e göre yapılmıştır. Çekme mukavemeti ve uzama testleri ASTM-D412'ye göre yapılmıştır. ASTM D624-07'ye göre bir yırtılma mukavemeti testi yapılmıştır. ASTM D2240'a göre Shore A sertlik testi yapılmıştır. Rezilyans testi ASTM-D1054'e göre yapılmıştır.

Nanoparçacıkların dağılımı, Alan emisyon taramalı elektron mikroskobu (FESEM) kullanılarak yapılmıştır. Ayrıca, agar well difüzyon yöntemi ile Staphylococcus aureus mikroorganizmalarına karşı antibakteriyel aktiviteleri ölçmüştür.

FESEM, ZnO ve HA nanoparçacıklarının silikon matris içindeki topaklanmalarını ve dağılımını ve klorofilden kaynaklanan gözenekleri göstermiştir. %10 klorofil içeren numune, su emiliminde önemli bir artış gösterirken, %1,5 ZnO ve 0,5 HA nanopartiküller eklendiğinde test edilen tüm mekanik özelliklerde oldukça önemli bir artış görülmüştür. Sertlik, nano katkıların konsantrasyonundaki artışla artmış ve artış takviye oranı ile doğrudan orantılıdır. Antibakteriyel sonuçlar, nanokompozit bileşiğin (SR+%10 klorofil +1,5 N-ZnO + %0,5 N-HA) Staphylococcus aureus mikroorganizmasına (20 mm'lik inhibisyon bölgesi) karşı iyi bir aktiviteye sahip olduğunu göstermiştir.

**Anahtar Sözcükler :** Soket Astar Protezler, Biyomalzemeler, Silikon kauçuk, Nano katkıları, Mekanik özellikler, Antibakteriyel.

**Bilim Kodu :** 91501

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## SYMBOLS AND ABBREVIATIONS INDEX

### SYMBOLS

$T_g$	: glass transition temperatures
$\text{kJ/mol}$	: kilo joule per mole
$E$	: Young's modulus
$\mu\text{m}$	: Micrometer
$^{\circ}\text{C}$	: Degrees Celsius

### ABBREVIATIONS

<i>SR</i>	: Silicone rubber
<i>ASTM</i>	: American Society for Testing and Materials
<i>Cl</i>	: chlorophyll
<i>HA</i>	: Hydroxyapatite
<i>EDS</i>	: Energy-Dispersive Spectrometry
$^{\circ}\text{C}$	: Degrees Celsius
<i>RTV</i>	: Room temperature vulcanization

## **PART 1**

### **INTRODUCTION**

#### **1.1.INTRODUCTION**

Amputation is a significant trauma that significantly disrupts the biomechanics of the musculoskeletal system, results in severe physical and psychological loss, and ultimately affects the individual's quality of life, social and professional life [1]. Studies in developed countries show that most lower extremity amputations are due to peripheral vascular diseases. The results of studies on this subject in our country show that trauma is the primary cause of amputation for both the lower and upper extremities. Tumours, acute and chronic infections, congenital limb deficiencies, metabolic diseases, paralysis, burns and frostbite also cause amputation. Other causes of amputation in developing, war-torn countries; include industrial or environmental accidents, terrorist attacks, diabetes, gangrene and infection leading to basic public health deficiency. These reasons increase the number of amputees at an alarming rate [2]. Loss of aesthetics and function after amputations have been tried to be compensated for by different prosthetic applications since the existence of human beings [3]. In general, essential factors for the use of prosthesis; are stump-socket compatibility, mechanical function of the prosthesis, and other qualities of the prosthesis (cosmetics, similarity to anatomical structures, weight, safety, durability) [4]. The essential function of the prosthesis is the realization of walking activity, and the most crucial characteristic is its adaptation to the stump. The compatibility between the stump and the prosthesis in the lower extremity is an important determinant of successful ambulation [5]. Insufficient stump-socket fit; It increases the piston movement, high-pressure areas and shear forces between the stump and the prosthesis. The weakening of the contact between the socket and the stump causes loss of proprioception and involuntary dislocation of the stump from the

prosthesis. With a good prosthesis fit and suspension, the forces between the stump and socket are effectively distributed,

While minimizing local high-pressure areas and shear forces, providing a comfortable fit [6].

Polymeric nanocomposites, a kind of compound material composed of a polymer and an inorganic filler with at least one dimension on the nanoscale scale, have acquired material characteristics in recent years [7]. Nanoparticles may enhance mechanical characteristics by increasing the number of crosslinking sites at the nanoparticle-matrix interface. Only a good filler spread in a base, such as a rubber matrix, may improve the material's properties [8]. The establishment of filler particles in elastomers inhibits the capacity of the chain to move freely and readily in rubberlike nanocomposites owing to interactions of base molecules with solids. Rubber materials are increasingly being used in various commercial applications due to the powerful performance of very modest quantities of filler particles on the mechanical characteristics of rubber. Nanocomposites exhibit significant advantages in medicinal applications, fire retardancy, mechanical qualities, thermal stability, and other scientific domains [9]. Knowing the characteristics used to determine the type of material required in the production area in which the possible use is, for example, in the field of space, introduced composite materials bear high temperature and density, and in the field of medicine, for compensation for parts of the human body, made composite materials with biocompatible specifications and high technology against bacteria growth [10]. For the reasons mentioned above, Rubber-reinforced nano-scale materials (nanocomposites rubber materials) usually appear to have good mechanical properties because nanoparticles strengthen more effective materials, leading to improved matrix properties, resulting in a lightweight composite material with low cost and ease of processing and an increased surface area, assuming good adhesion properties in boundaries compared to a rubber reinforced with the world via gauge material.

The biocompatibility of polymers is determined not solely by their chemical composition but is significantly influenced by various additional factors. The acceptance or rejection of a polymeric medical device by the body is contingent upon

the location and movement of the material, as well as the surrounding human environment, as previously noted [11]. Hence, identifying appropriate polymers that exhibit significant resistance to the factors above is crucial for biomedical purposes. Polyurethanes and silicones are the predominant polymer materials used in biomedical applications. Silicone rubber nanocomposites find application in diverse fields, such as ligament replacements, heart valve prostheses, vascular graft prostheses, breast prostheses, catheters, and cannulae. The material exhibits favourable biocompatibility, notable resistance to hydrolysis and bodily fluids, exceptional mechanical properties characterized by high tensile strength and elasticity, and a limited degree of degradation. Medical-grade silicone elastomer filled with zinc oxide is used in the medical field for breast augmentation and reconstruction through mammary prostheses [12]. The medical industry extensively uses silicone rubber. Among the various applications that hold utmost significance are internal or partially internal instruments, wherein the rubber comes in contact with the human body or skin. In biomedical applications, polymers must conform to specific criteria and standards to ensure their safe utilization within the human body. Primarily, the materials must exhibit biocompatibility, posing no harm to the human organism while demonstrating exceptional stability within the tissues [13].

Chlorophyll is a compound that is known as a chelate. A chelate consists of a central metal ion bonded to a large organic molecule, composed of carbon, hydrogen, and other elements such as oxygen and nitrogen.

Chlorophyll has magnesium as its central metal ion, and the large organic molecule to which it bonds is known as a porphyrin. The porphyrin contains four nitrogen atoms bonded to the magnesium ion in a square planar arrangement. Chlorophyll occurs in a variety of forms. chlorophyll absorbs energy to transform carbon dioxide and water into carbohydrates and oxygen. This is the process that converts solar energy to a form that can be utilized by plants, and by the animals that eat them, to form the foundation of the food chain .

## **1.2.OBJECTIVE OF THE WORK**

In general, many lower limb amputated operations are performed each year, and the main reason for this is peripheral vascular disease and/or diabetes, but other causes are different accidents, infections, and tumours. To carry out his routine, the patient often uses a prosthetic. Using prostheses makes the soft tissue in the residual limb bear body weight. The inner surface (lining) is part of the separation between the residual limb and the artificial part. One complication of synthetic liners is skin problems on the amputee's stump. The limb's skin is exposed to many non-normal conditions during weight-bearing and to shear stress forces, which may lead to edoema of the stump and blisters due to shear forces and stress at the end of the stump. In addition, it cannot evaporate sweat freely from the skin area where the liner is located. Increased moisture to the skin can lead to inflammation and bacterial infection that can occur in addition to those that lead to abscesses, cellulitis, pyoderma, and inflammation of the sweat glands. Using the lining of the nanocomposite material of silicone rubber and antibacterial materials such as nano zinc oxide, which is used as a separator between the skin and other components of the prosthetics, creates a more uniform distribution of pressure on the remaining part. This project aims to provide an antibacterial lining that prevents skin irritation from accumulating sweat. The lining produced is well porous, light in weight, and low in cost.

## **1.3.THESIS DESIGN**

This dissertation is divided into five chapters. The general introduction is presented in Chapter 1. The theoretical section of Chapter 2 provides the definition, categorization, and types of composite materials, as well as definitions of denture base materials and literature studies. The experimental work is covered in Chapter 3, which discusses the materials utilized, specimen fabrication, and test equipment. In chapter five, the findings and discussion of the experimental work, the work conclusions, and ideas for future investigations are discussed.



## **PART 2**

### **THEORETICAL BACKGROUND**

#### **2.1. INTRODUCTION TO NANOCOMPOSITE POLYMER**

Biopolymers constitute an important class of polymers that attract increasing attention and interest from researchers and industries. In contrast to synthetic polymers, which are produced from petroleum derivatives, therefore from non-renewable sources, biopolymers are produced by living organisms, such as plants, animals and fungi, via complex intracellular metabolic processes that involve enzyme-catalyzed reactions and reactions of polymerization[14]. It is essential to highlight that some authors include, in this category, polymers synthesized from raw materials of natural origin, such as poly(vinyl acetate) (PVA), poly(lactic acid) (PLA) and polyethylene, provided they are produced from bioethanol. They may also include those that are biodegradable[15]. However, the term biopolymers will identify polymers produced by living organisms unless otherwise specified. Among the most essential and abundant biopolymers, polysaccharides (for example, cellulose, starch, chitin, chitosan, alginates, hyaluronic acid), proteins (collagen, gelatin, zein, fibroin), polynucleotides, polyisoprenes (natural rubber) and polyesters (poly(b-hydroxybutyrate)/PHB, poly(b-hydroxy valerate) / PHV, poly(hydroxybutyrate-co-valerate)/PHBV) [16]. In addition to their wide availability and the fact that they are obtained from renewable sources, polysaccharides and proteins have been widely used in the development of new materials with essential applications in several areas due to their structural characteristics, physicochemical properties and biological activities, highlighting biocompatibility, biodegradability and non-toxicity.

The search for materials with optimized properties for applications in areas as diverse as engineering, medicine, automotive and aerospace has led to the large-scale use of composite materials. These are produced by combining two or more materials with different physical and/or chemical properties, resulting in a final multiphase material with intermediate characteristics of the constituent phases and superior final performance due to the optimized combination of properties [17]. The materials composites can be based on polymeric matrices (polymeric composites), ceramic matrices (ceramic composites) or even metallic matrices (metallic composites) [18, 19]. Among these, polymeric composites are widely used in several applications since polymers, acting as matrices, offer advantages over other materials, providing optimized properties [18].

Recently, several studies have been conducted to obtain polymeric nanocomposites through the combination of a polymeric matrix (continuous phase) and a dispersed phase (non-continuous) that has at least one of its dimensions in the nanometric scale, which can be zero-dimensional (e.g., nanoparticles) [20], one-dimensional (e.g., nanofibers) [21], and two-dimensional (e.g., nanoplatelets) [22]. Such materials are easily processable and can exhibit improved mechanical, electrical, optical, and other properties when compared to composites in which the dispersed phase is formed by macrostructures [18].

## **2.2. CLASSIFICATION OF POLYMER COMPOSITES**

The classification of polymeric composites depends on the nature of the components used in their formation and the preparation method used. Thus, different structures can be obtained and classified according to the size of one of the phases of the combination of materials to form the polymeric composite [23]. Composites can be classified according to the dimensions of the dispersed phase in microcomposite, intercalated nanocomposite and exfoliated nanocomposite. Microcomposites are materials in which micrometre-scale structures constitute the dispersed phase. When the dispersed phase consists of agglomerated nanomaterials in which the polymeric matrix is not intercalated, a composite of distinct phases is obtained (Figure 2.1), whose properties are similar to those of microcomposites [23].

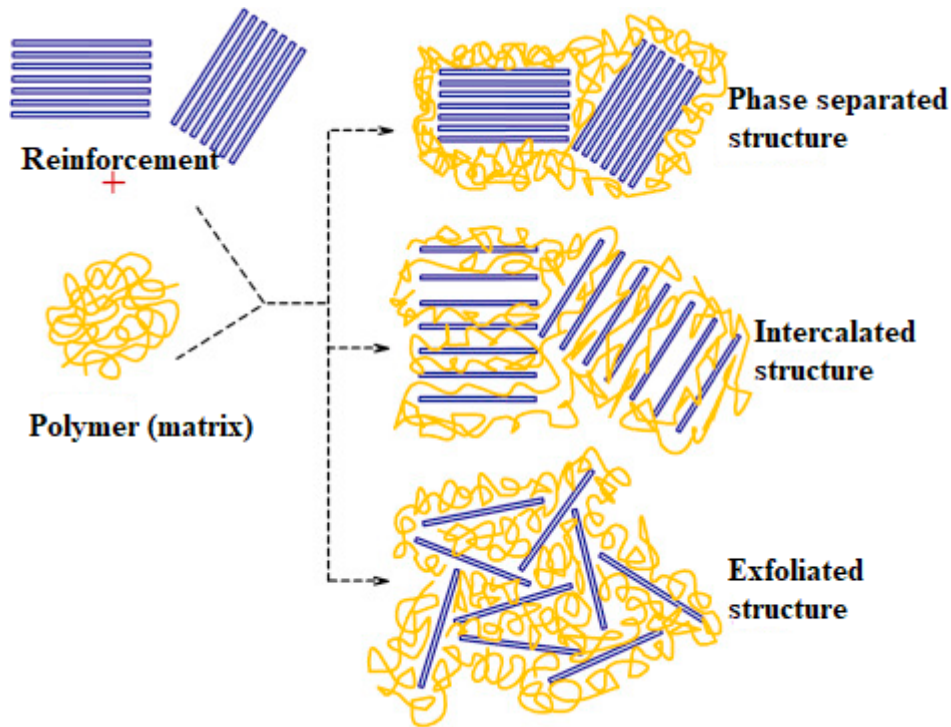


Figure 2.1. Possible structures obtained in the formation of composites [24].

In the case of the intercalated nanocomposite, there is a repetitive pattern of intercalation between the polymeric chains and the reinforcement. Dispersion, in this case, is also incomplete, resulting in a material formed by regions with a greater or lesser concentration of reinforcement, impacting mainly on the mechanical properties of the nanocomposite due to the heterogeneity and stress transfer throughout the nanocomposite. As for the exfoliated nanocomposite, the reinforcement is well separated and uniformly dispersed in the polymeric matrix. This type of structure is the most desirable for most applications, as it enables a better distribution of reinforcement in the polymeric matrix [25]. However, for each type of structure obtained (or level of dispersion), the physical, mechanical, and optical characteristics, among others, will be distinct in the resulting nanocomposites [25]. In addition to the different structures, the dispersed phase (reinforcement) can present different shapes and sizes, such as particles, lamellae and fibres, leading to the formation of particulate, fibrous and lamellar composites, according to shown in Figure 2.2 (a), (b) and (c), respectively[26].

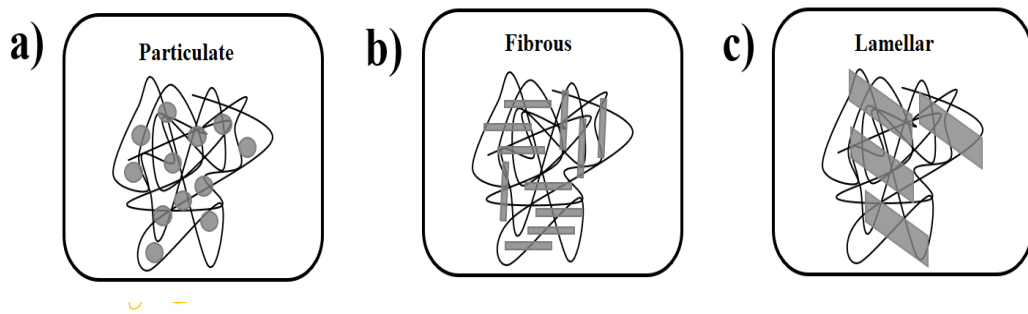


Figure 2.2. Classification of the different possible structures for the formation of polymeric composites: a) particulate, b) fibrous, and c) lamellar [26].

These different structures obtained depend on the nature of the components used, the materials used and the method of preparing the nanocomposite, which directly impacts the type of application desired for the material obtained [25].

The word 'nanocomposite' is a recent term, but the concept is not new, and the following paragraphs help to resituate its origin.

- Natural nanocomposites:

Various nanostructures and nanocomposites already exist in nature, such as bones and spider webs; some bacteria also manage to make nanostructures. Natural nanobiocomposites have a structure on a nanometer scale, like that of certain shells, called a brick made up of organic proteins and particles of calcium carbonate. These natural structures comprise elementary nanometric blocks of different natures and therefore come under the classification of nanocomposites. Most natural organic/inorganic nanocomposites self-assemble according to two mechanisms: - initial formation of the organic structure, then nucleation and growth of the mineral phase. This mechanism applies to most biological composites. The organic matrix can, however, restructure and reorganize itself during the mineral phase formation, thus approaching the second mechanism. - simultaneous assembly of organic and inorganic materials. Certain entirely organic or inorganic materials (such as teeth) may involve, during their synthesis, various types of materials which are not found in their final structure. The simplest examples of natural nanocomposites are biological compounds that manufacture nanoparticles within their cellular structure. Some grasses cause the

precipitation/condensation of SiO<sub>2</sub> nanoparticles in different forms (rods, sheets). Biological organisms can manufacture nanostructures (sea urchin spines, bones, shells, etc.) that are more complex than the nanoparticles mentioned above. Chemists try to reproduce these complex and often hierarchical natural organizations in the laboratory through biomimicry. Certain bacteria cause the precipitation of minerals whose structure is guided by proteins on the latter's surface [27].

- Synthetic nanocomposites:

The idea of improving the properties of materials by combining two phases with different properties is not new, even at the nanometric level. Throughout history, we find examples of ancient materials that can be considered nanocomposites, even if this approach was not initially intended. For example, particular colorations of Mayan paintings [27] are due to the inclusion of metallic nanoparticles and oxide in an amorphous silicate substrate, or even the lustre of certain pottery from the Italian Renaissance [28] is attributable to the presence of metallic nanoparticles of copper and of silver from 5 to 100 nm obtained by a reduction process. More recently, in 1917, carbon black was introduced into the composition of tires, the service life of which was thus multiplied by five. This carbon powder produced by controlled pyrolysis of hydrocarbons in the vapour phase consists of particles of 0.01 to 0.4 micrometres, while the average diameter of the aggregates varies from 0.1 to 0.8 microns. Carbon black is used as a reinforcing agent in rubber-based products such as tires, hoses, conveyor belts, and cables or as black pigments in inks, paints, coatings, ceramics, and plastics. It also manufactures insulating materials resistant to high temperatures or antistatic products.

- Microcomposite to nanocomposite:

Nanocomposites constitute a class of materials in their own right. Indeed, although they have the same composition as conventional composites, particularly concerning the nature of the matrix, their difference lies in the size of the components (matrix or reinforcement) and in the fact that certain specific properties only appear on the nanometer scale [29]. Composites with micrometric reinforcements have shown some of their limitations. Their properties result from compromises: improving strength, for example, comes at the expense of plasticity or optical transparency. Nanocomposites

can overcome some of these limitations and have advantages over conventional composites with micrometric reinforcements: a significant improvement in mechanical properties, particularly resistance, without compromising the material's ductility because the particles' small size does not create large concentrations of constraint. - increase in thermal conductivity and various properties, particularly optical ones, which conventional approaches to mixtures of components cannot explain. The nanoparticles, having dimensions below the wavelengths of visible light (380-780 nm), allow the material to retain its initial optical properties and a good surface condition. The reduction in the size of the reinforcements inserted into the matrix leads to a significant increase in the surface area of the interfaces in the composite. However, precisely this interface controls the interaction between the matrix and the reinforcements, partly explaining the singular properties of nanocomposites. It should be noted that the addition of nanometric particles significantly improves certain properties with much lower volume fractions than micrometric particles[30]. It can obtain: - for equal performance, a significant weight saving as well as a reduction in costs since fewer raw materials are used (without taking into account the additional cost of nano-reinforcements), - better resistance for structural dimensions similar, - an increase in barrier properties for a given thickness.

### **2.3. PROPERTIES, APPLICATIONS, BEHAVIOR AND PERFORMANCE OF POLYMER NANOCOMPOSITES**

The properties displayed by materials depend on the size scale in which this material is found or the extent to which such properties are measured. Because it is much easier for us to interact with what we can see and feel, we are much more familiar with the macro scale, and it is often more intuitive to understand and understand the properties and behavior of objects that are inserted in this scale that is, of materials ranging in size from meters, centimetres to a few millimetres. The properties presented by materials on the macroscale must be interpreted holistically, representing the average behavior of the entire object. For example, the density, the elastic modulus and the electrical resistance are associated with the object as a whole and are influenced by the parts that compose it [31]. However, when its dimensions are reduced to the nanoscale, a fixed composition material can show some effects not observable at the macroscale.

For example, electrical behavior, mechanical properties, color and reactivity characteristics can differ for the same material at the nano and macro scale[32].

The main change in downscaling is associated with the massive increase in the ratio between the surface area of the object and the volume it occupies. Thus, surface effects on nanometric materials contribute more significantly to the presented properties. This is the case, for example, of friction, which becomes much more significant than inertia, which depends on the object's mass. In the same way, intermolecular and electrostatic forces become more important and can be considered strong, whereas, on the macroscale, they are often ignored [31]. When reducing one of the dimensions of three-dimensional material, films (2D material) with nanometric thickness can be obtained (also known as thin films), which have characteristics such as electrical conductivity and light absorption different from the bulk material. Reducing one more dimension of the 2D material to the nanoscale gives rise to nanofibers (1D material) or nanowires, which have a high active surface area and can be used in applications such as filtration membranes. Finally, by reducing the three dimensions, some materials show more clearly quantum confinement effects and differences in the energy values of their valence and conduction bands, which can significantly alter their optical and electrical properties. Polymeric nanocomposites can be obtained by combining a polymeric matrix with nanomaterials to obtain a nanocomposite with specific characteristics significantly different from the properties (mechanical, thermal, electrical, optical, magnetic, etc.). Carbon-based nanomaterials, silicates and inorganic and metallic nanoparticles are some of the most used nanomaterials in combination with polymers to obtain nanocomposites [33]. That can be used as fibers, wires or tubes, in spherical shapes or layered structures [34].

In 1979, KATO et al. reported the mechanical properties of a nanocomposite consisting of nylon-6 obtained from aminocaproic acid and a montmorillonite-type filler [35]. In 1993, the R&D group of Toyota in Japan showed improved mechanical properties and thermal properties of nylon-6 after adding only 5% by mass of montmorillonite, a natural cationic clay—also permeability or fireproofing properties[36]. Polypropylene/organo-modified clay nanocomposites were prepared by melt-mixing using an internal mixer. A functionalized propylene maleic anhydride

(PP-g-MA) was used as a compatibilizer to improve the dispersion quality. The rheological measurements show that the  $G'$  modules are susceptible to the level of dispersion, and the degree of dispersion depends on the concentration of PP-g-MA and the mixing conditions. Rheological studies have also been carried out on the PS/Silicate nanocomposites prepared by in situ polymerization, which leads to the polymer chains' attachment and the excellent dispersion of the silicate layers, causing their exfoliation. Measurements of linear viscoelasticities show that the dispersion improves with lowering the molecular weight, which agrees with the weak interactions between the polymers and the silicate. On the other hand, the measurements of the non-linear viscoelasticities show that a significant fraction of the free polymer chains gives rise to a stress response [37]. The elongation force of the polymer nanocomposite is then markedly increased (0.46 to 3.81 MPa ) as well as the elongation at break, which means the absence of a break in the elasticity of the polymer by the intercalation of the particles [38].

For other nanocomposite systems derived from polyimides, epoxy or polysiloxane, there is an increase in glass transition temperatures  $T_g$  and an improvement not only in the mechanical strength of the materials but also a reduction in gas permeability by increasing the phenomenon of tortuosity, which allows their potential use in the food packaging industry. For example, the Nanocomposites/PVA system containing 5% by mass of a montmorillonite-type filler (MMT) has Young's modulus three times higher than PVA alone[39].

Wang et al. observe that the mechanical properties depend on the preparation method for some PS nanocomposites. The nanocomposites developed by several polymerization methods and using a reactive compatibilizer have mechanical properties superior to the polymer alone, and this in terms of elongation stress (5.9 to 8.1 Mpa), Young's modulus (0.74 to 1.14 Gpa) and elongation (1.1 to 0.8%) [40]. The dynamic mechanical properties of PS below the  $T_g$  increase with the increasing rate of MMT loading using vinylbenzyltrimethylammonium (VDAC) as a compatibilizer [41]. The Young's modulus, at 25°C, increases from 3.3 to 5.4 Gpa with only 7.6% by mass of MMT filler [42]. Similarly, for a smectite-nanocomposite of polyimide (PI), the  $T_g$  is increased compared to the polymer. Nanocomposites are also



suitable as a gas barrier by preventing volatile gas from escaping by creating long inter-platelet diffusion paths.

## 2.4. SILICONE ELASTOMERS

Silicon is a polymer composed of an inorganic siloxane backbone (Si-O). The most common silicon is poly(dimethylsiloxane), which has a backbone of silica and oxygen [43]. A schematic representation of the silicone elastomer is given in Figure 2.3. The synthesis of polysiloxanes results from a precursor reaction in which methylchlorosilanes are produced from methyl chloride and silicon [44]. The inorganic/organic hybrid nature of silicone elastomers gives them a unique combination of properties, putting them in a material form with the properties of both sides. Si-O bond (~433 kJ/mol-1) has higher binding energy than C-C (~355 kJ/mol-1). This provides higher heat resistance and thermal stability for the polymer grade[43]. In addition, the higher bond length (Si-O: 1.64, C-C: 1.53) and the absence of steric hindrance around the Si-O-Si bond, the structural features result in higher chain flexibility and Tg value. Silicone elastomers have high binding energy (444 kJ/mol). It also contains two methyl groups for each silicon. The ratio between methyl and ethyl groups is between 0.1 and 0.2.

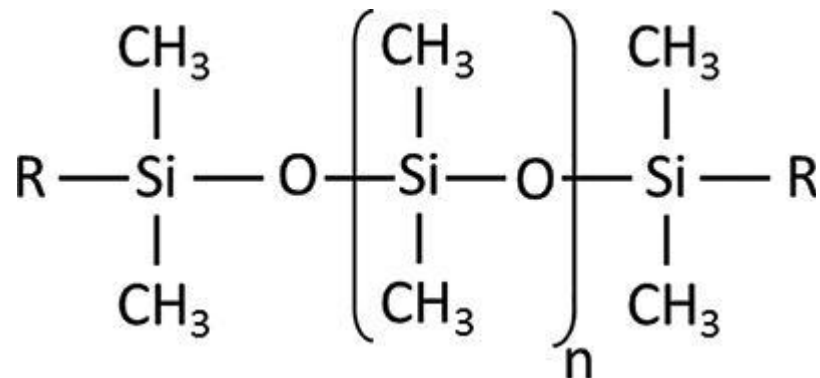


Figure 2.3. Chemical structure of silicone rubber[43].

The number of units in Figure 2.2 is connected with similar units to form a chain of "n." Side groups called R in the structure;

-CH<sub>3</sub> .

-CH=CH<sub>2</sub> .

- Ph.

-CH<sub>2</sub>-CH<sub>2</sub>-CF<sub>3</sub>

It can be in the form. Silicone rubbers are named according to the structure of the attached R group. In order;

MQ (methyl-polysiloxane).

VMQ (vinyl-methyl polysiloxane).

PVMQ (phenyl-vinyl-methyl polysiloxane).

FVMQ (fluoro-vinyl-methyl polysiloxane)

Commonly seen along the polysiloxane chain, side groups other than methyl are phenyl and vinyl groups. The chemical components' placement along the siloxane chain determines the material properties [44]. The superior properties of silicone rubbers make these materials (different filling materials) usable for electrical engineering, medium-high voltage lines, and conductor cable insulation compared to others. The low surface energy of silicon allows it to exhibit excellent hydrophobicity. There are many examples in the literature about using this feature of silicone elastomers in outdoor insulation applications.

Silicone elastomers have lower mechanical strength when compared to other elastomers, such as EPDM. However, its mechanical properties do not change much over a wide temperature range, and its useful operating range varies between -55°C-230°C. This range varies depending on the amount of filler used in the formulation (recipe). Despite their excellent properties and durability, silicone rubbers are subject to deterioration over time when exposed to various environmental and chemical factors and high temperatures[44].

#### **2.4.1. Reinforcements in Silicone Elastomers**

Silicone elastomers often contain reinforcing silica (glass or quartz) to strengthen the structure. Because its mechanical properties are weaker compared to other polymers. Silica has reactive groups that bind to the silicon structure and affect its hardness, toughness and other mechanical properties. Besides silica, different fillers have been added for other properties, such as erosion and weather resistance [44]. UV rays cause damage to the polymer network. Some fillers act as catalysts, reducing the energy

required to break the Si-O bond. Selected fill types must follow two rules; 1) Demonstrate long-term stability under expected conditions 2) Inertness to other ingredients in the recipe is expected to preserve the silicone functionality. Additives added to silicone rubber are given below

- Accelerators
- Plasticizers
- Anti-aging materials (Antidegradants)
- Mold release agents
- Activators
- Filling materials

Compared with other elastomers, silicone rubber requires few additives because the essential properties are determined by the siloxane polymer used. Particularly notable is that silicone rubber is free of curing accelerators or retarders, organic plasticizers and organic antioxidants. Additives include stabilizers, masticating aids and colourants. Stabilizers are available for special applications to optimize heat and media resistance properties. Silicone rubber is generally transparent and can be coloured as desired: from transparent through translucent to opaque. It should be remembered that some additives are inherently coloured such as titanium dioxide [45].

#### **2.4.1.1. Cross-linking Agents**

It causes the formation of cross-linked elastomeric structures by causing a chemical reaction. The elastomeric structure changes from a soft, sticky material to a hard, temperature-stable material by chemical cross-linking. In silicone rubber, crosslinking occurs between carbon atoms in the side chains. All crosslinks are made up of carbon-carbon (C-C) bonds. Organic peroxides are the most common vulcanizates used in high-voltage insulation.

#### **2.4.1.2. Auxiliary Additives**

It prevents the disintegration of the cross-links between the polymer and the vulcanizate. It prevents these bonds from breaking and forming new bonds. Two

additional additives, Type I (agents), accelerate curing speed and cure hardness. Type II additional additives (agents) increase hardness while not affecting the curing rate.

#### **2.4.1.3. Filling Materials**

It strengthens the physical properties of the elastomer. There are two types of filling materials; It is divided into Booster type or Extender-expander type. Quartz, titanium dioxide, clay, zinc oxide, and chalk powder are fillers used as extenders or extenders. Alumina trihydrate (ATH) provides high resistance to electrical trace formation and combustion in all insulator compounds. High-fill elastomers have good arc resistance. However, (ATH)  $\text{Al}(\text{OH})_3$  filler cannot be added much because it does not allow the recovery process between stress events in traditional trace tests or other standards [46].

#### **2.4.1.4. Coupling Agent**

Binding additives (agents) form a chemical bond between the filler and the elastomer. In electrical insulators, they bridge between ATH and polymer and increase electrical properties, modulus and tensile strength [47].

#### **2.4.1.5. Plasticizer Additives**

They are used as an aid to mixing, adjusting the viscosity or providing flexibility at low temperatures. The most important feature of the silicone rubber mixture, cross-linked with the additives described above, is that it is hydrophobic in the outdoor environment and for high-voltage insulators. The leakage current is reduced if no water is retained on the polymeric surface. In addition, the hydrophobic surface is cleaned as water drops slide. Removal of contamination or contamination again reduces the leakage current. Studies on hydrophobicity have concluded that silicone rubber alloy is much better than silicon-coated porcelain and EPDM [46].

### 2.4.2. Crosslinking of Silicone Elastomers

Vinyl and other reactive groups in the polymer chain are usually found as side groups and end groups. These groups allow the formation of cross-links during the chemical reaction. The type and type of crosslinking depend on reactive groups, crosslinking agents, inhibitors and catalysts. Cross-link formation is given in Figure 2.4

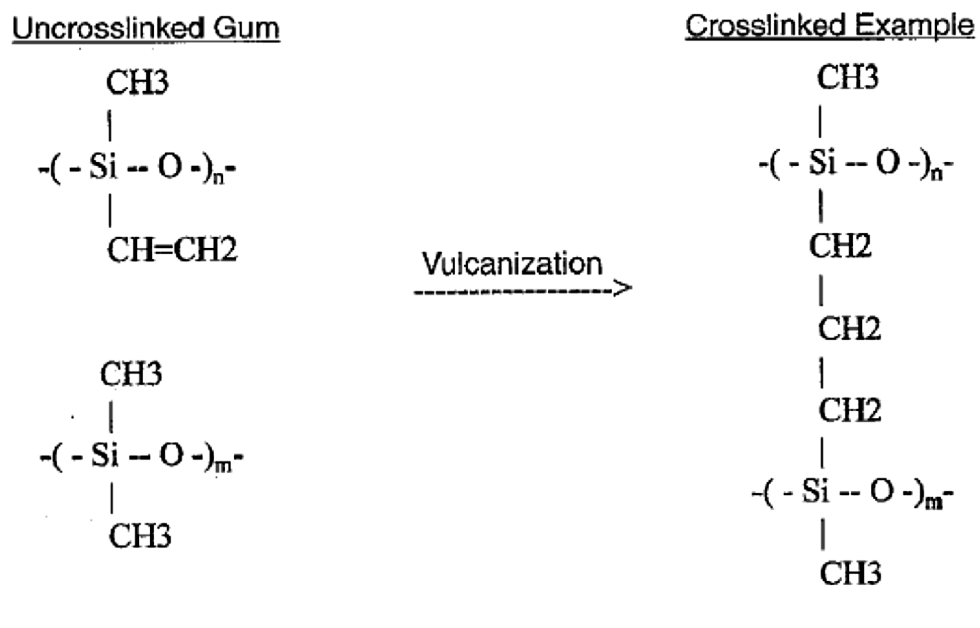


Figure 2.4. Schematic representation of a typical crosslink in silicon[44].

Vinyl and other reactive groups are often found as side and end groups. These groups allow the formation of cross-links during the chemical reaction. The type and type of crosslinking depend on the reactive groups in the polymer chain, crosslinking agents, inhibitors and catalysts [44]. There are two basic crosslinking systems in elastomers, sulfur and peroxide. Organic peroxides and platinum are used in the crosslinking of silicone elastomers. In addition to being odourless and colourless, platinum provides better physical properties than peroxide crosslinking. However, they are less preferred than peroxides due to their high cost compared to peroxides and the high vulcanization temperature requirement.

Organic peroxides are structures formed by bonding at least two oxygen atoms attached to an organic group. Peroxide decomposes with heat, forming free radicals

forming active polymer chain groups. With the interaction of the active parts formed on the polymer chains, the chains are linked, and cross-linking occurs. The mechanism of cross-linking of silicone elastomer with peroxide is shown in Figure 2.5 [48].

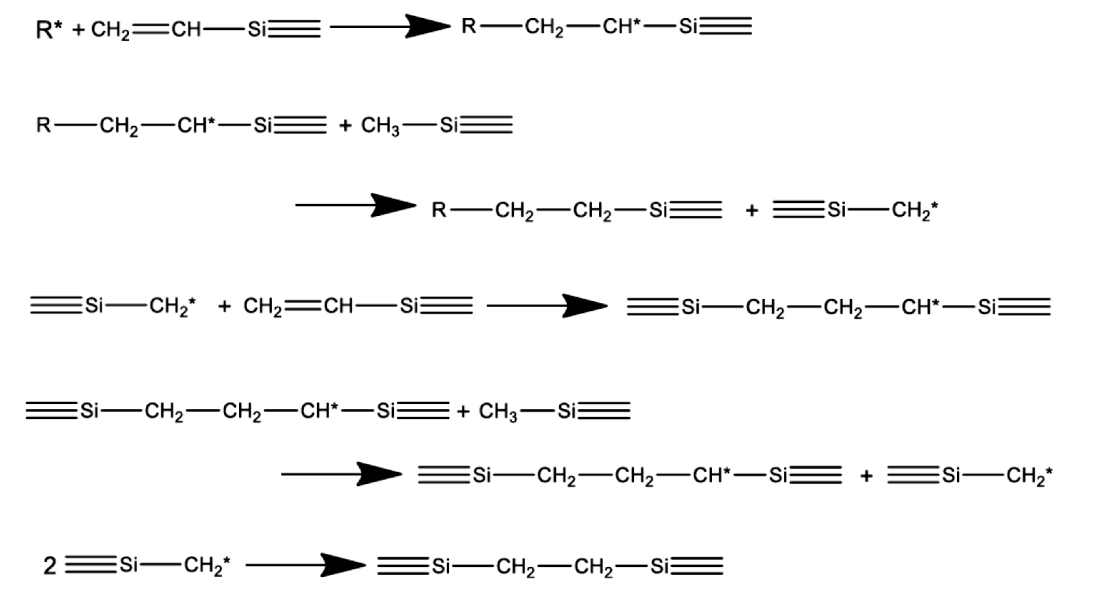


Figure 2.5. Peroxide crosslinking mechanism of silicone elastomers.

#### 2.4.2.1. Classification of Peroxides

The chemical structure of the organic group attached to the oxygens in peroxides allows the peroxide to be classified as dialkyl, diacyl, peroxy ketal and peroxy ester. The advantages and disadvantages of some peroxides in these peroxide classes and frequently used with silicone elastomers are given in Table 2.1.

Peroxyketals react more quickly due to their low half-life. Peroxyketals give high-firing reactions at low temperatures compared to dialkyl peroxides. However, since peroxy ketals contain weak and strong free radicals, they show less efficient cross-linking than dialkyls. On the other hand, Diacyl peroxides form highly active free radicals when they decompose. However, since they require high firing temperatures and have a long half-life, they are preferred in processes that require little cross-linking[49].

Table 2.1. Some types of peroxide used[49, 50]

Peroxide Type	Molecular Representation	Molecular Structure	Active Oxygen Amount %	Usage Area
Diacyl peroxide		<p><b>Di(2,4-dichlorobenzoyl) peroxide</b></p>	50	Horizontal and vertical extrusion technology
Dialkyl peroxide		<p><b>2,5-Dimethyl-2,5-di(tert butyl peroxy)hexane</b></p>	45	Injection technology and molding Min. 7 bar pressure required
Diaralkyl peroxide		<p><b>Dicumyl peroxide</b></p>	99	Molding technology Min 3 bar pressure required
Alkyl aralkyl peroxide		<p><b>Di(tert-butylperoxyisopropyl)benzene</b></p>	40	Molding technology, autoclave, air tunnels No pressure required

## **2.5. CLASSIFICATION OF SILICONE RUBBERS**

Silicone rubber is divided into high-temperature heating vulcanization (HTV) and room-temperature heating vulcanized (RTV) according to the curing temperature.

### **2.5.1. Room Temperature Vulcanized Silicone Rubber (RTV)**

The formation of the cross-link in the structure of silicones cured at room temperature occurs with a condensation-type reaction. The base polymer can be linked with the crosslinking agent, the catalyst. High tear resistance stands out and can be produced in varying degrees of hardness. Vulcanized rubber has temperature limitations (- 60 ~ + 200 °C), excellent electrical properties, hydrophobicity, ozone, and weather resistance. The machinability of RTV silicones is easier than HTV silicones. They can maintain their chemical properties at high-temperature changes [51].

### **2.5.2. High-Temperature Vulcanized Silicone Rubber (HTV)**

High Hot vulcanized silicone rubber (HTV) is one of the most important organic silicone products. HTV silicones are generally white, opaque, paste-like, high-viscosity materials. It contains 0.5% polydimethylvinyl siloxane with a vinyl side chain structure. Vulcanization occurs as a result of an addition-type reaction. Platinum salts and peroxides act as catalysts.. Catalyst, crosslink structure and type are effective on tear resistance; it is harder than RTV. It becomes a colourless, odourless, non-toxic final product with reinforcement agents. The final product has excellent electrical insulation, arc resistance, corona, electric spark strong, waterproof, moisture-proof, anti-impact, and anti-seismic properties [51].

## **2.6. SILICONE RUBBER NANOCOMPOSITES**

The preparation and characterization of organic-inorganic nanocomposites have garnered significant interest in material research during the last decade. Nanocomposites have the potential to increase the range of polymer applications thanks to their superior qualities, which include resistance to high temperatures,



dimensional stability, increased barrier properties, flame retardancy, and improved thermo-mechanical properties. Nanofillers enhance Polymers' hydrophobicity, electrical conductivity, relative permittivity, and thermal conductivity. The impact of filler inclusion on the properties of silicone rubber for use as an outdoor insulator has received much attention [52]. Important uses may be found in biological and chemical sensors, tissue engineering, drug screening, and optical devices when hydrophilic nanofilms are selectively deposited on silicone rubber substrates to generate micropatterns. Polydimethylsiloxane (PDMS) nanocomposites with nanoscale SiO<sub>2</sub> particles were generated using a simple and mild sol-gel copolymerization of tetraethoxysilane and cross-linking reaction [53]. The findings demonstrated that the nanocomposite membranes had outstanding oxygen-enriching characteristics for air purification, good membrane-forming ability, superior mechanical qualities, and strong solvent resistance.

The tensile behaviour of siloxane rubber may be altered by adding various fillers, most of which are nonreinforcing. Compared to mixing ferrite into a rubber matrix, the lightweight benefits of siloxane rubber blended with carbon black are clear [54]. To achieve a sensitive, flexible tactile sensor material with both flexibility and tactile function [55], a combination of carbon black and silicone rubber-packed nano-SiO<sub>2</sub> was used as the significant raw material. A novel material and a technique for preparing it as a flexible tactile sensor will be shown. When applied to touch sensors, this novel material and technique open up a wide range of potential applications, from delicate humanoid robot skin to medical applications. Silicone-based composites greatly benefit from adding nanoscale multi-walled carbon nanotubes (MWCNTs) dispersed throughout the matrix. After functionalizing MWCNTs with a silane compound, a silicone rubber/MWCNTs nanocomposite was effectively synthesised. This allowed for a uniform distribution of functionalized MWCNTs throughout the silicone matrix. Compared to pure silicone rubber, the tensile strength and modulus of silicone rubber/functionalized MWCNTs (1 wt%) composites increased by around 50% and 28%, respectively [56]. In order to combine the benefits of two popular biomaterials, a new nanocomposite of hydroxyapatite (HA) and silicone rubber (SR) has been developed. This study created the nano-composite by combining n-HA (nano-hydroxyapatite) slurry, modified by a silane coupling agent, with silicone rubber. The

mechanical characteristics of the composite may be significantly enhanced, and it is discovered that this is largely due to the homogenous dispersion states of the n-HA particles in SR. We used micrometre-sized HA (l-HA) and SR composites as reference points. It concludes that the n-HA/SR composite's tensile strength can significantly improve relative to the l-HA/SR composite [57]. Silicone rubber was filled with silica nanoparticles, and the surface characteristics of the resulting material were studied. The poly (St-SO<sub>3</sub>-P<sup>+</sup>Bu<sub>3</sub>R)-grafted silica found within silicone rubber has potent antibacterial activity. Silicone rubber has been shown to reduce the number of Staphylococcus aureus and Escherichia coli that may reproduce on its surface [58]. Carbon nanotubes are made of carbon nanotubes, a kind of carbon nanotube. The initial modulus of the test specimens increases dramatically as a function of filler load, but the final characteristics decrease. This demonstrates that the reinforcement was successful because of the special qualities of the carbon nanoparticles. After an initial rise as a function of strain, all of the composite samples' enhanced moduli disappeared between 10% and 20% strain [59]. Sodium montmorillonite and a siloxane surfactant containing quaternary ammonium were used to create the siloxane-modified montmorillonite clay. As part of the rapid-cure liquid silicone rubber (LSR) matrix, we used siloxane-modified montmorillonite clay and market-modified montmorillonite and bentonite clays. The compression set increased by 40%, tear strength by 24%, and water vapour permeability by 20%, all of which were attained [60].

Graphene nanosheets (GN) were successfully dispersed in silicone rubber (SR) matrix to create a unique electrically conductive nanocomposite. Sonicating expanded graphite in an alcoholic water solution yielded the powder used to make GN. The percolation threshold of SR/GN nanocomposite was around 0.009, significantly lower than that of composites with standard graphite, due to the unique shape of GN 30-80 nm in thickness with a high aspect ratio, which adds to the benefit of building the conducting network. Since the SR/GN nanocomposite has a very low elastic modulus, it exhibits outstanding piezoresistive behaviour at very low pressures [61]. Withstanding numerous washings in the washing machine, rough abrasion, strong acid or base, boiling water or beverages, and excellent stain resistance, a superhydrophobic fabric coating made of cross-linked polydimethylsiloxane elastomer containing well-

dispersed hydrophobic silica nanoparticles and fluorinated alkyl silane has been developed [62]. Ball milling was used to create a conductive silicone rubber (SR) composite that included both carbon nanotubes (CNTs) and carbon black (CB). Mechanical parameters, including tensile strength and strain to failure, are enhanced in the SR composite (SR with 2.5 phr CB and 1.0 phr CNT hybrid fillers) due to the excellent dispersion and synergistic effects of the CNT and CB. In addition, the nanocomposite's great sensitivity to tensile and compressive stress results from the CNT and CB's construction of conductive pathways, which occurs at a relatively low concentration. Long-term property measurements reveal that the SR composite maintains good electrical characteristics despite being subjected to various strain histories. These exceptional characteristics indicate that the SR composite may find use as a strain and pressure sensor [63]. Using a "packing-filling" technique, we were able to create a homogenous silicalite-poly(dimethylsiloxane) (PDMS) nanocomposite membrane on capillary support that was ultrathin (300 nm). Before the PDMS phase was packed into the gaps between the nano-crystals, the porous alumina capillary support was layered with silicalite-1 nano-crystals using a dip-coating process (packing). For the pervaporative recovery of iso-butanol from an aqueous solution (0.2–3% wt%) at 80 °C, the membrane exhibits an extremely high flux (5.0–11.2 kg m<sup>2</sup> h<sup>-1</sup>) and an excellent separation factor (25.0–41.6). Applications in fermentation-pervaporation-coupled processes are very desirable due to these characteristics [64]. Nanoscale interactions between artificial nanostructures and living organisms are the focus of bionanotechnology. Using organomodified nano clay with negatively charged silicate layers, biomedical-grade silicone rubber was changed. To improve cell behaviour, the nanoparticle loading was optimized. The addition of nanoparticles boosted the substrate's mechanical characteristics, including its strength and stiffness, without causing any observable toxicity. The use of nanofillers enhanced cell viability and multiplication, according to the results. Cells respond appropriately by rearranging their cytoskeletal fibres in response to the matrix's enhanced mechanical properties. The findings may be used in tissue engineering to improve cell behaviour in in vivo applications where superior sub-strata were previously lacking [65]. The combination of hydroxyl-terminated poly-dimethylsiloxane with organoclay has allowed the synthesis of a new exfoliated silicone rubber/clay nanocomposite. Na-montmorillonite was treated with the swelling agents HTAB and TPAC to create organoclay. The

findings demonstrated that in the range of 1–10% TPAC-mont concentration, the nanometer-scale silicate layers of TPAC-mont were dissolved in the silicone rubber matrix. The nanocomposites offer a significant improvement over either the pure polymer or the standard aero-silica-filled silicone rubber in terms of mechanical characteristics and thermal stability. TPAC-mont/silicone rubber was shown to have a 200–300% improvement in tensile strength and a 100% increase in elongation at break compared to pure silicone rubber [66]. VPMPS, HPDMS, catalyst, and 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane-modified alumina trihydrate were combined to create a liquid silicone rubber nanocomposite. Jung conducted tests on the mechanical and electrical properties of insulating materials, finding that they had a high tensile strength and a good short-circuit property [67]. Silicone rubber compounds are resistant to heat and chemicals, and their rapid curing speeds up factory packing and assembly processes. A ready-to-process compound may be used directly by professionals to produce an end product, or it can be combined with other compounds to produce a product with unique technical needs. Silicone rubbers have been indispensable in high-end technological applications and are finding an ever-expanding range of uses in emerging industries. When combined with the appropriate technology, silicone rubber enabled novel approaches to production, especially in the realm of reorganising and automating industrial processes. Many high-end processing and manufacturing applications that prioritised low costs without sacrificing quality favoured it. As a result, it's important for firms to have a solid understanding of how to utilise a wide range of tools and resources to their advantage.

## **2.7. APPLICATIONS OF SILICON RUBBER NANOCOMPOSITE**

Several lower limb amputations are performed each year, with the most common causes being victims of car bombs, peripheral vascular disease, and/or diabetes, as well as various accidents, infections, and tumours. If the patient can continue daily activities, he typically uses a prosthesis [68]. The soft tissue in the residual limb bears body weight due to prostheses. Liner receptacle that separates the residual limb from the prosthetic component. Amputees do not use synthetic liners if they are unpleasant, as they transmit soft tissue burdens to the prosthetic limb and must be designed to provide patient comfort. The development of skin disorders in the amputee limb is one

of the disadvantages of using synthetic liners. During weight-bearing, the epidermis of the limb is exposed to numerous anomalous conditions. The skin is exposed to shear stress forces, which can cause edoema of the stump and sores. Stress at the extremity of the stump is exacerbated by the poor nutritional status of the skin, vascular insufficiency, or local pressure from a poorly made prosthesis [69]. In addition, the liner prevents perspiration from evaporating readily from the epidermis where it is worn. In addition to abscesses, cellulitis, pyoderma, and inflammation of the perspiration glands, increased hydration can cause bacterial infection and inflammation of the epidermis [70]. Silicone rubber is used in a variety of medical applications. The most essential of these applications is the internal or semi-internal apparatus that makes contact with the human body or epidermis. In order to be utilised securely within the human body, polymers used in biomedical applications must adhere to specific regulations and requirements. They must first be biocompatible, non-toxic to the human body, and possess high tissue consistency [13]. Multiple factors, including chemical structure, determine the biocompatibility of polymers. Depending on the placement and movement of the material, as well as the adjacent human environment, the body can either embrace or deny a polymeric medical device. Therefore, for biomedical applications, it is essential to choose polymers with high resistance to the conditions above [11].

## **2.8. REQUIREMENTS OF LINING SOCKETS**

A prosthesis aims to provide the amputee with the capacity to carry out daily tasks in a simple, natural, and comfortable way while fitting any artificial limb [71]. A prosthesis comprises a liner, a socket, a limb, and any necessary structural and mechanical elements for an above-knee amputation. A liner is utilised as a residual limb-socket buffer to protect the leg and skin from additional harm while providing comfort; however, not all prosthetic legs have one. The liner is often created using silicone, silica gel, polyurethane, or even more rigid polymers. Each material, however, has a distinct combination of mechanical benefits and drawbacks [72]. Because of their ability to stick to the skin, operate as an abrasion barrier, and disperse pressures, liners are often used in standard practice. In the past, Pelite and other open and closed-cell foams were used to make prosthetic liners. It is now possible to roll on

the residual limb for longer periods and with a more effective cushioning effect [73] using silicone or another elastomer-based lining. According to bench tests, because they are soft, compressible, and comparable to biological tissues, elastomeric gel liners minimise shear stress on the skin and provide additional cushioning on bony prominences. Urethane liners offer better skin adhesion and prevent skin breakdowns due to their high friction coefficient.

In contrast, silicone elastomers offer better suspension and are preferred for softer stumps to reduce the relative displacement between the socket and the residual limb tissues. Roll-on liners provide a better fit than distal locking mechanisms since they may be attached to an air evacuation system based on a unidirectional valve or a VAS system (liner-fit suction). The Seal-In liner in Fig. 2.6a is an example of a hypobaric seal that may be used with a valve or VAS [74].

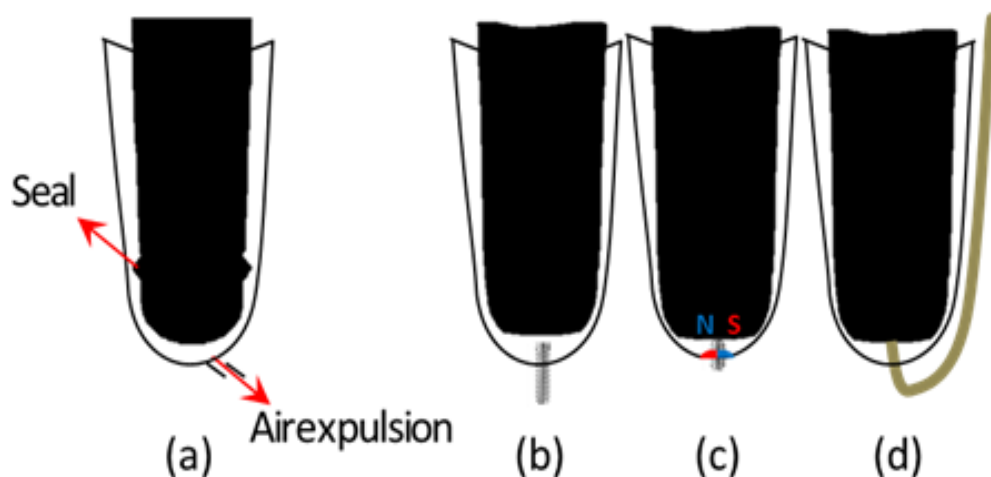


Figure 2.6. From left to right: a) Seal-In, b) Pin-lock, c) Magnetic-lock, d) Lanyard strap [74].

A combination of socket design and materials and a unique suspension system determines how pressures and shear loads are distributed on the tissues and how temperature and volume variations affect the residual limb. Volume changes may suggest a poorly fitting prosthesis, but they may also signal a shift in the distribution of pressure and shear stresses on the remaining tissues of the limb. Because of the barrier established by the socket and liner might lead to friction phenomena that alter the thermoregulation system, resulting in perspiration, discomfort, and odour [75].

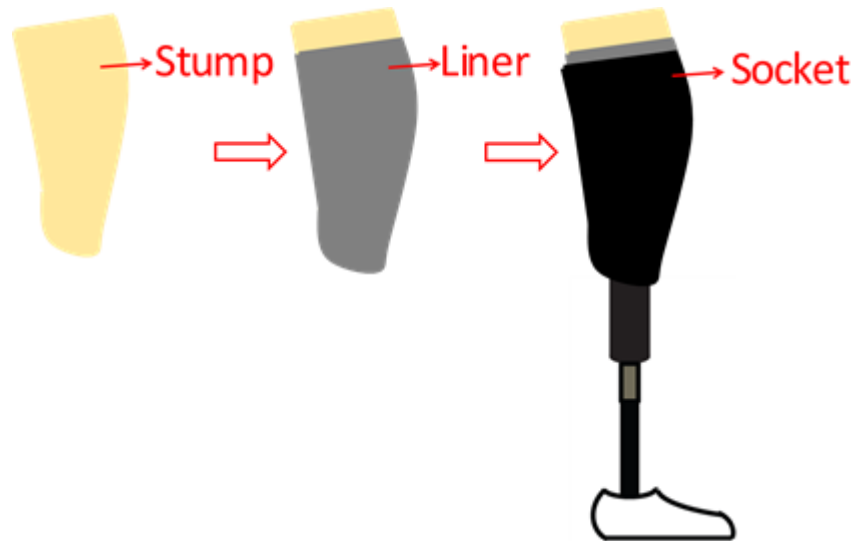


Figure 2.7. The socket provided with a liner between it and the stump [75].

## 2.9. STRUCTURE AND MECHANICAL PROPERTIES

In order to meet the requirements of "ideal medical prosthetic material" and the necessity of the most appropriate material, liner prosthetic material must be examined for various mechanical qualities. These tests consist of the following:

- Hardness is the degree to which an object resists indentation under standard test circumstances. A compound of an elastomer's intrinsic hardness and its processed hardness, hardness is the outcome of these two qualities. The material's chemical composition lends support to this conclusion. Each elastomer's hardness may be adjusted via the vulcanization process. Measuring its hardness may determine how flexible and bendable a material is. It may be tested for consistency and other qualities to gauge how similar a material is to human soft tissues. Surface hardness measures how well a material resists being scratched, sliced, worn, indented, or penetrated. A hardness tester doesn't have to break the bank, and readings may be taken on irregular surfaces. Small, Shore A-scaled microhardness tests are commercially available. Different indenters are used under lower weights to restrict the depth to which the indenter penetrates the test piece [76], allowing testing of specimens thinner than the standard 6 mm.

- Properties under tension (stress-strain) In order to quantify the "ultimate properties" of a material, such as its strength and deformability, the tensile strength test is often used. A rubber sample is stretched to its breaking point to determine the tensile strength at break value. Up to around 900%, depending on the compound, is a common elongation the test piece goes through before breaking. The dynamic stress resistance of silicone rubber was no higher than that of organic rubbers. However, Shin-Etsu has solved this shortcoming by creating silicone rubbers with 8–20 times the flex fatigue resistance of standard products [77]. The compounding materials used significantly impact the tensile curves of various rubber compounds. The modulus is the stress per unit area of the initial cross-section at a certain length change [78]. The modulus is the tension at a certain length. The ASTM D412 standard is used to test modulus at 100%, 200%, and 300% of its original length. The following may be determined from the rubber tension curve [79]:

  - 1, the breaking tensile strength (in megapascals).
  2. Elastic modulus (MPa) at 100%, 200%, and 300%
  3. The percentage of total length reached just before the break
- Tear resistance is an essential feature of long-lasting prostheses, particularly when adhesives are used for retention. If the prosthesis has low tear strength, it might easily rip when the adhesive is removed from the prosthesis's margin for cleaning or when the prosthesis is removed for maintenance. The tensile strength of rubber is evaluated using the ASTM D 624 tear test [79]. The force required to create a new surface constantly is measured in a tear test by focusing it on an intentional fault or abrupt discontinuity. The desired sample form is cut and then stretched from a flat sheet using a tensile machine. The force required to initiate complicated tearing depends on the geometry of the test piece and the kind of discontinuity. The site of the greatest stress concentration is one possible crack initiation site. The fracture widens and develops into a ripping motion once initiated. Drawing conclusions about product performance from tear strength test data is challenging. The results of a tear test and a tensile test agree on a ranking system for rubbers. In general, silicone has a tear strength of 9.8 kN/m. It was possible to find high-strength kinds with tear strengths between 29.4 and 49.0 kN/m by modifying the



polymer and carefully choosing the fillers and cross-linkers. When tear strength was needed, these materials were perfect for moulding huge goods, reverse tapered shapes, and intricately formed things [80].

- Resilience The ratio between the inventor's energy after the impact and its energy before the impact (given as a percentage) is described as rebound resilience. Only one half-cycle of deformation is applied to the test component. In various test procedures, a free-falling indenter applies strain to a rubber test sample. It demonstrates a rubber vulcanizate's capacity to absorb and return impact energy, which is affected by rubber type, vulcanization circumstances, curing components, application temperature, and filler levels. This is a critical property for predicting vibration damping in certain applications. Because rubber is viscoelastic, temperature affects resilience measures [81].
- Specific gravity measures the mass of a given volume of material compared to that of the same volume of water at 23°C. Density is the mass per unit volume of a substance. Assuming that water has a density of one kg/litre, it is measured concerning water. A test article is weighed in air and water using the ASTM D 792 [82] technique. Archimedes' principle, which states that a substance immersed in a liquid appears to lose weight in proportion to the weight of the liquid displaced, is demonstrated by measuring specific gravity. Knowing the weight of the material and the weight of an equivalent volume of water, the specific gravity, which by definition is the ratio of the weight of a given volume of material to the weight of an equivalent volume of water, can be calculated.
- The silicone rubber's compression set exhibited uniformity across a broad spectrum of temperatures, from negative sixty degrees Celsius to two hundred and fifty degrees Celsius. The compression set of organic rubber exhibits a relatively low value at room temperature; however, it experiences a significant increase as the temperature rises. Silicone rubbers that incorporate appropriate curing agents are highly recommended for producing moulded items requiring low compression when using silicone rubber. As per the guidelines outlined in ASTM D 395-03 [83] for conducting elastomer compression tests, the specimen dimensions must adhere to specific standards. These standards dictate that the thickness of the specimen should measure  $12.5 \pm 0.5$  mm, while

the diameter should measure  $29.0 \pm 0.5$  mm. The elastomer specimens underwent compression testing using a compression testing machine. The compressive load was incrementally applied at a rate of 1 lb.

- Silicone rubber exhibits superior thermal stability compared to other types of rubber, enabling it to endure both high and low temperatures. Moreover, it exhibits exceptional resilience to low temperatures. The ageing process refers to the deterioration of polymers and alterations in their mechanical characteristics due to environmental factors. The degradation of polymers can be attributed to various factors, including chemical and physical mechanisms. When acting in concert, light, temperature, and humidity can pose a significant risk to the structural integrity of polymers. This combination of factors is often called a triple threat for polymers. Individually, each of these factors has the potential to inflict harm. However, when combined, they exhibit a synergistic effect that exacerbates the damage inflicted on the polymer [84].
- Water absorption calculates how much water is absorbed under certain circumstances. Water absorption is affected by factors such as the kind of plastic used, the additives used, the temperature, and the exposure period. The data gives insight into the materials' performance in wet or humid settings. This test technique for the rate of water absorption has two purposes: it serves as a guide to the percentage of water absorbed by a material and, therefore, as a guide to the effects of exposure to water or humid conditions on such qualities, and it serves as a control test for product uniformity. The ideal diffusion of liquids into polymers is a function of immersion time squared [85]. The time required for saturation is highly dependent on the thickness of the specimen. The effect of water absorption on SR used as matrices for composite applications has damaging effects, and the nature of the damage itself, whose degree and intensity depend on the type of rubber, temperature, type and amount of filler, post-cure treatment, and other factors, makes the evaluation very complex because processing and the environment play a critical role in how resistant the polymeric material will be. The SR prosthetic liner may collect sweat and sebum while lying on live human skin for lengthy periods. Absorption may induce structural changes in materials, leading to prosthesis deterioration. The pH of human skin is 5.5 (mildly acidic). Sweat is

a salty, watery substance that sweat glands create. When sebum and perspiration combine on the skin's surface, they produce a protective layer that shields the skin from "the elements" (such as wind or pollution) while inhibiting the development of dangerous germs and fungus. Any colour variations in the elastomeric prosthetic material are also caused by skin secretions and other solutions [86]. The introduction of water into the SR matrix results in the formation of new H-bonds, as seen in Figure 2.8.

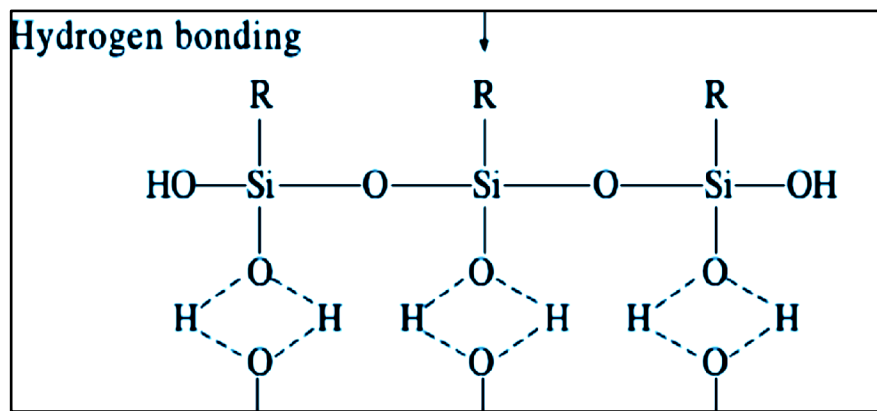


Figure 2.8. Effect of water absorption on the silicone rubber chain[87].

## 2.10. CHALLENGES IN PROSTHETICS

Ancient prostheses were made of metal and wood and had limited functionality. These prostheses, which were cumbersome and poorly adapted to the residual limb, had limited utility [88]. Updated technologies and the introduction of novel materials, such as silicone liners, have improved the fit and functionality of prostheses. However, satisfaction with prostheses is not always maximum. The ability to properly wear prosthetic components significantly impacts the use, comfort and wear of the prosthesis [89]. With the increasing use of silicone liners in lower leg prostheses, it is more important than ever to wear the prosthesis correctly [90]. Since then, liners with different material properties have been introduced, and manufacturers of silicone liners touted prosthesis fit and spring benefits over the standard prosthesis with

supracondylar fitting, condylar bedding Munster (KBM) fitting, patellar tendon bedding (PTB) fitting, or conventional prosthesis fitting [91].

### **2.10.1. Skin Perspiration**

The thermal environment in prosthesis cases and reduced quality of life and prosthesis use, comfort and satisfaction can put amputees at high risk for skin irritation [92]. This article examines the importance of heat and sweat stress in prosthetic sockets by shedding light on the prevalence of the problem. The socket is the primary component of a prosthesis that provides structural coupling, control, and appropriate power transmission at the residual limb interface [90]. The socket comfort directly influences the function and extent of prosthesis use in amputation patients. A good fit and suspension of the prosthesis require a full contact fit, restricting airflow and ventilation at the socket-skin interface. Insufficient socket ventilation and low moisture permeability of the socket wall contribute to increased residual limb skin temperature and accumulation of sweat in the socket. By inhibiting the function of the sweat glands, antiperspirant medications, topical ointments, powders, and aerosols can reduce sweating. To avoid this problem, we need to make breathable and antibacterial materials [91]. These materials have an unpleasant odour and are associated with the risk of allergic reactions and systemic disorders.

### **2.10.2. Sweating and Bacterial Growth**

The skin sweats more than normal because the liner of the prosthesis is snug and warm, and the perspiration has nowhere to spread and dry off. Intertrigonal dermatitis may develop in damp environments [93]. As an added complication, bacterial infections manifest as folliculitis, furunculosis (or boils), cellulitis, pyoderma, and Hidradenitis [94], particularly in regions prone to *Staphylococcus*. Prosthetic infection risk factors include user cleanliness, skin wetness and hairiness, and environmental temperature. Poor nutrition, inadequate blood flow, or localised pressure from an ill-fitting prosthesis may all contribute to the development and persistence of ulcers [95]. Contact dermatitis is a rare but severe reaction that may occur after an amputation if the patient is sensitive to the silicone used in the socket or liner. Many areas of skin,

including those around the mouth, nose, genitalia, and anus, are hospitable to harmless bacteria. However, staph bacteria may enter a wound when the skin is pierced or damaged for any reason, producing an infection. Sometimes, *S. aureus* infections might be rather dangerous. This occurs when germs enter the bloodstream via a cut or scrape in the skin. Figures 2.9 illustrate how this might spread illness to other body regions, including the lungs, bones, joints, heart, blood, and central nervous system [96]. Infections caused by *S. aureus* in other regions of the body are far rarer than those caused by *S. aureus* on the skin. People whose immune systems have been compromised by another illness or medicine, such as cancer treatment, are at increased risk of developing them [97].

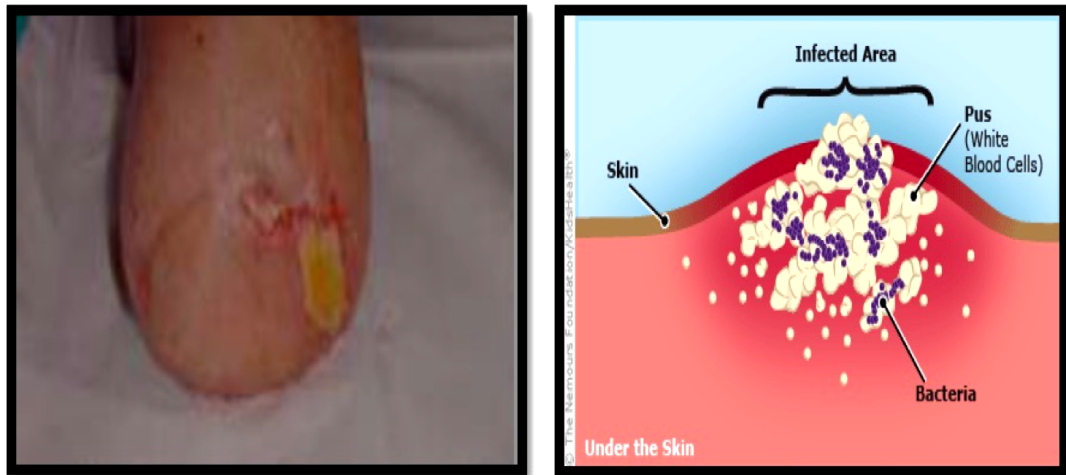


Figure 2.9. Stump infected with bacteria after amputation [98].

## PART 3

### METHODOLOGY AND EXPERIMENT

#### 3.1. MATERIALS

##### 3.1.1. Silicon Rubber(SR)

The rubber-silicone utilized in this study was purchased from the Company of Technology (Sunny Zhou). The RT-800 silicon rubber platinum hardener combined with silicone was chosen for its superior properties :

- i. The ability to withstand acid, alkali, and high temperatures (up to 250 degrees Fahrenheit) and time effects.
- ii. It has a low viscosity and flows easily. Simple to pour out.
- iii. Curing may be done either at ambient temperature or by applying heat.
- iv. Little wrinkling. Cross-linking without releasing low-molecular compounds. There is no change in volume. Less than 0.1% of the original size has been lost.
- v. Good resistance to tearing and tensile strengths. Soft silicone items like breast enhancers, shoulder pads, and artificial organs are made using life-casting silicone. Table (3.1) lists the many characteristics of SR

Table 3.1. Properties of Silicon Rubber [99].

Property	Value
Appearance	Translucent
Curing time at 25 °C	24 hours completely cure
Viscosity (mPa.s)	5000-7000
Hardness shore A	8-12
Elongation %	400
Tear strength( MPa)	1
Tensile strength( MPa)	4

### 3.1.2. Reinforcement Materials

The present study prepared nanocomposite silicon rubber materials as matrix material, reinforced with nano Zinc oxide and hydroxyapatite and added with chlorophyll as water absorbent. Nano zirconium oxide, nano-hydroxyapatite as a reinforcement and chlorophyll as a water-absorbing agent. Nano zinc oxide with a particle size of 20 nm was obtained from Sigma Aldrich. Nanohydroxyapatite particles with an average diameter of 10 nm were purchased from Sigma Aldrich. Chlorophyll was extracted using celery plants as the chlorophyll source and hexane as the solvent.

## 3.2. METHODOLOGY

### 3.2.1. Chlorophyll Extraction

Because chlorophyll is particularly sensitive to oxygen, light, and heat, celery by-products were freeze-dried, vacuum-packed, and stored in the dark. Hexane was used as a reference solvent for the extraction of chlorophyll from freeze-dried celery.

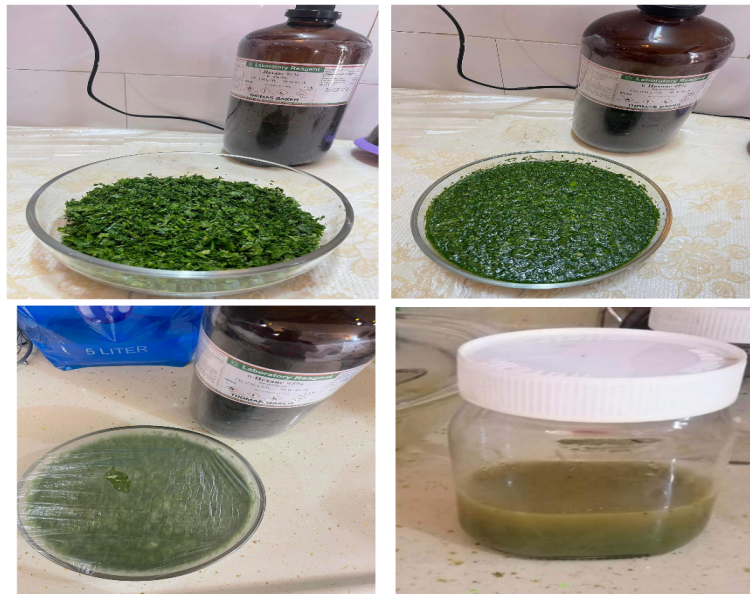


Figure 3.1. Extraction of chlorophyll.

The extraction was carried out at room temperature. The first thing is celery; it chops it finely and put in a glass container and add the hexane to it and immersed in it so that the hexane becomes higher than the amount of celery, and then the glass container is tightly closed to ensure that the hexane does not volatilize and left for 24 hours after which the chlorophyll is filtered. It is ready for use, as shown in Figure 3.1, in the extraction process.

### 3.2.2. Preparation of Nanocomposite Components of the Prosthetic Liner

The recipe includes silicone rubber as a matrix, chlorophyll as a filler that absorbs water from the environment, and Zinc oxide and hydroxyapatite nanoparticles as bifunctional agents that provide reinforcement and antibacterial properties. Many mechanical tests are required to fabricate silicone rubber nanocomposite material for prosthetic liner supports, such as tensile strength, tear resistance, impact, and Hardness. Physical tests, including temperature and water absorption, are required as people age. The proper recipe for these applications necessitates improving these parts by preparing reinforcement materials such as ZnO and mixing these reinforcements at different ratios with the recipe to provide a laboratory sample of various recipes for mechanical tests using ASTM standard moulds, as shown in Table 3.2.

Table 3.2. Standardized requirements for the manufacture of prosthesis liners [100].

Property	Value
Specific Gravity	1.115- 1.140
Hardness (shore A)	30- 48
Tensile strength (MPa)	Min. 1
Modulus of elasticity (MPa)	Min. 0.8 at 300%
Elongation (%)	Min. 235
Tear strength (MPa)	Min. 0.9

The process to produce the silicone rubber-based nanocomposite has three stages and is as follows:



- 1- Chlorophyll extracted from the celery plant is added to the silicone rubber in three concentrations (10, 20 and 30%), and then the tensile strength and water absorption are measured to determine the best ratio in terms of tensile strength and water absorption.
- 2- In the second step, after determining the best chlorophyll percentage (10%), zinc oxide is added to the mixture of (silicone gum + 10% chlorophyll) in three portions (1.5, 3 and 4.5% by weight), then many mechanical tests are carried out to determine the best percentage of zinc oxide in terms of mechanical properties.
- 3- The third and final stage involves the addition of nano-hydroxyapatite in various weight ratios (0.5, 1 and 1.5) to the mixture consisting of (silicone rubber + 10% chlorophyll + 4.5% zinc oxide), after which the final nanocomposite is analyzed for its mechanical and biological properties (antibacterial test).

Throughout the sample modification stage, the moulds for mechanical testing were lubricated, and the silicone rubber composites were poured into these molds. Then leave the molds overnight at room temperature. Figure 3.2 summarizes the overall program used in the present work.

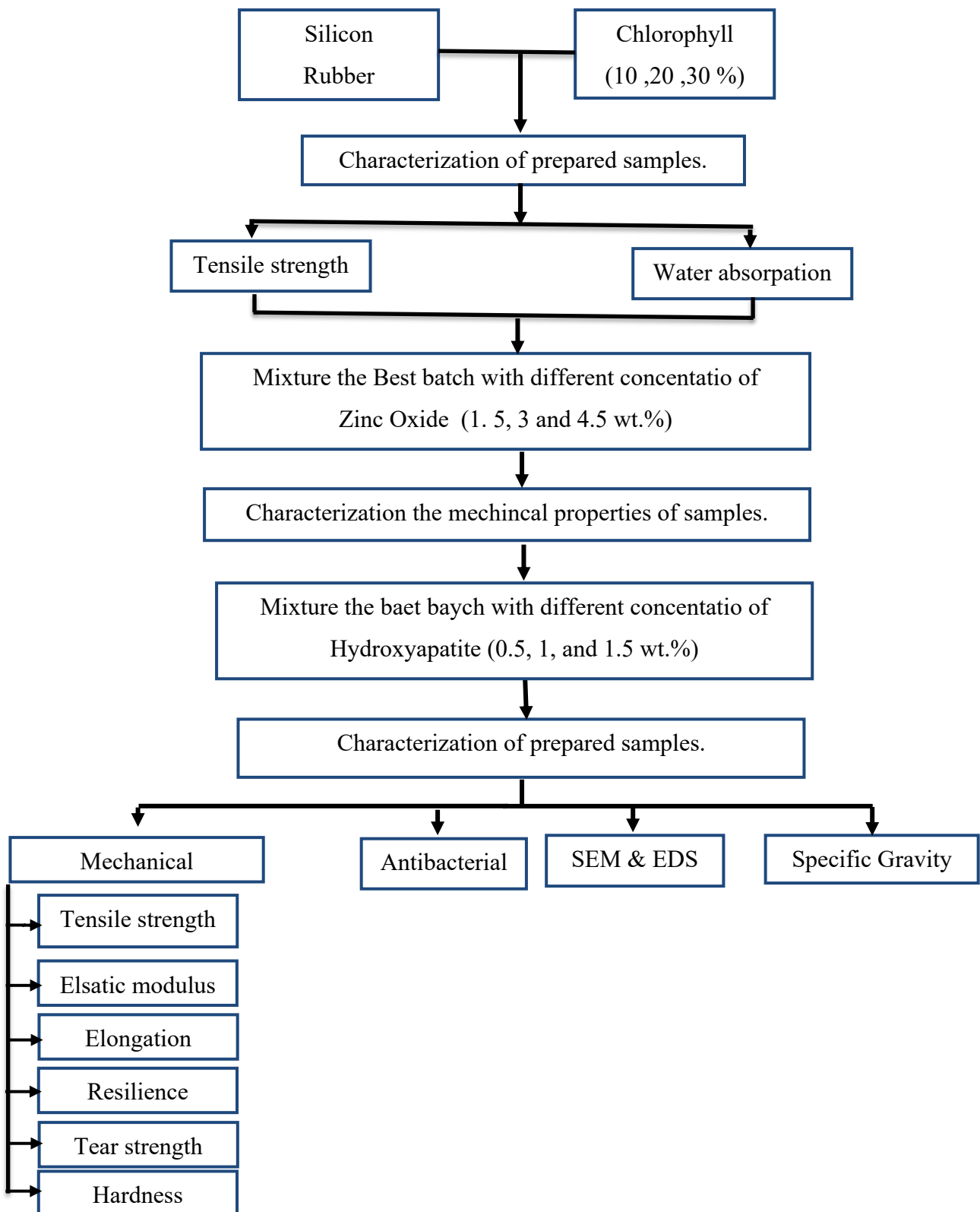


Figure 3.2. The experimental program of the present study.

### 3.3. SPECIMEN PREPARATION

#### 3.3.1. Preparation for Water Absorption Test

ASTM 570-98 [106] mandates using water absorption to quantify the amount of water absorbed under specific conditions. This serves as a reference point for assessing the effects of exposure to water or wet conditions on the properties of the liner. The water absorption process is influenced by various factors, such as the type of plastic, the additives incorporated, and the temperature and duration of exposure. The experiment involved immersing the samples in water at ambient temperature for 24 hr to evaluate their water absorbency, a crucial factor in manufacturing liner sockets. The water absorption percentage in the sample is calculated from the weight change using the following equation:

$$\text{water absorption} = \left( \frac{W_2 - W_1}{W_1} \right) \times 100\% \quad \dots\dots\dots(3.1)$$

Where  $W_1$  is the initial weight of the specimen,  $W_2$  is the weight of the specimen after water immersion [86].

#### 3.3.2. Preparation for Specific Gravity And Hardness Test Specimens

The mold used to prepare these samples has a cylindrical shape with a diameter of 30 mm and a thickness of 4 mm, as shown in Figure 3.3 a . Test specimens were prepared according to ASTM D2240 for testing Shore A durometer hardness as shown in Figure 3.3 b. For this purpose, four test specimens were produced, and the hardness test was carried out using a Shore A scale [101]. A reasonable amount of recipes is poured into the mold, and then the mold is left and placed on a flat surface at room temperature for 24 hours.

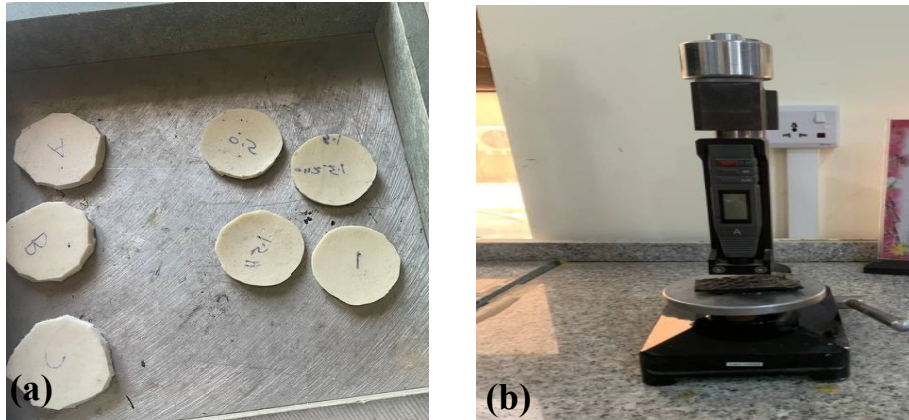


Figure 3.3. a) Specific gravity and hardness specimens, b) Shore A durometer Hardness

The shape is the same hardness as the specific gravity, while the specific gravity is checked with a GP-120 S type density meter (Matsu Haku, Chain) according to ASTM D792 [102], as shown in Figure 3.4. In this test, the sample is weighed in air, and the weight is then checked with water. The discovery of specific gravity lends credence to Archimedes' principle, which states that the apparent loss in weight of an object immersed in a liquid is equal to the weight of the liquid displaced. Knowing the weight of the material and the weight of an equal volume of water, specific gravity can be calculated, defined as the weight of a given volume of material divided by the weight of an equivalent volume of water [103].



Figure 3.4. Specific gravity Instrument.

### 3.3.3. Preparation for Tensile, Elastic Modulus and Elongation specimens

The dimensions of the mold used to prepare specimens for the tensile and elastic modulus and elongation experiments were as follows: a length of 150 mm, a width of 150 mm and a thickness of 3 mm. The mold is used to grease and pour in the required amount of recipes. Then the mold is left for one day, after which the sample (dumbbell sample) is manually cut with a hand press, as shown in Figure 3-5, to allow a tensile test on the produced samples. The evaluation of the tensile strength and the elongation percentage was carried out according to the standard ASTM-D412 [104].

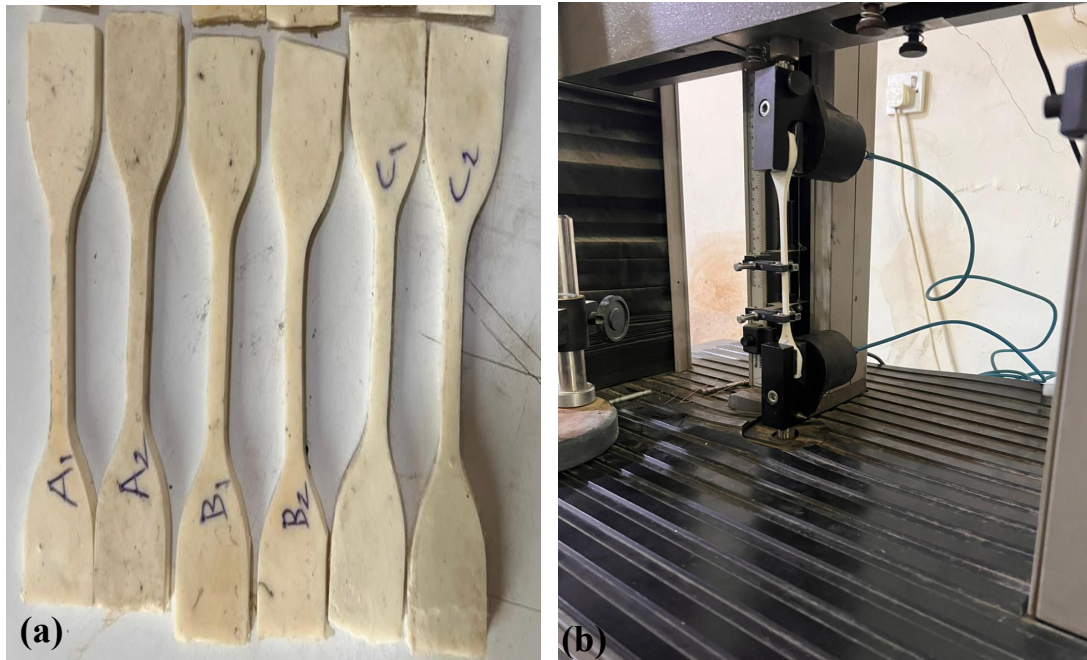


Figure 3.5, a) Tensile specimens, b) Tensile specimens under tension Instrument

### 3.3.4. Preparation for Tear Specimens

The tear resistance samples were prepared by putting the recipe into a mould with dimensions of (150x150x3) mm. The preparation of tear test samples follows the same procedure as that of the tensile test samples. The dimensions and shape of the sample are depicted in Figure 3.6.

The tear resistance test is conducted using the Monsanto T10 tensometer at a speed of 500mm/min in accordance with the ASTM D624-07 standard [105]. The calculation of tear resistance was performed using the following equation:

$$Tear = \frac{F}{D} \quad \dots\dots\dots (3.2)$$

A specimen's tear resistance (T) is measured in units of N/mm, while the force required to break the specimen (F) is measured in units of N. Additionally, the thickness of the specimen (D) is measured in units of mm.



Figure 3.6. Tear specimens.

### 3.3.5. Rebound Resilience

Rebound resilience is the percentage difference between the inventor's energy before and after being impacted. Only one-half cycle of deformation is applied to the test specimen. These techniques use a free-falling indenter to apply a strain on a rubber sample under test. Dependent on rubber type, vulcanization settings, curing chemicals, application temperature, and fillers quantities, it demonstrates a rubber vulcanizate's capacity to absorb and return impact energy. Predicting the vibration damping in a given application relies heavily on this property [106]. The test is done according to



standard ASTM-D1054 [107] using rebound resilience device type (Wallace R2-DunlopTripsometer), as shown in Figure 3.7.



Figure 3.7 Rebound resilience test Instrument.

### 3.3.6. Scanning Electron Microscope (SEM)

Chemical and elemental analysis of the manufactured nanocomposite composite was performed using Microstructure and energy dispersive spectrum (EDS). Using a Carl Zeiss ultra plus Gemini FESEM model scanning electron microscope, researchers from Karabuk University's Scientific Technology Application and Research Centre (MARGEM) analysed the produced nanocomposite based on silicon rubber nanocomposite Figure 3.8.



Figure 3.8 Carl Zeiss ultra plus Gemini FESEM.

### 3.4. ANTIBACTERIAL TEST

*Staphylococcus aureus*, a gram-positive bacterium, was used to test the antimicrobial effect. The best sample (SR+10%Cl +1.5% n-ZnO,0.5 % n-HA) was tested by the agar well diffusion method to assess the kinetics of bacterial growth rate. Tiny sprinkles of filter paper containing antibiotics are placed on a plate where bacteria are growing, and an inoculum is made from the bacterial suspension with a sterile swab on a Muller Hinton agar tray. The disc contains the antibiotic, which will spread throughout the agar. A pronounced ring or zone of inhibition around the disc indicates poor development if the bacteria are sensitive to the antibiotic. The sample's resistance, intermediate level or sensitivity can be determined using specific comparators that analyze the size of the inhibition zones. Plates were incubated at 37°C for 24 hours before the breaking point was determined from tables. After that, calculated how many millimetres wide the zone of inhibition was.

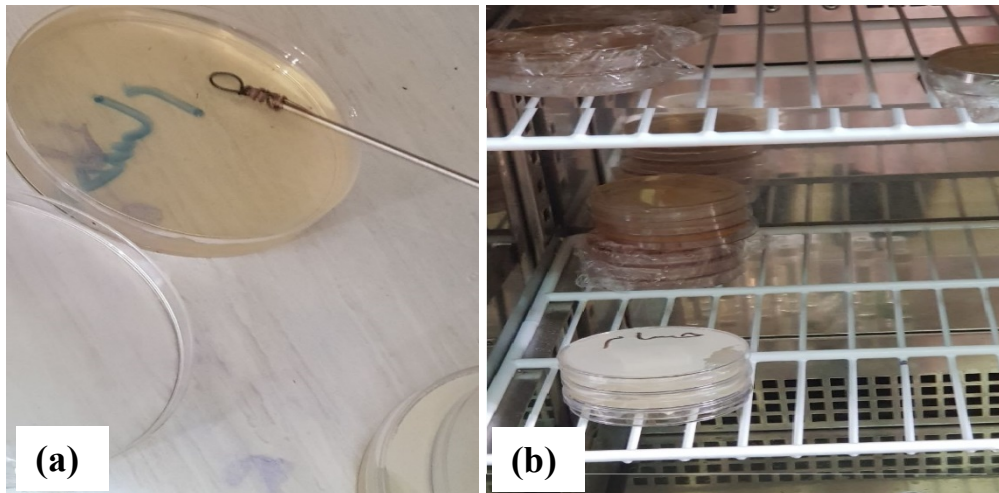


Figure 3.9 a) Culturing bacteria, b). Bacteria culture instrument and specimens.



## **PART 4**

### **RESULTS AND DISCUSSION**

#### **4.1. INTRODUCTION**

This chapter deals with the production of nanocomposite components based on silicone rubber. Silicone rubber contains additives that can promote or hinder growth. Mechanical properties such as (tensile strength, elastic modulus, tear strength, hardness, etc.) of test specimens were also measured to demonstrate the suitability of these alloys for biomedical applications. For this reason, a test was developed to evaluate the influence of different additives on the degree of biological growth. Bacteria (*Staphylococcus*) was used to test bacterial growth on the nanocomposite.

#### **4.2. THE EFFECT OF ADDING CHLOROPHYLL TO SILICONE RUBBER**

##### **4.2.1. Water Absorption**

Absorption properties are most commonly assessed using weight change after immersion in water at 37°C. Silicone rubber is a synthetic elastomer with excellent resistance to water and other liquids. It is often hydrophobic and does not readily absorb water [108]. When chlorophyll is added to silicone rubber in a way that changes its surface chemistry or shape, it improves its hydrophilicity and, therefore, its ability to absorb water. Increasing the chlorophyll content in silicone rubber can improve its hydrophilicity and water absorbency. Polar functional groups in chlorophyll, such as hydroxyl groups (-OH) and carbonyl groups (C=O), can interact with water molecules through hydrogen bonding[109]. However, the exact effects would be determined by the chlorophyll content, the type of inclusion, and the chemical structure of the silicone rubber, as shown in Figure 4.1.

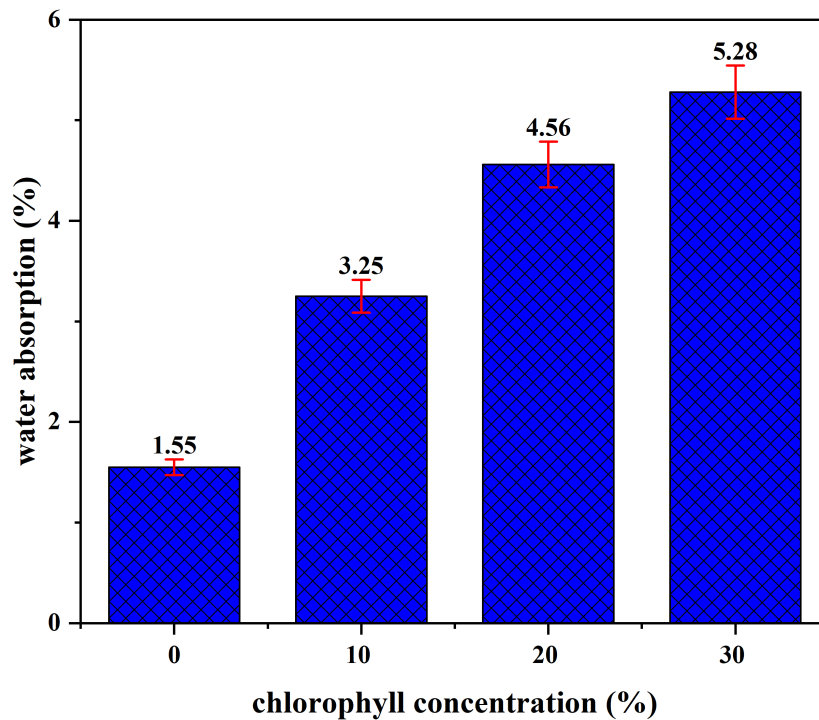


Figure 4.1. Water absorption of silicone rubber nanocomposite.

#### 4.2.2. Tensile Strength

Adding varying percentages of chlorophyll to silicone rubber in order to determine the optimal addition for constructing a high-performance, water-absorbent prosthetic liner. The optimal result contains 10% chlorophyll, as this concentration provides the highest mechanical properties. The presence of an infill material will inevitably affect the samples' properties. However, these modifications may be irrelevant or even advantageous. The filler enhanced the samples' hardness, tensile strength, and shear strength, as described. As a result of chlorophyll's high hydrophilicity, it absorbs the perspiration that has accumulated between the liner and the stump, in addition to reducing expenses. The tensile strength decreases as the percentage of chlorophyll increases. This is due to the high percentage of chlorophyll resulting in inadequate chlorophyll particle distribution in the nanocomposite composite. Also, the interface bonding and unique mechanical interlocking within the chlorophyll particles through the matrix are reduced, resulting in a decrease in the tensile strength of the composites

at high mixing ratios compared to small ones, as depicted in Figure 4.2, which corresponds to what Glenn et al. [110] reported.

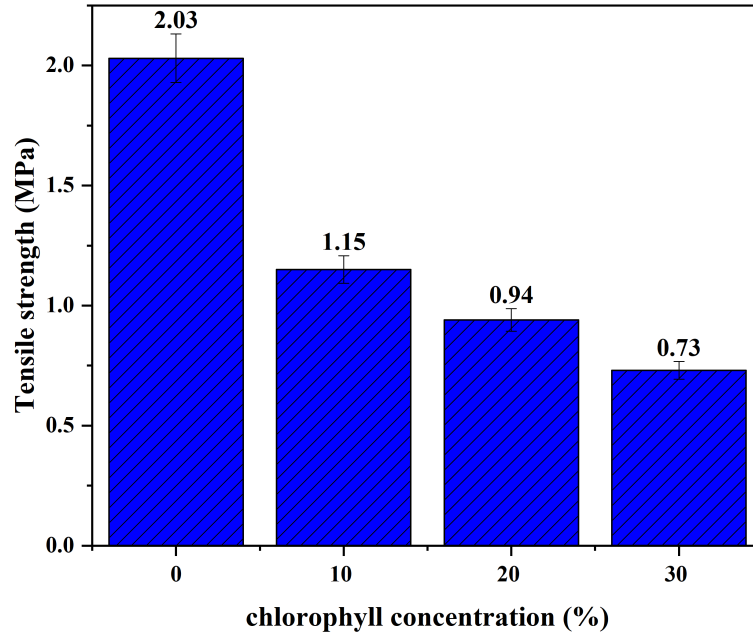


Figure 4.2. Tensile strength of silicone rubber nanocomposite

### 4.3. THE EFFECT OF ADDING N-ZnO TO SILICONE RUBBER WITH 10% CHLOROPHYLL

Nano ZnO's effect on the mechanical characteristics of a silicone rubber/chlorophyll (10%) composite shows: Silicone rubber is a two-component system consisting of a polymer and a hardener that, once combined, form cross-links between the chains, according to Linglong Feng's [111]. Depending on their quantity and chemical structure, the additives may either increase cross-link density or decrease it. The mechanical characteristics of polymers may be significantly enhanced by filling them with nanoparticles. The nature of the filler and the procedure used to apply it are crucial to the success of such enhancements. Therefore, there is a negative correlation between increasing nano ZnO concentration in the composite and tensile and tear strength values. This may occur due to particle aggregation during composites preparation and manufacture, which causes an increase in particle size and therefore affects diffusion as well as mechanical and antibacterial characteristics.

### 4.3.1. Specific Gravity

For the addition of 1.5% nano ZnO, the weight per unit volume increases, the specific gravity rises due to particle interference between rubber chains, and the material becomes denser per unit volume, as shown in Figure 4.3, as predicted by Al-Husnawi [112]. Also, the percentage of specific gravity decreased as the ZnO addition ratio increased, possibly due to the presence of hydroxyl groups, as shown in the graph. In general, the decrease in specific gravity may be caused by the generation of gases from additives by silicon's heat and hardener reactions resulting from the presence of functional groups in its structures.

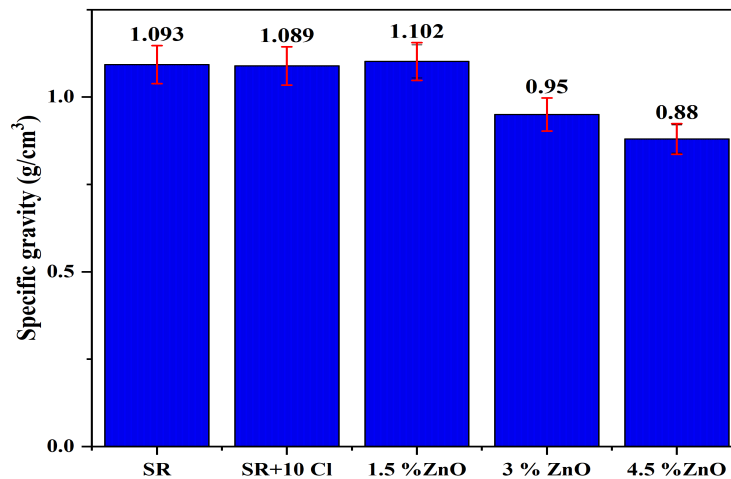


Figure 4.3. Effect of the nano ZnO on the specific gravity.

### 4.3.2. Tensile Strength

The addition of (0, 1.5, 3,4.5)wt.% ZnO resulted in a reduction in tensile strength as the concentration of nano ZnO increased. Even with the addition of ZnO, the mechanical characteristics remain high. This phenomenon may explain why ZnO increases the contact surface area between rubber chains, resulting in a rigid structure with higher tensile strength (2.24 MPa). While at high concentrations of ZnO, aggregates will form in the rubber matrix. As shown in Figure (4.4), this causes poor dispersion, which weakens the link between chains and reduces tensile strength [112, 113].

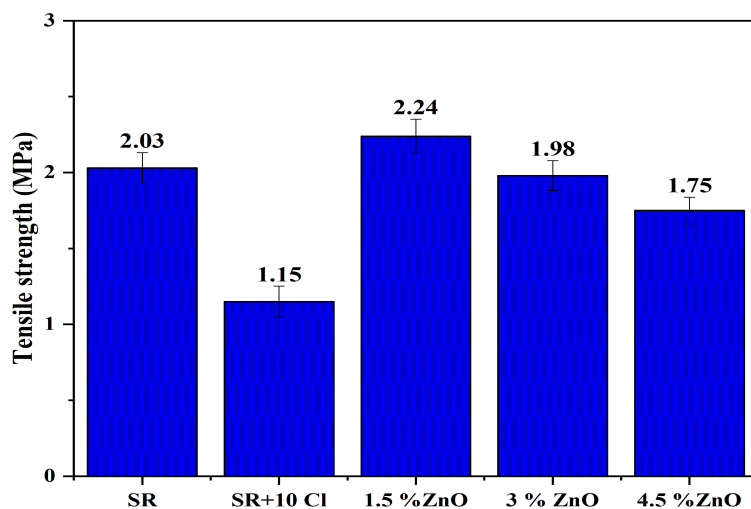


Figure 4.4. Effect of the nano ZnO on the Tensile strength.

### 4.3.3. Elongation

Figure 4.5 shows that the elongation property decreases when nano ZnO is added. This is because the rubber is highly stretchy, so when the very fine particles fill the spaces, it will restrict the movement of chains due to the diffusion of very fine ZnO nanoparticles through the rubber chains, which are responsible for riveting the rubber chain, leading to a decrease in the elongation property, as confirmed by a study[114].

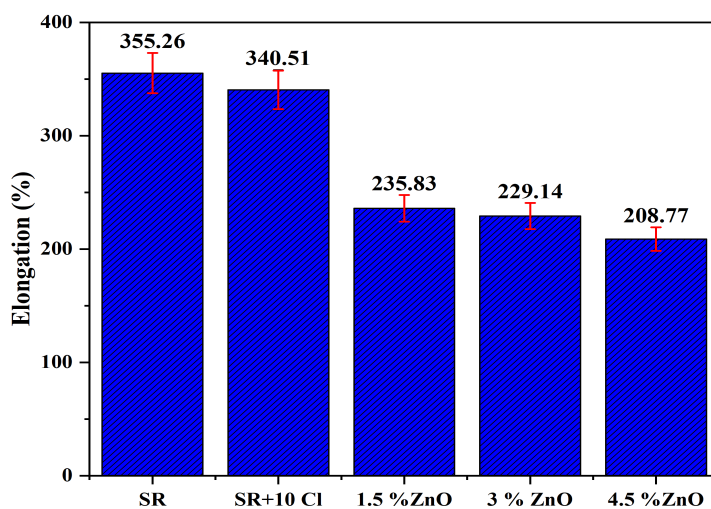


Figure 4.5. Effect of the nano ZnO on the Elongation.

#### 4.3.4. Modulus of Elasticity

As can be seen in Figure 4.6, the ZnO additives reduce the elongation properties, and their diffusion between the chains can impede the elastic movement of the polymer chains, requiring greater strength to yield those chains, both of which naturally have a positive effect on the elastic modulus of silicone rubber. This finding corresponds with that of [115], which found that increasing the amount of ZnO nanoparticles added led to a decrease in the modulus of elasticity as the rubber chain slid in the direction of the applied force.

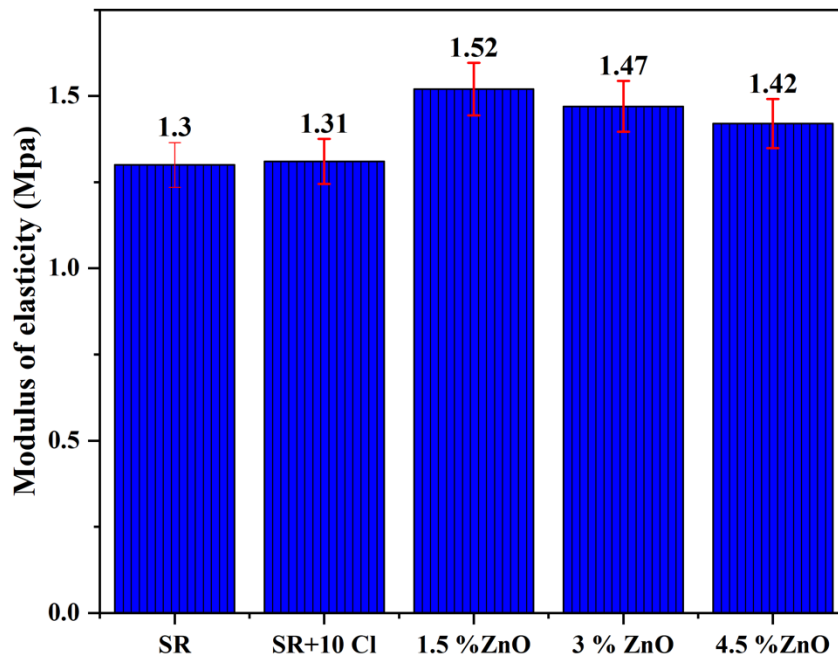


Figure 4.6. Effect of the nano ZnO on the Modulus of elasticity.

#### 4.3.5. Resilience

As can be seen in Figure 4.7, the addition of ZnO UMN results in a decrease in the rebound resilience. It is quite likely that the existence of agglomerates at greater filler concentration is associated with the decline in resilience. The findings by Al-Husnawi [112] show that adding ZnO progressively enhanced the resilience of the SR, which was the desired result. This was accomplished by increasing the filler content, which

in turn worked to generate surplus material that contributed to the rise in resilience force.

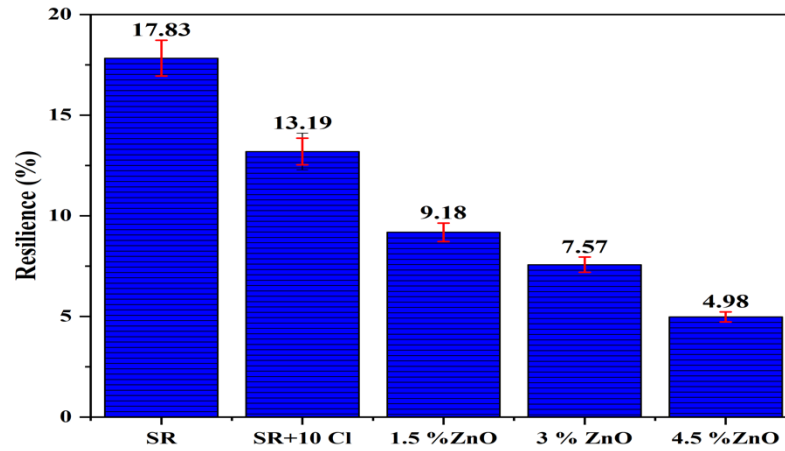


Figure 4.7. Effect of the nano ZnO on the Resilience.

#### 4.3.6. Tear Strength

As shown in Figure 4.8, adding even a small amount of ZnO improves tear resistance because of its relationship to the tensile characteristic. For the same reason that the particles will disperse equally across rubber chains and enhance the mechanical link between them, as discussed above in the context of the tensile characteristic. This results in enhanced durability against tears. When nano ZnO content is increased, tear resistance is reduced. Uneven distribution of nano ZnO nanoparticles in the rubber matrix and aggregate between chains reduces tear resistance. The results of the study confirm with [114].

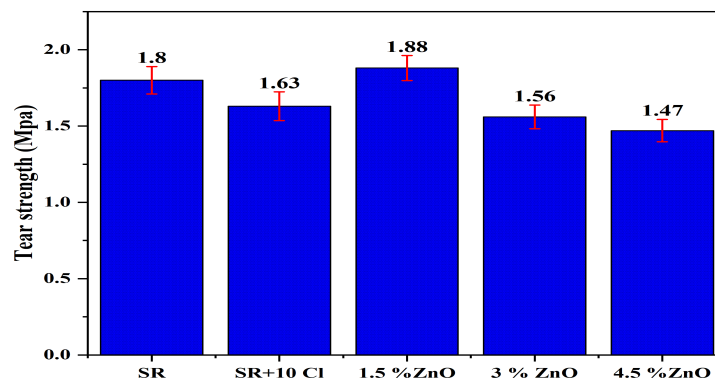


Figure 4.8. Effect of the nano ZnO on the Tear strength.

#### 4.3.7. Hardness

As shown in Figure 4.9, adding only 1.5% ZnO significantly improves the recipe's hardness and resistance to external pressures. ZnO may function as physical crosslinks because filler and rubber interact physically or chemically. It is believed that the overall effect of crosslinking of the polymer network, polymer-filler interactions, which may be physical and chemical, and the formation of occluded rubber gives a high hardness value, consistent with [113]. The filler can be physically entrapped in the rubber and shared in the load-bearing process in the matrix, leading to higher hardness.

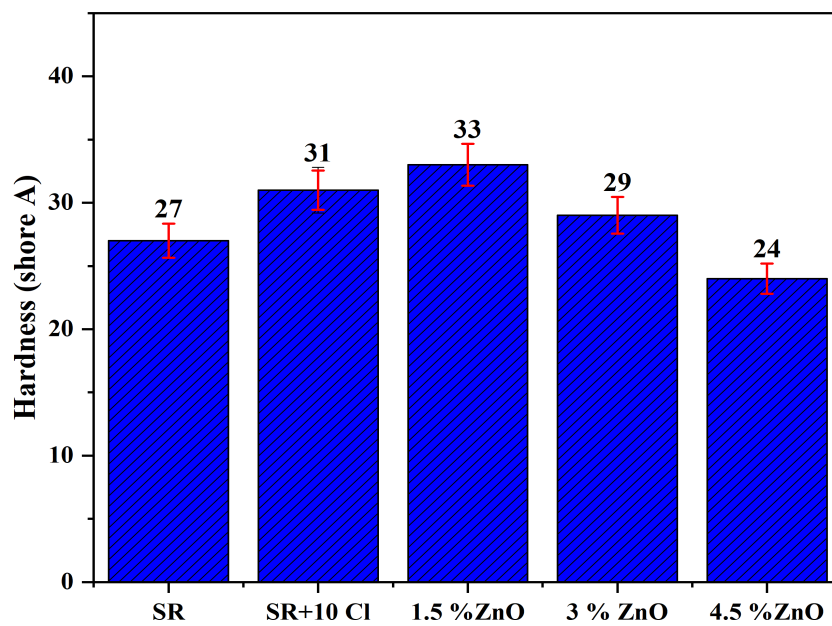


Figure 4.9. Effect of the nano ZnO on the Hardness.



#### **4.4. THE EFFECT OF ADDING N-Hydroxyapatite TO SILICONE RUBBER WITH 10% CHLOROPHYLL**

##### **4.4.1. Tensile Strength, Elongation and Modulus**

The tensile strength and percent elongation test results indicate that incorporating HA nanoparticles improved these properties. In particular, a decrease was observed at the 1.5% HA nanoparticle concentration. However, at a concentration of 0.5% HA, a highly significant increase in tensile strength and percent elongation was observed compared to the conventional and control groups. The other groups demonstrated a statistically insignificant increase compared to the conventional and control groups. The results for tensile strength and elongation percentage can be found in Figures 4.10 and 4.11, respectively. Aziz et al. stated that the cured silicone elastomer's tensile strength and elongation are significantly influenced by the crosslinking system, crosslink density, and the interaction between fillers and polymer chains.[116]. Eleni et al. noted that the molecular weight and degree of crosslinking of polymers significantly impact the elasticity and strength of maxillofacial silicones.[117]. One of the mechanisms that reinforce the material is the incorporation of nano-HA, which facilitates polymerization, resulting in an increased crosslink density and enhanced strength and stiffness of the polymer.

Additionally, it inhibits the rupture of polydimethylsiloxane chains, consequently augmenting its tensile strength. Incorporating nanoparticles increases the interfacial area between elastomeric chains, enhancing the tensile strength and imparting a more rigid structure Al-maamori et al. [118]. According to Sengupta et al. [119], prosthetic lining materials should exhibit tensile strength values within the range of 1 N/mm<sup>2</sup>. As such, any alterations in the tensile strength values observed in this investigation may be deemed clinically satisfactory. According to Kong et al. [120], the interaction between the fine particulate filler and the matrix can increase the elongation at the break of the filling system. According to Lewis and Castleberry's [121] study, the optimal range for percent elongation is between 400 and 800%. Hence, all alterations in percentage strain values observed in this study can be deemed clinically acceptable. At elevated levels of HA nanoparticle loading, the interaction between fillers leads to

the formation of agglomerated morphology. The phenomenon of particle agglomeration results in a reduction of the aspect ratio of the HA nanoparticle, leading to a decrease in the contact area between the particles and the polymer matrix.

Furthermore, the agglomerated nanoparticles have the potential to function as stress concentration sites within the composites. According to Han et al. [122], particles detach and debond from the polymer matrix when subjected to tensile mode deformation. As a result, it was observed that the tear strength, tensile strength, and percent elongation decreased at a concentration of 1.5% HA. The results of this study's tensile strength align with those reported by Tukmachi and Moudhaffer [123], despite using distinct nanoparticles combined with M-511 silicone.

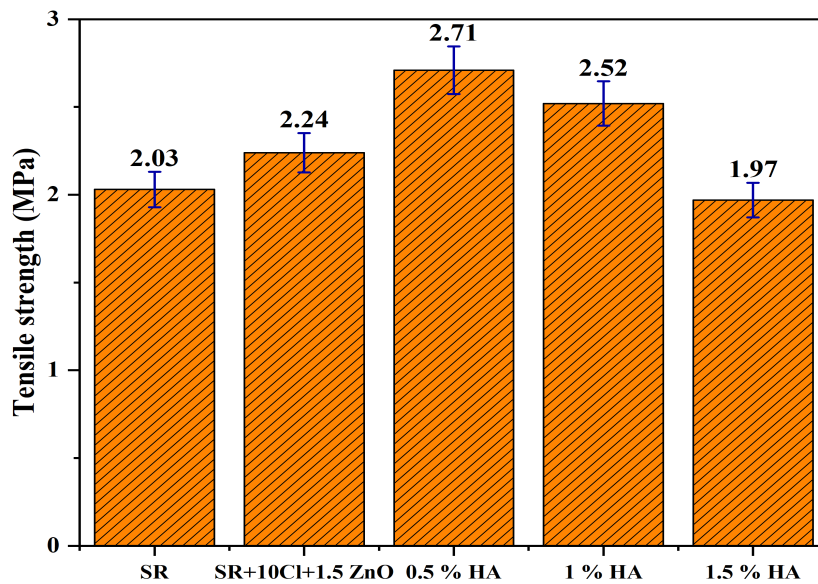


Figure 4.10. Effect of the nano HA on the Tensile Strength.

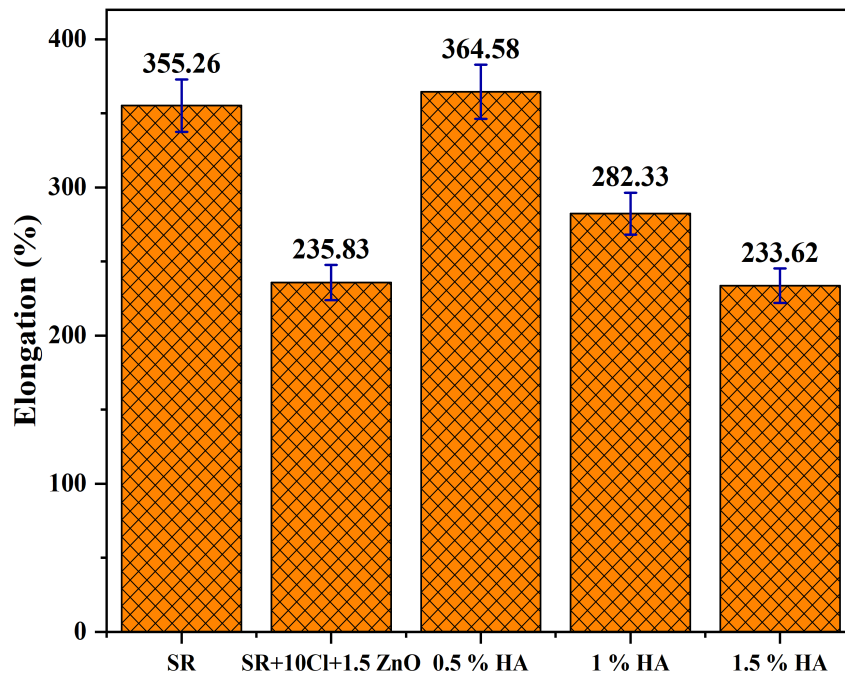


Figure 4.11. Effect of the nano HA on the Elongation.

The modulus of elasticity test results states that an increase in nano-HA leads to an increase in modulus, while a decrease is observed in the 1.5% HA group. Particularly, the 0.5% HA group exhibited a statistically significant increase in modulus compared to the conventional and control groups. The result of the modulus functioning is shown in Figure 4.12. The observed increase in modulus can be attributed to the presence of nanoparticles in the continuous phase of the silicone elastomer. This leads to an increase in cross-linked structure formation of the silicone material, resulting in an increase in both cross-sectional area and force. The modulus exhibits a decreasing trend with the incorporation of 1.5% HA nanoparticles, which leads to increased strain, as depicted in Figure 4.12. This increase in strain causes a corresponding increase in the dimensional change of the HA-containing samples, ultimately reducing the composites' stress-bearing capacity. This behaviour is consistent with that reported [124].

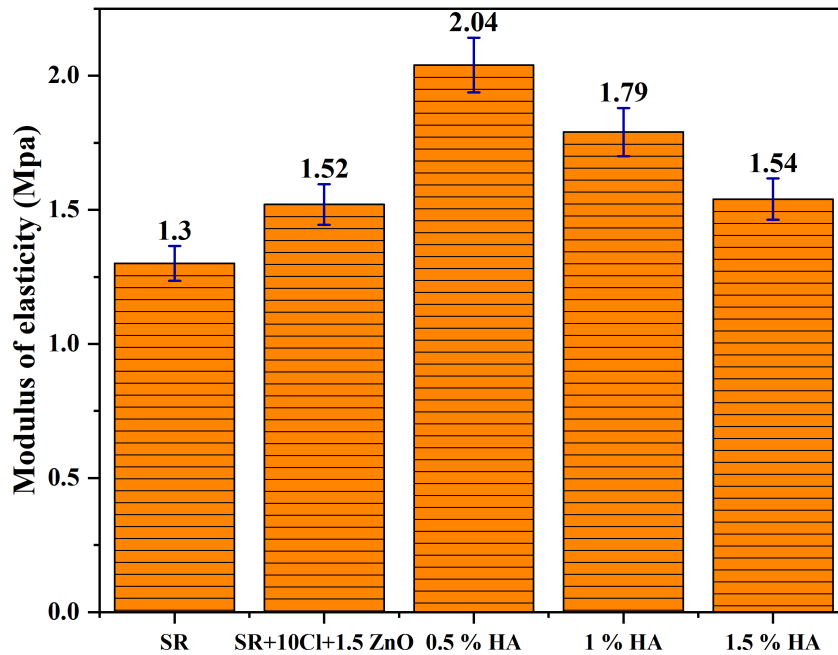


Figure 4.12. Effect of the nano HA on the modulus of elasticity.

#### 4.4.2. Tear Strength

The tear strength of silicone prosthetic liners is considered the most crucial property from a clinical perspective. According to Aziz et al. [116], attempting to remove the prosthesis from the facial tissue for cleaning at night can indicate the integrity and durability of the thin rim of the prosthesis. The findings of the tear strength test indicate that the tear strength exhibited an upward trend with an increase in nano-HA, while it decreased in the 1.5% HA and 0.5% HA groups. This increase was highly significant in comparison to both the conventional group and the control group. The tear strength outcome is depicted in Figure 4.13. The addition of HA appears to enhance the tear strength, potentially attributable to the nanoparticles' influence on the silicone elastomer's continuous phase. This effect promotes the development of cross-linked structures within the silicone material, increasing both cross-sectional area and strength. Incorporating nano-sized particles into silicone elastomers results in material reinforcement, as reported by Li et al. [125]. The propagation of strain energy within the polymer near and surrounding the developing cracks could elucidate the observed augmentation in tear strength. As the cracking progresses, the nanofillers dissipate the

energy within the polymer matrix, increasing tear strength. This, in turn, necessitates a higher force and stress to fracture the polymer matrix completely, as noted by Donnet and Custodero [126]. It has been reported that the recommended tear strength values for silicone prosthetic linings are a minimum of 0.9 N/mm. The outcomes derived from this investigation are deemed clinically satisfactory and have surpassed the recommended threshold. Notably, higher tensile strength is advantageous as long as it does not compromise other properties, as and Lewis and Castleberry [121] stated. As a result of the swelling and softening of the silicone caused by ethanol alcohol, there was a marginal and statistically insignificant reduction in tensile strength, elongation percentage, and tear strength observed between the conventional group and the control group. This finding aligns with previous studies conducted by Qamar et al. [127].

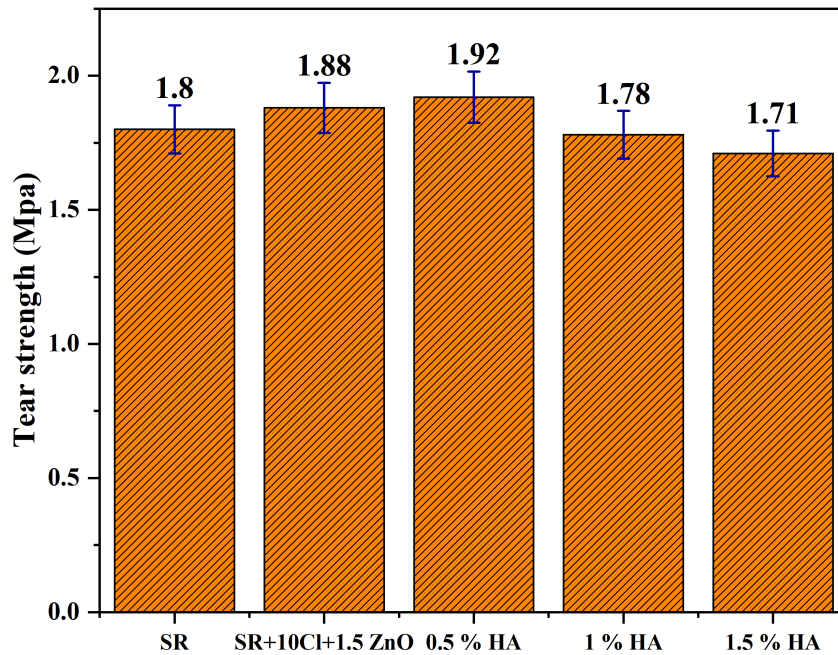


Figure 4.13. Effect of the nano HA on the Tear strength.

#### 4.4.3. Hardness

The softness of a material is measured by its hardness, which is determined by indentation loading [128]. The property of hardness, similar to tensile and tear

strength, is essential because it plays a crucial role in determining a material's flexibility. It is preferable to have a material with similar flexibility to the surrounding defect, as reported by Hatamleh and Watts [129]. Figure 4.14 shows the results of the hardness test for all groups. Increasing the ratio of HA to the reinforced silicone elastomers results in a corresponding increase in hardness value. Increasing the filler concentration leads to a direct and proportional increase in the hardness value. The observed phenomenon can be attributed to the reinforcing effect of HA as a filler that increases the resistance of the formulation to external forces [118]. In addition, nanoparticles have been reported to facilitate polymerization [130]. It is likely that according to the findings of Goiato et al. [131], it resulted in increased silicone polymerization and hardness. An alternative explanation is that the Shore A hardness of the silicone elastomer with nano-HA was more significant compared to the pure silicone elastomer. The observed phenomenon can be attributed to nanoparticles' influence on the silicone elastomer's elastic modulus. Notably, a significant proportion of these nanoparticles are located on the surface of the silicone. This finding contrasts the results of a previous study by Xia et al., which was confirmed [132]. According to Methananda et al. [133], there is a proportional relationship between the Shore A hardness and the modulus of elasticity of silicone elastomers. In addition, the dispersion of nanoparticles in the silicone elastomer leads to an increased crosslink density and, thus, an increase in the hardness of the material.

According to Figure 4.14, a reduction in hardness can be observed with an HA loading of 1.5%. This could be related to the interfacial and physical bonding between the filler and the SR matrix. Conversely, hardness depends on the HA molecular distribution within the SR composites. The literature suggests that integrating HA molecules into the soft matrix can increase the elasticity of the polymer chains, resulting in composites with reduced stiffness. These interactions reduce the hardness of the investigated SR matrix fillers. The HA nanoparticles content has increased again. It has been reported that the ideal hardness range for silicone prosthesis liners is between 30 and 48. The knowledge gained from this study is considered clinically satisfactory. The result of this Shore A hardness study agrees with the findings of Han et al. [122] which contradicts the conclusion of Nobrega et al. [134] that including nanoparticles decreases the hardness before aging. The observed phenomenon could be due to the

inclusion of nanoparticles in the silicone matrix. This can impede the mixing of the polymer chains and increase hardness after accelerated aging. It is worth noting that facial silicone is a continuously polymerizing material; therefore, its degree of polymerization can increase with age [131]. The result of this Shore A hardness study is consistent with previous studies by Tukmachi and Moudhaffer (2017) [123], despite using different nanoparticles in the context of M-511 silicone.

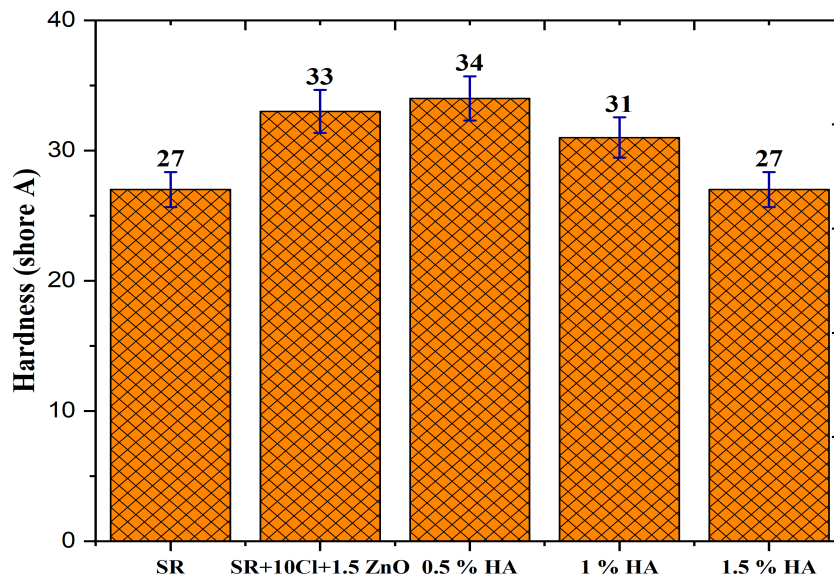


Figure 4.14. Effect of the nano HA on the Hardness.

#### 4.4.4. Specific Gravity

Incorporating HA nanoparticles increases weight per unit volume, leading to an increase in specific gravity, as depicted in Figure 4.15. This is attributed to the interference of particles between rubber chains, resulting in a denser material per unit volume, which is consistent with the findings of reference [164]. As depicted in Figure 4.15, there is a reduction in specific gravity as the content of 1.5% HA nanoparticles increases. This phenomenon occurs due to air diffusion through the closed cell in the sample, resulting in increased volume and decreased specific gravity. This result has also been reported by Frohlich [135]. According to reports, the optimal range for

Specific Gravity in silicone prosthesis liners is between 1.115-1.140 g/cm<sup>3</sup>. The results obtained from this study are considered to be clinically satisfactory.

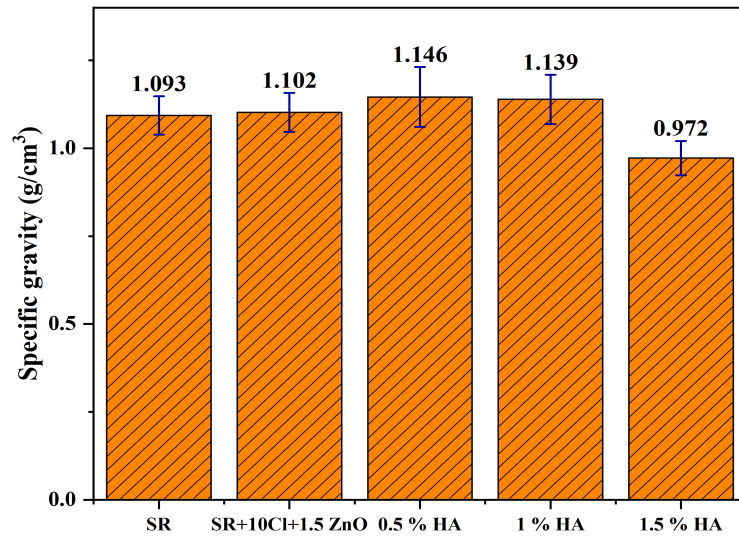


Figure 4.15. Effect of the nano HA on the Specific Gravity.

#### 4.4.5. Rebound Resilience

The results presented in Figure 4.16 indicate a decrease in rebound resilience upon introducing HA nanoparticles. The decrease in toughness is probably related to the presence of agglomerates at increased filler concentrations. As expected, the incorporation of HA nanoparticles resulted in a gradual improvement in the toughness of the SR with increasing filler content. This phenomenon is consistent with a study [112] that found that excess material increases the restoring force.



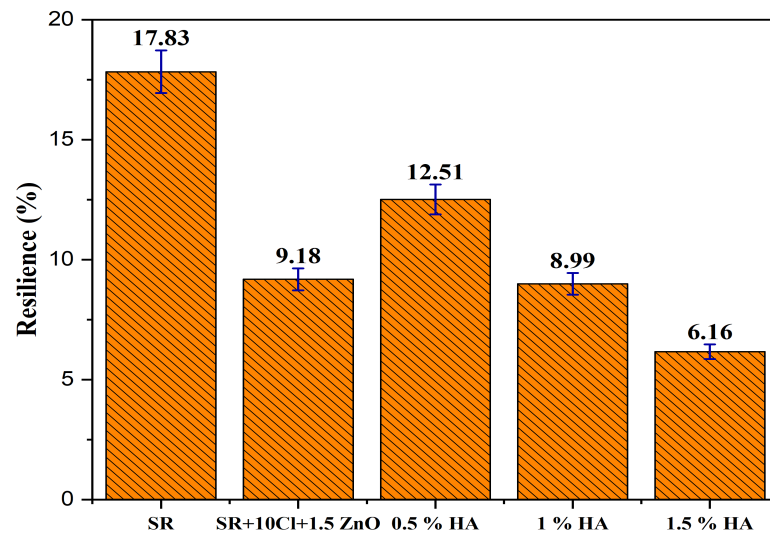


Figure 4.16. Effect of the nano HA on the rebound resilience.

#### 4.5. MICROSTRUCTURE ANALYSIS

The mechanical properties of materials are significantly influenced by the dispersion state of the nanoparticles (ZnO and HA) fillers within the rubber compound. The agglomeration of nanoparticles reduces their contact surface area and interactions with other components in the cross-linking system. This, consequently, can cause a decrease or increase in the mechanical properties of the nanocomposite based on silicon rubber. In order to analyze the morphology of the nanocomposites, scanning electron microscopy (SEM) was used to assess the ZnO/HA nanoparticle fillers within the rubber compounds.

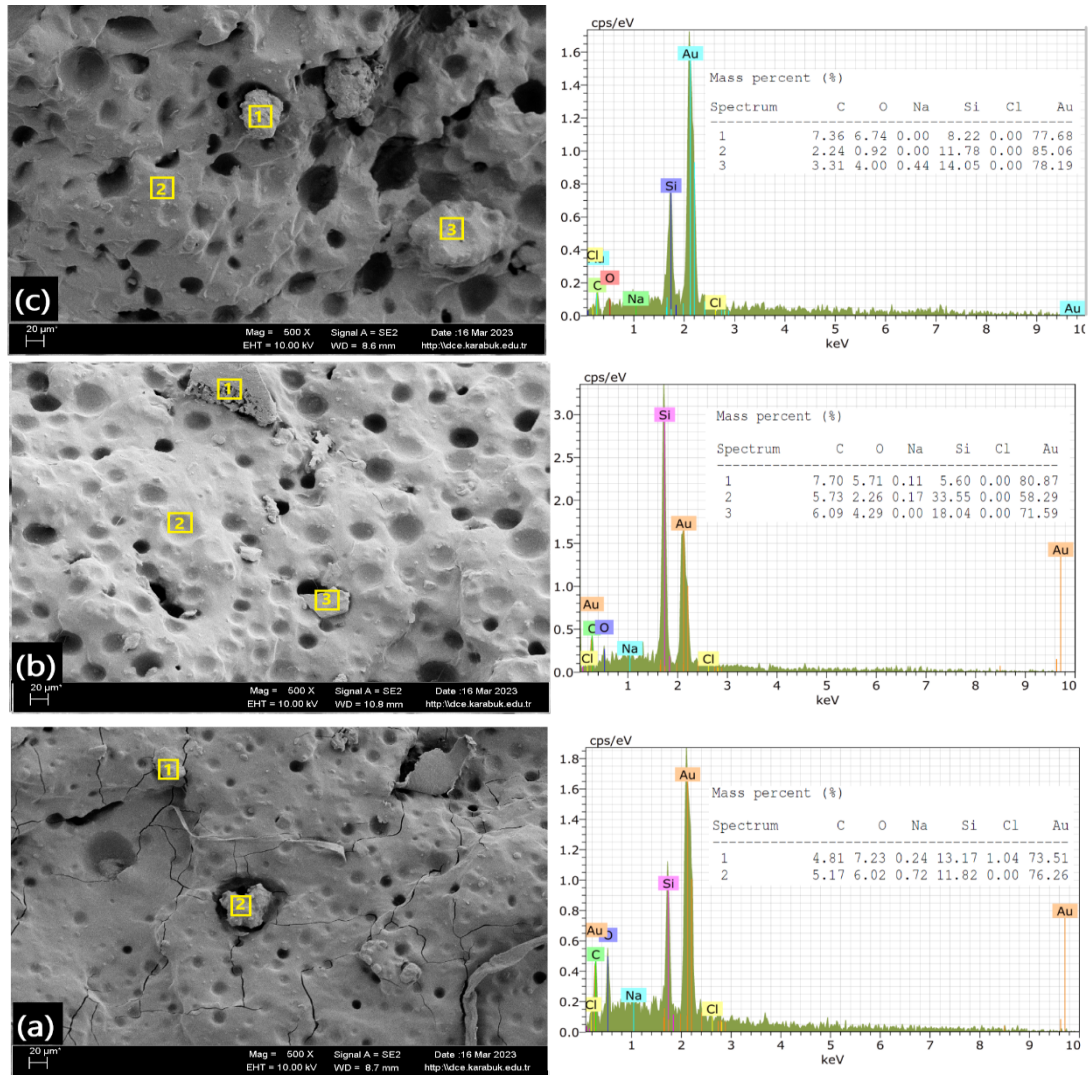


Figure 4.17 SEM for Silicone rubber with a)10 %,b) 20%, and c) 30% chlorophyll.

Figure 4.17 represents the impact of chlorophyll addition on silicone rubber, revealing the presence of both open and closed pores and voids. These structural features significantly influence the water absorption level, with an increase in porosity leading to a corresponding increase in water absorption for the silicone rubber-based compound. Figure 4.18 depicts the morphology of ZnO nanoparticles incorporated into a silicon rubber composite material. The dispersion of zinc oxide (ZnO) and hydroxyapatite (HA) nanoparticles within the silicone rubber composites is uniform throughout the matrix, as shown in Figure 4.18. It has been observed that specific ZnO nanoparticles exhibit a propensity to aggregate, thereby forming larger particles. A significant quantity of hydroxyl groups is posited to promote the agglomeration of the

nanoparticles. Figure 4.19 presents that adding HA/ZnO nanoparticles results in a superior dispersion. This outcome can be attributed to surface modification and weaker inter-particle interactions. Incorporating nanoparticles in the SR/HA/ZnO nanocomposite results in an augmented cross-linking density of the composites. However, an excessively high cross-linking density may ultimately reduce the mechanical properties' strength. Hence, optimizing the filler ratio of nanoparticles is crucial to attaining superior mechanical properties. The SR/HA/ZnO nanocomposites exhibit superior tensile strength and elongation at break compared to the SR/ZnO nanocomposites. This can be attributed to the increased cross-linking density and enhanced interfacial interaction between the surface of the nanoparticles and the silicone rubber matrix [136].

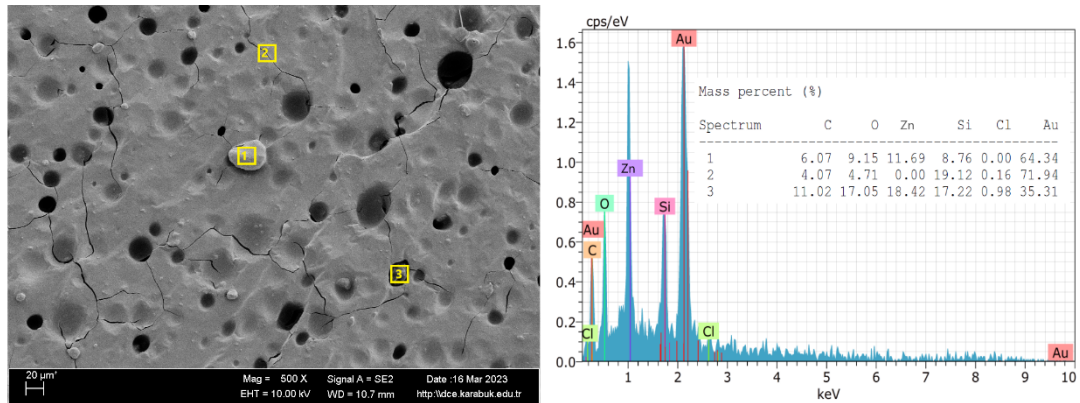


Figure 4.18 SEM for Silicon rubber composite ( SR+10 Cl+1.5% nano ZnO).

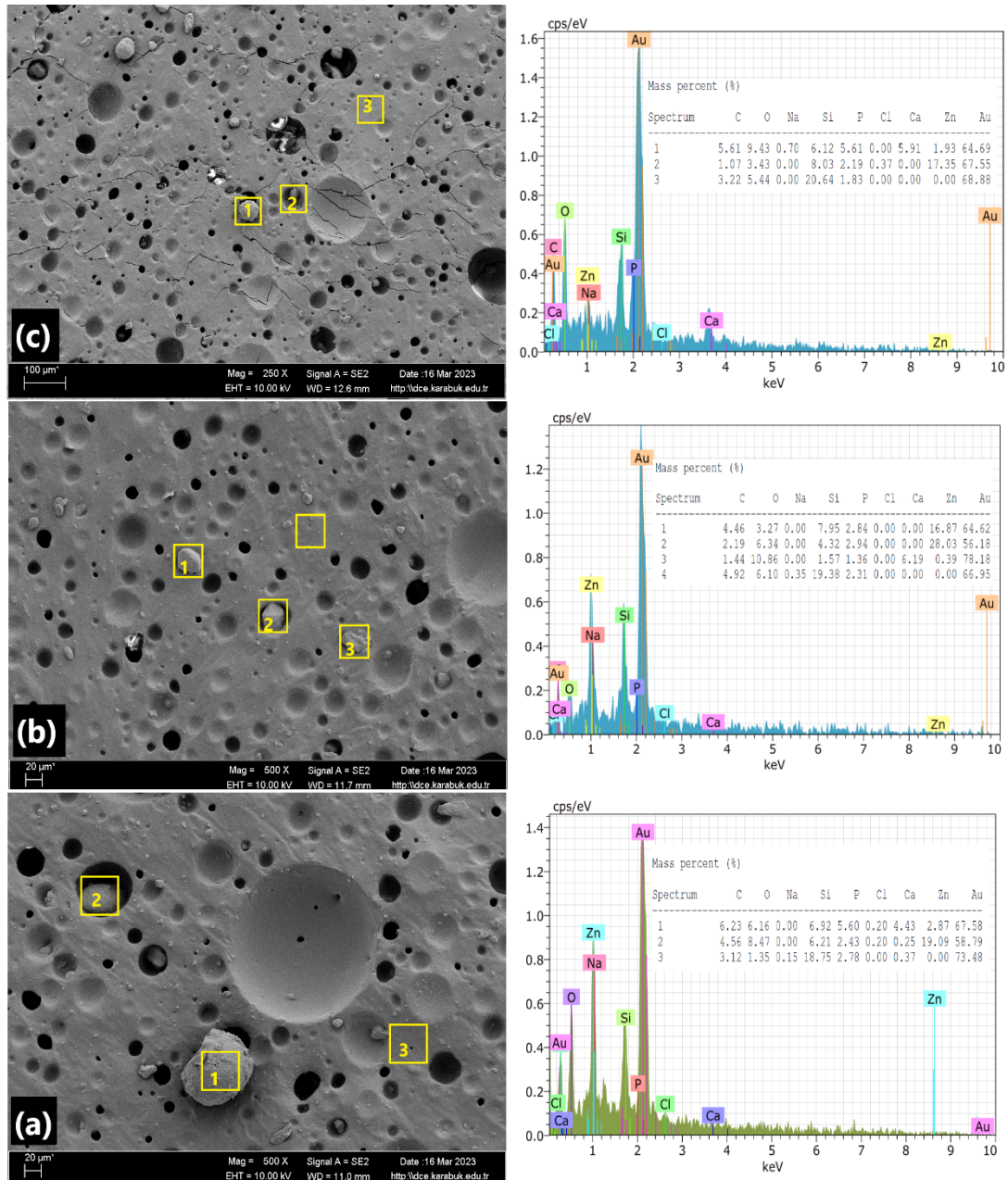


Figure 4.19 SEM for Silicon rubber ( SR+10 Cl+1.5% nano ZnO).with a)0.5 %,b) 1%, and c) 1.5 % nano HA.

#### 4.6. ANTIBACTERIAL TEST

Figure 4.20 shows the antibacterials for the silicone rubber incorporated with 10 % chlorophyll, 1.5 %ZnO and 0.5 hydroxyapatite (HA) and zinc oxide (ZnO) particles against Staphylococcus aureus bacteria which are gram-positive and gram-negative,



respectively, the inhibition zone was 20 mm. The following are the plausible mechanisms:

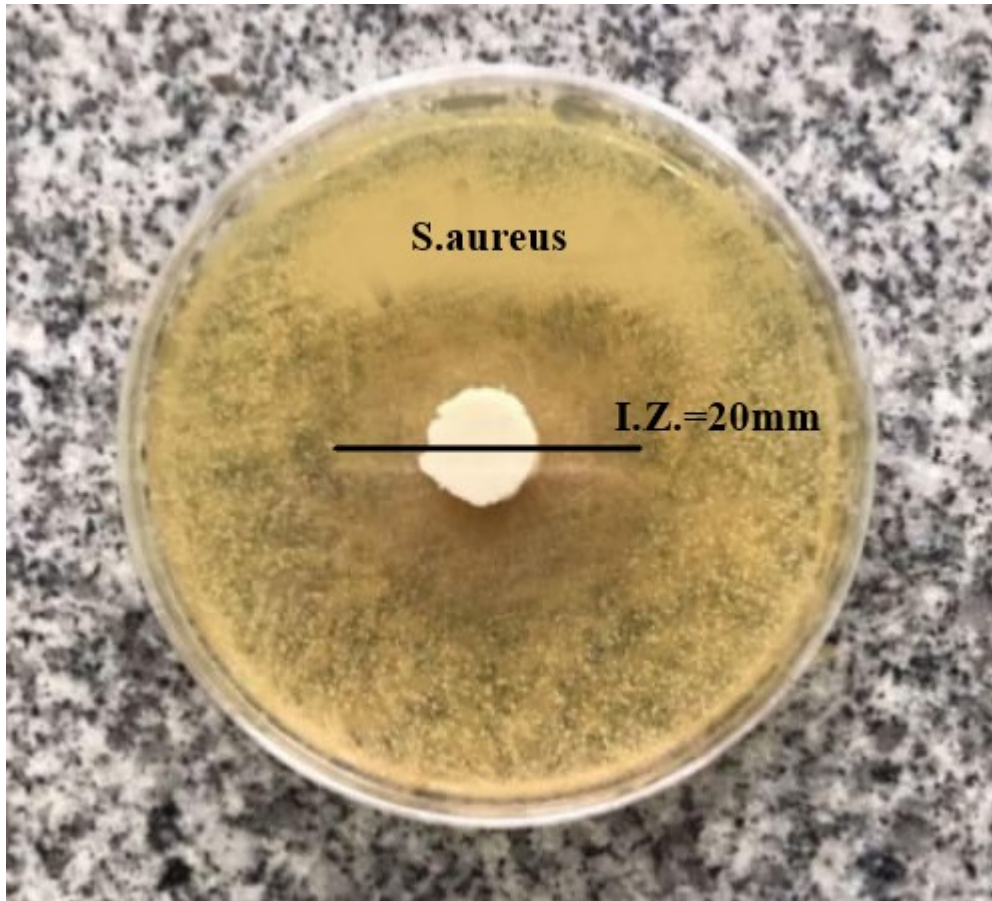


Figure 4.20. The negative results of staphylococcus bacteria growth on the nanocomposite's surface (SR+10%Cl +1.5% n-ZnO, 0.5 % n-HA).

The antibacterial properties of ZnO particles are attributed to the discharge of  $Zn^{2+}$  ions, which can cause harm to bacterial cell membranes and result in the leakage of intracellular components [137]. Zinc ions ( $Zn^{2+}$ ) have been observed to interact with proteins containing sulfur in bacterial cells, leading to a disruption in their usual physiological function. Incorporating Zinc Oxide (ZnO) into silicone rubber can potentially induce bactericidal effects upon contact.

The antibacterial action of HA particles alone is insignificant. Nevertheless may function as transporters for antibacterial compounds like silver nanoparticles and

medicines, which can subsequently diffuse out of the HA and kill bacteria[138]. Therefore, HA can be a means of delivering other antibacterial agents.

The surface morphology and porosity of silicone rubber can be altered by incorporating HA and ZnO filler particles, which can lead to a mild antibacterial effect by damaging bacterial cell membranes upon contact. The filler particles possess the capability to ensnare bacteria and impede their propagation.

The production of reactive oxygen species (ROS), such as superoxide radicals and hydrogen peroxide, can occur on the surface of zinc oxide (ZnO) when exposed to light or in high pH conditions. The ROS (reactive oxygen species) have the potential to function as antibacterial agents by inducing the oxidation of bacterial proteins and DNA [137]. The incorporation of ZnO into silicone rubber may potentially yield photoinduced antibacterial properties.

The liberation of  $Zn^{2+}$  ions from ZnO typically occurs over an extended duration, resulting in sustained antibacterial effectiveness. Similarly, the immobilization of antibacterial agents onto hydroxyapatite (HA) can result in a diffusion of said agents over time, thereby conferring enhanced durability to the antibacterial properties.

By obtaining these mechanical and physical qualities, silicone rubber with addition of nano ZnO and HA can be used as a liner for amputated limbs, making it more acceptable and pleasant for the patient. As compared with the physical and mechanical properties of the standard prosthesis liners, shown in figure 4.1

Table 4.1. Compare of the stander and present value of the prosthesis liners.

<b>Property</b>	<b>Stander Value</b>	<b>The present value</b>
Specific Gravity	1.115- 1.140	1.146
Water absorption (%)	Not available	3.25
Hardness (shore A)	30- 48	34
Tensile strength (MPa)	Min. 1	2.71
Modulus of elasticity (MPa)	Min. 0.8 at 300%	2.04
Elongation (%)	Min. 235	364.58
Tear strength (MPa)	Min. 0.9	1.92

## PART 5

### CONCLUSIONS AND RECOMMENDATION

#### 5.1. CONCLUSIONS

Silicone rubber has been identified as the optimal material for socket lining in prosthetic applications, as it enhances patient comfort and overall prosthesis functionality. The mechanical and physical properties of materials play a crucial role in enhancing the longevity of the lining and ensuring optimal protection of the amputated limb. Silicone rubber polymers were synthesized using intermediates modified with n-HAp and n-ZnO, and the nanocomposite products were characterized by SEM, water absorption, mechanical properties and antibacterial, and the following results were obtained:

1. Adding chlorophyll to silicone rubber increased water absorption when the percentage of chlorophyll and the porosity percentage increased; however, it decreased tensile strength; the best percentage was when adding 10% chlorophyll, which gives good mechanical properties.
2. It has been observed that using a small amount of nano ZnO as a filler in the nanocomposite compound of the prosthetic liner is more effective than using a high quantity. This is due to its ability to fill the spaces in the liner efficiently.
3. The optimal percentage of ZnO MN is 1.5% because it increases tensile strength, tear resistance, hardness, and resilience. ZnO nanoparticles aggregate between chain links and are unevenly distributed in a rubber matrix, diminishing the material's effectiveness.
4. Mechanical properties can be improved by adding HA nanoparticles to a compound composed of (SR+10% CL+1.5%) N-ZnO; a concentration of 0.5% HA nanoparticles showed a highly significant difference and improved the overall tested mechanical properties, while a concentration of 1.5% ZnO showed declines in mechanical properties.



5. SEM analyses showed that nHAp and n-ZnO have a nano-sized particle structure, and these spherical particles are dispersed in the polymer matrix.
6. The utilization of the hand-laying method in preparing samples resulted in the formation of pores.
7. Based on the findings, it can be concluded that ZnO nanoparticles are safe to use in medical applications because they inhibit bacterial growth by damaging the bacterial cell membrane and forcing the extrusion of the cytoplasmic contents, killing the bacterium.

## **5.2. RECOMMENDATIONS**

Here are some recommendations for socket lining in prosthetic applications based on silicon rubber nanocomposite :

1. Fabrication method: silicon rubber nanocomposite can be prepared using various techniques, including compression molding.
2. Investigate the effects of UV light and cleaning solution on silicone prosthetic liners to determine their degradation rate.
3. Investigate the wettability of surfaces and the permanent deformation characteristics of silicon rubber nanocomposite.
4. Study the Aging effects on mechanical and physical characteristics of n-ZnO and n-HA nanoparticles-reinforced maxillofacial silicone elastomers.

By obtaining these mechanical and physical qualities, silicone rubber may be used as a liner for amputated limbs, making it more acceptable and pleasant for the patient.

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## **RESUME**

Husam awaid ABED is a material engineer who graduated from the Faculty of Materials Engineering, Polymer and Petrochemical Industries University of Babylon - Iraq. He received His Bachelor's degree in 2017. He is currently studying for her Master's degree at Karabük University in the field of Materials Engineering.