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Preparation and Evaluation of above Knee-Prostheses Liner soft Socket

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﴿قَالَ رَبِّ اشْرَحْ لِي صَدْرِي ۝ وَيَسِّرْ لِي أَمْرِي ۝
وَاحْلُلْ عُقْدَةً مِّن لِّسَانِي ۝ يَفْقَهُوا قَوْلِي﴾

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Supervisor Certification

We certify that this thesis entitled **"Preparation and Evaluation of above Knee-Prostheses Liner soft Socket"** is Prepared by (**Hajer Abed Al-Samd Mohamed Ali Mahdi**) under our supervision at the University of Babylon/ College of Materials Engineering/ Department of Polymer and Petrochemical Industries in partial fulfillment of the requirements for the Degree of Master in Materials Engineering/Polymer.

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Date: / / 2022	*Date: / / 2022*

TO my family..
My safety in this world.
daughter..
Shafaq
friends..
All the love and thanks for your spport.

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Abstract

Lower limb prostheses have three types: above the knee, through the knee and below the knee. The limb above the knee consists of several parts, one of the most important of these parts is the socket, which in turn needs an inner lining that works to stabilize the socket with the amputated part and prevents direct friction between the socket and the skin as well as prevent putrefaction growth.

This lining needs to improve its biological and mechanical properties. So the purpose of this work is to make a socket lining for amputees that will be able to withstand the weather in Iraq, which usually causes the prosthesis to sweat, accompanied by an unpleasant odor.

In this work, a polymeric socket lining was manufactured in three stages. In first stage, an Interpenetrating Polymer Network (IPN) was prepared from polyurethane (PU) resin and silicon rubber (SiR) resin and their own hardeners. In this stage, PU was added to the SiR with different weight ratios (0, 10, 15, 20, 25, 30 and 35). For PU, the ratio of hardener (isocyanate) to resin is 30:70, while for SiR it is 1.5:100.

In the second stage, a tertiary blend where prepared by adding nano chitosan powder by 3 wt% to the previous IPN to improve its antibacterial ability. In the third stage, and for further improving of the antibacterial activity, the tertiary blend was covered by chitosan layer. To tightly connect this layer, Glutraldehyde and (3-chloropropyl) triethoxysilane (CPTES) cross-linker system was used.

Several structural and physical tests were carried out, such as X-Ray diffraction (XRD), Infrared Fourier Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), wettability, Thermo gravimetric analysis (TGA), hardness, tensile strength, elastic modulus, elongation, fatigue, rebound resilience, specific gravity and water absorption.

Also, the antibacterial activities against Staphylococcus aureus and Pseudomonas microorganisms were measured by two biological tests; Agar Well Diffusion method and biofilm formation assay.

Characterization results showed that there was no chemical reaction between SiR and PU in the IPN, the crystallite size increased from 20.06 to 26.51 at $2\theta=12^{o}$, the tertiary blend is immiscible. AFM test shown porosity increased and roughness decrease, TGA/DTG test shown that decomposition of the blend at 420ºC and weight loss about 46.29%. The chitosan layer reduces the contact angle from 80.989º to 63.523º.

Physical results showed that the hardness increased by 60% and the elastic modulus by 40%. with the PU content and the maximum IPN damping occurred at 20% PU. Other mechanical properties in terms of tensile stress and fatigue life have been reduced. The water absorption capacity increased up to 6.8%, which means increased absorption of sweat and a reduction in the appearance of embarrassing odors for patients in the hot summer months.

The antibacterial results showed that both SiR and the IPN have no abilities, while the tertiary blend has good ability especially against Pseudomonas microorganism and the 30 min immersed in (CPTES/acetone) solution gave the best results (inhibition zone of 10.5 mm and inhibition efficiency of 42.8% vs. 8.3mm and 38% respectively).

Biofilm formation results showed that Pseudomonas (G^{-ve}) microorganism have less tendency (better) than Staphylococcus (G^{+ve}) to form this film. The best sample in privation biofilm formation is the coated sample which immersed for 3o min, since its OD is 0.089 nm.

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Abbreviations

Abbreviations	Description
A.K	Above Knee
APTES	3-aminopropyltriethoxysilane
ATRP	Atom transfer radical polymerization
B.K	Below Knee
CO_2	Carbon dioxide
CoFs	Coefficients of friction
CPTES	3-chloropropyltriethoxysilane
EVA	Ethylene vinyl acetate
GRF	Ground reaction force
HTV	High temperature vulcanizing
IPN	Inter Penetrating Network
MDI	Methyldiphenylisocyanate
NGOs	nongovernmental organizations
PDMS	Poly-di-methyl-siloxane
PTB	Patellar Tendon Bearing
PUF	Polyurethane foam
RTV	Room temperature vulcanizing
SB	Sodium Bicarbonate
SH	Strain hardening
SiR	Silicon Rubber
TDI	Toluendiisocyanate
T.K	Through Knee
TSB	Total Surface Bearing
UV	Ultraviolet

Chapter One

Introduction

1.1 Introduction

The term "prosthesis" is a Greek word which comes from "prostithenai". A prosthetic is a man-made device that performs the function of a missing bodily component. Prosthetic limbs, or artificial limbs, are fabricated devices that provide amputees with a replacement for their missing limb, restoring some function. Lower limb prosthetic devices must restore the capacity for walking if they are to be effective [1 and 2].

Lower limb amputation has become an area of increasing concern for those working in modern healthcare due to its increasing prevalence in society. This is not only due to the increase in amputations arising from warfare, but largely from the aging population and the increase in lifestyle related illnesses, such as diabetes and peripheral vascular disease, which can result in amputation [3].

Lower limb prostheses are generally developed with three principal parts: socket, pylon (leg section), and foot [4], as shown in figure (1.1). A socket is an essential component of prosthetic limbs; it serves as a connection between the residual limb and the prosthetic components [5].

Fig. 1.1: Prosthesis Parts [5].

There are two type of socket: hard socket (external) and soft socket (internal), that one which this study about it, most modern sockets are used with an intermediate liner, the principal role of these liners is to improve amputee safety and comfort by adding a cushioning layer between the residual limb and the prosthetic socket.

The cushioning performance of the liners depends on their mechanical properties [4]. The socket connects the residual limb (stump) to the remaining portions of the prosthetic device. Due to the uniqueness and complexity of each patient's residual limb, designing and mounting the socket is the most difficult process.

There are two methods for making socket as shown in figure (1.2) where SLS: Selective laser sintering, CAD/CAM: Computer _aided design/computer _aided manufacturing and MSS: Modular socket system [5].

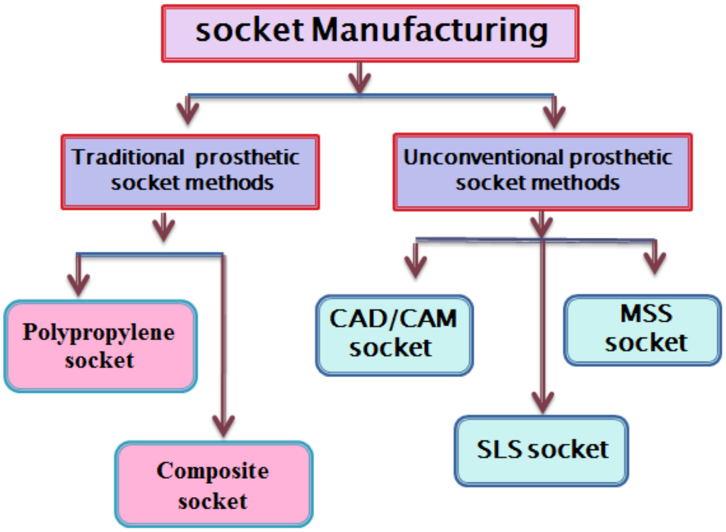


Fig. 1.2: Socket manufacturing methods [5]

The prosthetic socket, which acts as an interface medium between the prosthesis and the residual limb, is the most important component. The socket design must be perfectly tailored to the user's needs in order to achieve satisfactory load transmission, efficient ambulatory control, and stability [6 and 7].

Lower limb consist of two types knowing traditionally as, Trans-tibial which is at the level below the knee and transecting both the tibia and fibula, and Trans-femoral which is at a level above the knee joint [1 and 8].

The liner serves to couple the limb to the socket, accommodate changes in limb shape and volume, and distribute concentrated socket stresses. Clinically, a liner must be matched to a patient based on a number of characteristics that include limb shape, tissue quality, socket design, anticipated volume change, and activity level [8].

Prosthetic sockets are custom made for each amputee, yet there are no quantitative tools to determine the appropriateness of socket fit. Ensuring a proper socket fit can have significant effects on the health of residual limb soft tissues and overall function and acceptance of the prosthetic limb [9], the main materials used for made socket liner was: silicone, TPE, PU.

During recent years, polymeric nano composites that form a kind of compound materials of a polymer and inorganic filler component which has at least one dimension in the nanometre scale developed the material properties [10].

Nanoparticles can lead to improve the mechanical properties due to the increase the number of crosslinking sites at the nanoparticle-matrix interface. The enhancements in the materials characteristics can achieved, if it is good filler dispersed in a base, such as rubber matrix [11].

1.2 Motivation

The lower limbs consist of several parts and one of the most important of these parts is the socket, which in turn needs an inner lining that works to fix the socket to the amputated part, protect the stump and make wall easy to the patients. In general, Iraq is one of the importing countries for the bushings, which are manufactured within the atmosphere of those European countries whose temperatures are clearly different from Iraq, From the beginning of April to October of each year, the patient suffers from the inability of the limb to bear high temperatures, so the patient often abandons the limb due to heavy sweating that occurs in addition to fluid retention, which makes the limb uncomfortable and has an environment suitable for bacterial growth, the reasons mentioned above In addition to the cost led us to work on this research.

1.3 Aim of Work

The aim of this project is to making a material for a soft socket (liner) that matches the weather in Iraq and comforts amputee patients.

1.4 Objectives

To achieve the aim of this project, the following steps carried out:

1. Choosing the appropriate materials for the application (silicone rubber and polyurethane)
2. Mixing materials in different proportions, making it as Inter penetration network IPN.
3. Adding chitosan to IPN to improve antibacterial properties, making it as tertiary blend.
4. Make the tests (physical, structural, morphological and antibacterial).

1.5 Thesis Layout

This thesis is divided into five chapters. The general introduction are introduced in chapter one. Chapter two includes: the theoretical part which includes definition, classification and types of composite materials and denture base materials definition and literature reviews. The experimental work is discussed in chapter three which describes the used materials, manufacturing of specimens and test equipment. Chapter four involves results and discussion of the experimental work, the work conclusions and gives suggestions for future studies in chapter five.

Chapter Two

Theoretical Part and Literature Review

2.1 Introduction

Ancient artificial limbs were crafted from metal and wood and had minimal functionality. Heavy and ill-fitting to the residual limb, these prostheses had limited usefulness [12 and 13].

Prosthesis fit and function have improved as a result of updated technologies and the introduction of new materials, such as silicon liners [14]. However, prosthesis satisfaction is not always maximized. The ability to appropriately wear prosthetic components has a significant impact on prosthetic wear, use, and comfort [15]. With the increased use of silicon liners in trans-tibial prostheses, proper prosthesis wearing is even more critical to maintaining good prosthetic function [16]. Since then, liners with a variety of material properties have been introduced, and manufacturers of silicon liners have propagated advantages in prosthesis fit and suspension when compared to the "standard" prosthesis with a supracondylar fitting, Kondyl Bettung Munster (KBM) fitting, patella tendon bearing (PTB) fitting, or conventional type prosthesis fitting [14 and 17].

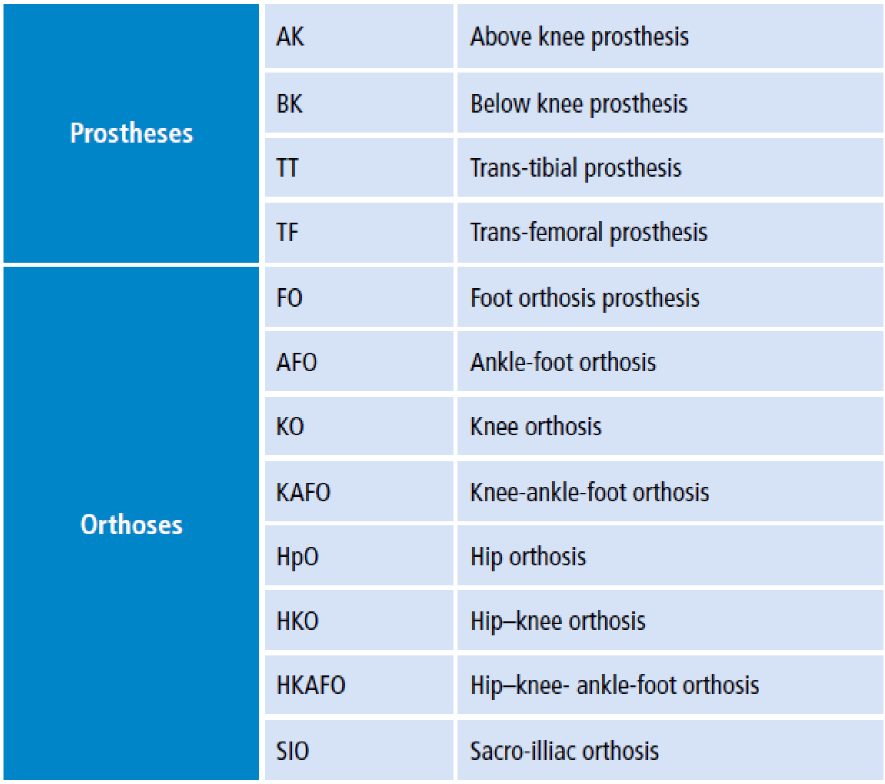
Diabetes and vascular disease are the leading causes of lower limb amputation [18]. There are four main levels of major lower limb amputation: below knee, through-knee, above-knee, and through-hip. These four types of amputation have been shown to provide the best chance of using prosthesis, which is why amputation is not performed directly at the level of the most distal viable tissue [19].

In Iraq especially in Kerbala city at Jaafar Al Tayar Center for Amputees from 2016 to 2021 more than 600 cases of amputated patients and by each case they were classified as shown in table (2.1), while table (2.2) shown nomenclature for lower limb Prosthesis and Orthosis.

Table 2.1: Type of patients at Jaafar Al Tayar Center for Amputees from 2016 to 2021

Above Knee	132
Below Knee	466
Through Knee	7
Upper limb	11

Table 2.2: Nomenclature for lower limb Prosthesis and Orthosis [20]



Prostheses	AK	Above knee prosthesis
	BK	Below knee prosthesis
	TT	Trans-tibial prosthesis
	TF	Trans-femoral prosthesis
Orthoses	FO	Foot orthosis prosthesis
	AFO	Ankle-foot orthosis
	KO	Knee orthosis
	KAFO	Knee-ankle-foot orthosis
	HpO	Hip orthosis
	HKO	Hip–knee orthosis
	HKAFO	Hip–knee- ankle-foot orthosis
	SIO	Sacro-illiac orthosis

2.2 Requirements of lining Sockets

In the fitting of any artificial limb, the goal of the prosthetic is simply to restore to the amputee the ability to perform everyday activities in an easy, natural, and comfortable manner [21].

For an above knee amputation a prosthetic is composed of a lining, a socket, a limb and any structural and mechanical components. Although not all prosthetic legs utilize one, a lining is used as a residual limb-socket buffer to prevent any further damage to the leg and skin while also providing comfort. Traditionally speaking, the lining has been made with silicone, silica gel or polyurethane; even some with harder plastics. However, each material has its own unique set of mechanical properties and disadvantages [22].

Liners are widely employed in standard practice because of their capacity to adhere to the skin, provide an abrasion barrier, and distribute stresses [23]. Previously, prosthetic liners were constructed of open and closed cell foams like Pelite. Rolling on the residual limb with silicone or other elastomer-based liners now allows for greater longevity and a more effective cushioning effect [24]. Bench testing indicates that elastomeric gel liners reduce shear stress on the skin and provide more cushioning on bony prominences since they are soft, compressible, and similar to biological tissues [23 and 24].

Because of their high friction coefficient, urethane liners provide better skin adhesion and thus avoid skin breakdowns, whereas silicone elastomers provide better suspension and are thus preferable for softer stumps, in order to minimize the relative displacement between the socket and the residual limb tissues [25].

Roll-on liners can also be connected to an air evacuation system based on a unidirectional valve or a VAS system (liner-fit suction), providing for a better fit than distal locking devices. Finally, hypobaric seals combined with valves or VAS can be employed (Seal-In liner in Fig. 2.1a) [26].

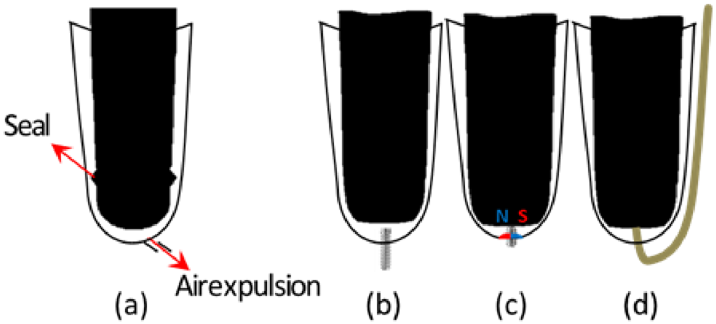


Fig. 2.1: From left to right: Seal-In (a), Pin-lock (b), Magnetic-lock (c), Lanyard strap (d) [26]

The distribution of pressures and shear loads on the tissues, as well as temperature and volume changes influencing the residual limb, are determined by a specific mix of socket shape and materials, in conjunction with a unique suspension system. All of these characteristics are interconnected: volume variations may indicate a poor fit of the prosthesis, but they may also indicate a changing distribution of pressures and shear stresses on the limb residual tissues. This can result in friction phenomena that, when combined with the barrier formed by the socket and liner, change the thermoregulation system by causing sweating, irritation, and odor [25].

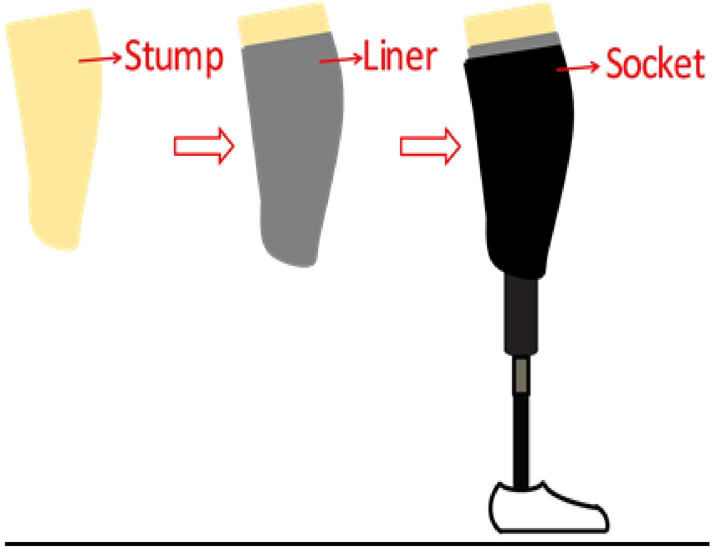


Fig. 2.2: Representation of a socket provided with a liner between it and the stump [25]

2.3 Polymer Materials

Polymers are long molecules (macromolecule) composed of repeating structure units typically connected by covalent bonds to form the polymer. These long molecules are bonded together by weak "Van der Waals" and hydrogen bonds, or by these plus "covalent cross – links" [27].

Polymers are low weight, good corrosion resistant material with low strength and stiffness and they are not suitable for use at high temperature. They show some of the features of a material near their melting point, they creep and elastic deflection which appears on loading increases with time. This is just one important way in which polymers differ from metals and ceramics, and it necessitates a different design approach. These polymers formed too many shapes, ranging from plastic bags to mechanical gears to bath tubes. Engineering polymers are designed to give improved strength or better performance at elevated temperatures. Some of the engineering polymers can perform at temperatures as high as 300 °C.

There are three types of polymers that include thermoplastics, thermosets and elastomers, which have many useful physical properties [28]. Figure (2.3) shows types of polymers used for external lower limb prosthetic and orthotic.

2.3.1 Thermoplastic Polymers

Thermoplastic has polymer chains that are not cross-linked therefore it turns to a liquid when heated and freezes to a rigid state when cooled sufficiently. Utmost thermoplastics are of high molecular weight whose chains are associated through weak Van der Waals forces such as "PE" polymer stronger dipole-dipole interactions and hydrogen bonding (nylon) [29].

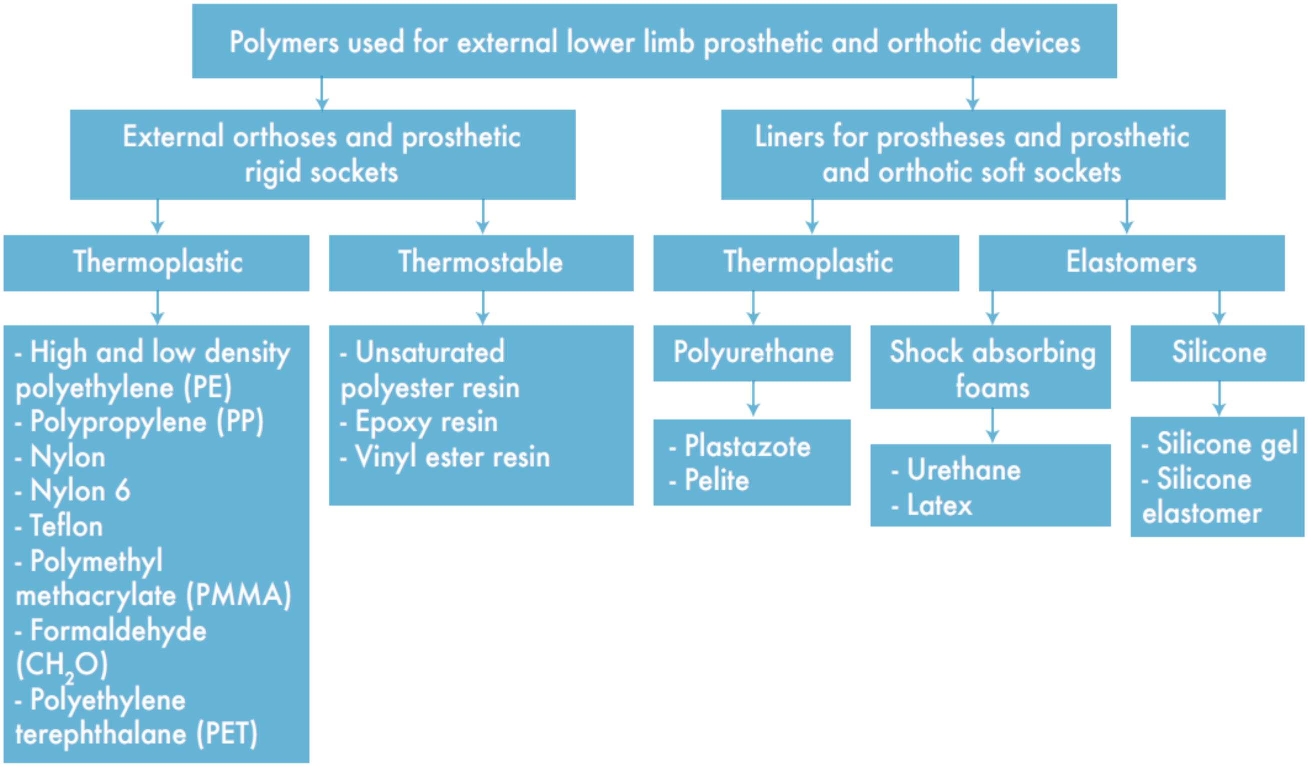


Fig. 2.3: Polymers used for external lower limb prosthetic and orthotic devices [20]

2.3.2 Thermosetting polymers

Thermosetting polymers such as epoxy resins have not been so common in orthopaedics because of variable biocompatibility, durability characteristics. These materials can have much better processing characteristics than the thermoplastics and allowing the fabrication of more sophisticated composite structures [30 and 31].

2.4 Polymer Blends

A polymer blend or polymer mixture is a colleague of a class of materials in which two or more polymers are blended together to create a new material with different physical properties. By combining in an advantageous manner, the properties of the alloying components and in some cases the properties of the blends are superior to those of the individual components. The technology of polymer blends improved materials with full set of desired specific properties at the lowest cost, e.g. a combination of strength, toughness and solvent resistance, etc. Blending also benefits the manufacturer by offering improved process ability, product uniformity, quick formulation changes, plant flexibility and high productivity [32 and 33].

2.4.1 Types of polymer blends

According to thermodynamics points of view, polymer blends can be classified to two types miscible and immiscible. Only a few commercially significant polymer blends are based on miscible and partially miscible (i.e., miscible within a narrow concentration range) polymer pairs. It is uncommon to combine two or more polymers and produce a blend with useful properties, and when creating a new polymer blend from immiscible resins, a specific strategy for mixture compatibility is required to ensure optimum physical performance and long-term stability [34].

2.4.1.1 Miscible (Homogeneous) polymer blend

Miscible polymer blends consist of single phase structure and miscible system thermodynamically has metastable properties between the components of blend. The produced miscible polymer blends must obey the thermodynamic criteria of miscibility which provide this type of polymer blends [35 and 36].

2.4.1.2 Immiscible (Heterogeneous) polymer blend

A blend exhibits more than two phases. One unusual property of immiscible blends is, that one, made from two amorphous polymers which has two glass transition temperatures, since the two components are phase separated, they and their T_g separate. In fact, scientists frequently evaluate a blend's Tg to determine whether it is miscible or immiscible. If two Tgs are discovered, the blend is immiscible. If only one Tg is seen, the mix is most likely miscible.

If an immiscible blend is helpful, the inhomogeneity generated by the separate phases is on a small enough scale that it is not noticeable disusage (blends that are miscible in certain useful ranges of composition and temperature, but immiscible in others, are also called compatible blends) [35].

Figure (2.4) shows idealized expected property combinations from blending of two polymers that are either miscible (solid center line), immiscible and un-compatibilized (bottom line), or immiscible and compatibilized (top line) [37].

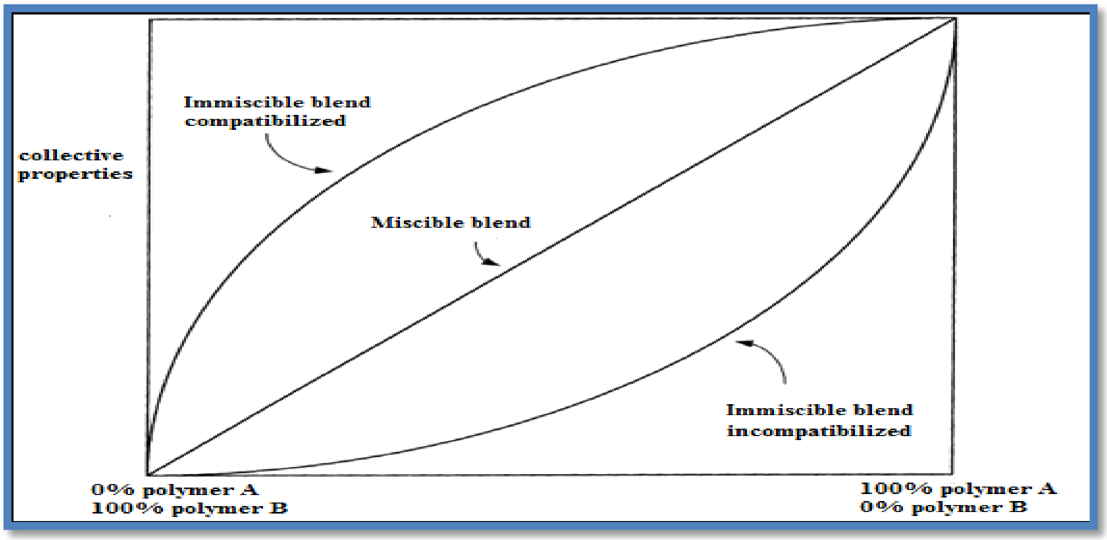


Fig. 2.4: Potential effect on polymer blend properties with component concentration [38]

2.4.2 The advantages of blending [39]

A. Blending can improve resin or product performance by:

1. Developing materials with all needed qualities at the lowest possible cost.

2. Improving the performance of engineering resins by adding less expensive polymers.

3. Improving specific characteristics.

- Toughening of brittle polymers without the use of low molecular weight additions.
- Adding a stiffer, heat-resistant resin to the mix may boost modulus and dimensional stability.
- Adding semi-crystalline polymer to an amorphous resin to increase solvent and chemical resistance.
- By combining flammable and non-flammable polymers, flame resistance is improved.
- Polymers with -OH or -SH functionality in blends produce permanently anti-static blends (e.g., ethylene oxide-coepichlorohydrin with ABS/PC blend).
- Biodegradable materials created from biodegradable resin.
- Blending allows for the production of multi-layered integrated structures.

4. Making it possible to recycle industrial and/or municipal plastic trash.

5. Blending technology allows for the restoration of high molecular weights of partially degraded polymers, allowing for the creation of high performance items from plastic waste.

B. Blending could improve process-ability

1. The high glass transition temperature (Tg) resin can be treated at temperatures considerably below the thermal degradation limit by integrating a miscible resin with a lower glass transition temperature (Tg) (for example, PS/PPE mixes).

2. The use of an immiscible, low viscosity resin, such as LCP/PEEK blends, lowers pressure drop between dies or runners, enhancing productivity.

3. Blending with resins that have high strain hardening (SH) on their own (e.g., LDPE in a PO blend) or that generate long chain branches when reactively blended (e.g., PS in a PO blend) results in mixes with a regulated degree of SH. These materials perform better in technologies requiring a large extensional flow field, such as film blowing, blow molding, wire coating, and foaming.

4. Elastomeric particle insertion increases gas bubble nucleation, which stabilizes the foaming process, reduces bubble size, and lowers final foam density.

5. The addition of a biodegradable resin to an engineering or speciality resin enables for the formation of a controllable amount of foaming gas during the later stages of processing, especially injection molding.

6. The molecular weight distribution is extended by blending different grades of the same resin, making processing easier and more stable (as well as better mechanical performance).

7. Product uniformity (and consequently plant efficiency) is improved by blending (and thus plant efficiency).

8. Blending enables for quick formulation changes, increasing plant flexibility and output.

2.5 Interpenetrating polymers networks (IPN) [40]

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

When two or more polymers are mixed, the resulting composition can be called a multicomponent polymer material. There are several ways to mix two kinds of polymer molecules; as in an extruder, results in a polymer blend. If the chains are bonded together, graft or block copolymers result: Bonding between some portion of the backbone of polymer I and the end of polymer II, the result is called a graft copolymer; chains bonded end to end result in block copolymers. Other types of copolymers include AB-cross-linked copolymers, where two polymers make up one network, and the IPNs, and semi-IPNs (SIPNs).

In many ways, IPNs are related most closely to block copolymers. In the block copolymer systems, the length of the block determines the size of the domains. Correspondingly, the cross-link level (length of chain between cross-links) plays a major role in determining the domain size of IPNs. Short blocks or short chain segments between cross-links both make for small domains under many conditions. However, there are some important differences. Short block lengths are important because they increase miscibility between component polymers. For the case of IPNs, there is growing evidence that cross-links decrease the miscibility of the system relative to the corresponding blend, for systems in which the linear component polymers are miscible.

2.5.1 Kinds of IPNs

IPNs can be made in many different ways. Brief definitions of some of the more important IPN materials are as follows:

- **Sequential IPN.** Polymer network I is made. Monomer II plus cross-linker and activator are swollen into network I and polymerized in situ; as in Figure 2.5A. The sequential IPNs include many possible materials where the synthesis of one network follows the other.

- **Simultaneous interpenetrating network (SIN).** The monomers or pre-polymers plus cross-linkers and activators of both networks are mixed. The reactions are carried out simultaneously, but by noninterfering reactions. An example involves chain and step polymerization kinetics; as in Figure 2.5B.
- **Latex IPN.** The IPNs are made in the form of latexes, frequently with a core and shell structure. A variation is to mix two different latexes and then form a film, which cross-links both polymers. This variation is sometimes called an interpenetrating elastomer network (IEN).
- **Gradient IPN.** Gradient IPNs are materials in which the overall composition or cross-link density of the material varies from location to location on the macroscopic level. For example, a film can be made with network I predominantly on one surface, network II on the other surface* and a gradient in composition throughout the interior.
- **Thermoplastic IPN.** Thermoplastic IPN materials are hybrids between polymer blends and IPNs that involve physical crosslinks rather than chemical cross-links. Thus, these materials flow at elevated temperatures, similar to the thermoplastic elastomers, and at use temperature, they are cross-linked and behave like IPNs. Types of cross-links include block copolymer morphologies, ionic groups, and semi-crystallinity.
- **Semi-IPN.** Compositions in which one or more polymers are cross-linked and one or more polymers are linear or branched are semi-IPN (SIPN).

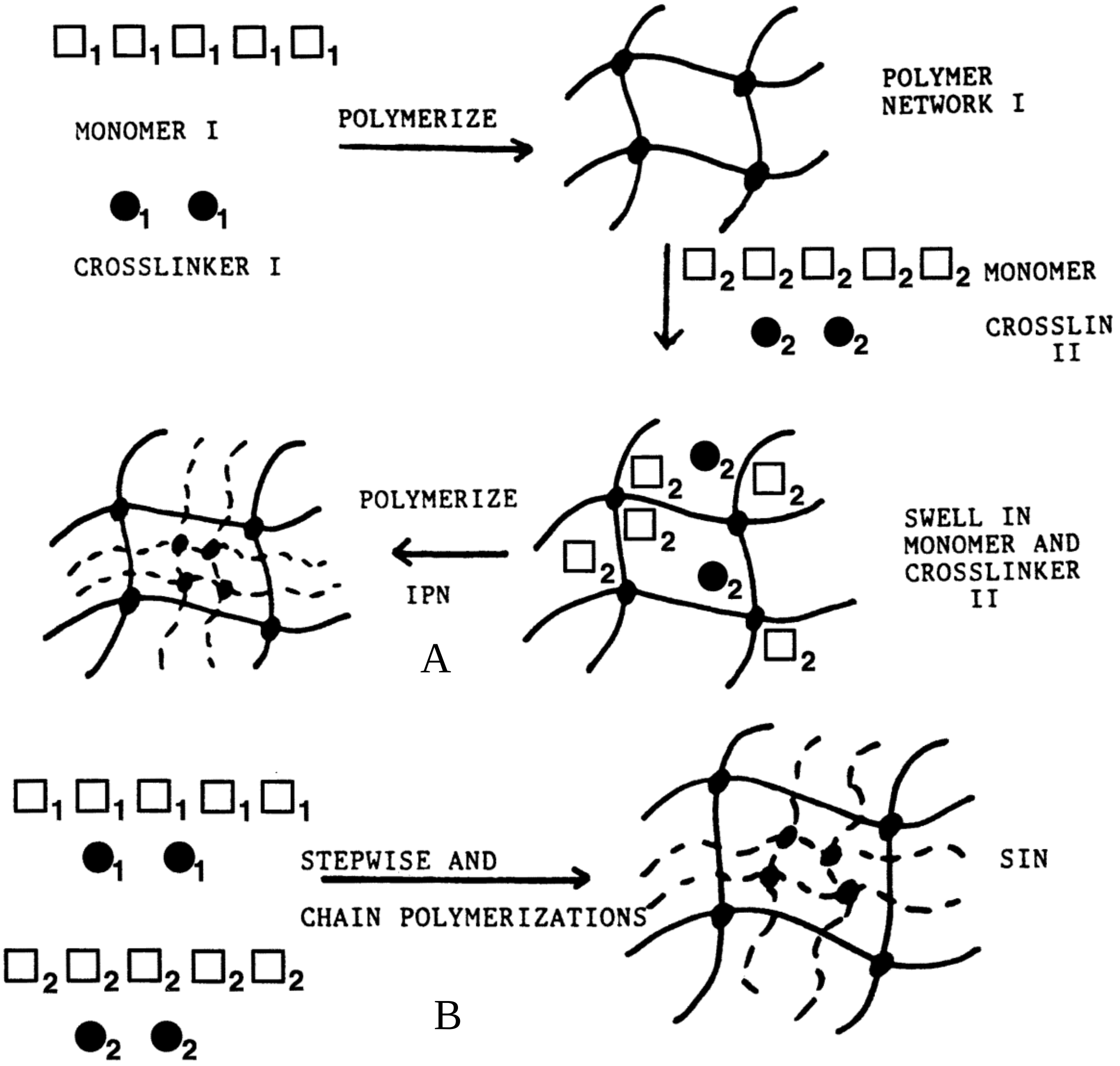


Fig. 2.5: Basic synthesis methods for IPNs. A, Sequential IPNs; B, simultaneous interpenetrating polymer networks (SINs)[40]

2.6 Biopolymers

Biopolymers are polymers produced by living organisms. They have all lived on our planet for millions of years, giving microbes enough time to evolve enzymes capable of destroying their structure and rendering them biodegradable. Their environmental impact at the end of life is often modest [41]. However, in at least two cases, this is not the case:

1. When the biopolymer is exposed to an unfavourable environment for biodegradation. Because it lacks oxygen and water, a landfill, for example, does not provide appropriate conditions for biodegradation. Under anaerobic conditions (the absence of oxygen), the biopolymer, like organic waste in general, degrades, producing biomass, methane (CH_4), carbon dioxide (CO_2), and water, as well as other small molecules (NH_3, N_2, N_2O, H_2S, and so on). Methane is a far more potent greenhouse gas than CO_2 and, unlike CO_2, is not easily reabsorbed by plants.

2. Once mixed with other polymers in a recycle stream, the biopolymer will behave as a pollutant because biopolymers are not generally recyclable and degrade under recycling processing conditions [41].

2.6.1 Requirements of biomaterials

Biomaterials must have unique features that can be adjusted to satisfy the needs of a certain application. A biomaterial, for example, must be biocompatible, non-carcinogenic, corrosion-resistant, and have minimal toxicity and wear [42].

2.6.2 Classification of biomaterials

Biomaterials are usually categorized into two types: i) biological biomaterials, ii) Synthetic biomaterials. another classification: i) biostable, ii) biodegradable [42, 43].

2.7 Nano composite

In recent years, there has been an increasing interest in materials applications in medical areas. Here we define a Nano composite as the combination of two distinctly dissimilar materials, by the degree of dispersion, interfacial properties and also, properties of the individual components determined the overall behaviour of composite materials. A

Nano composite is termed when at least one of the materials within the composite has a Nano-scale [43].

Due to the high-performance effect of small amounts of additives compared with other fillers, low-weight benefits can be expected. A huge interfacial specific surface area can reach up to 1000 m^2/g filler, which is a major specific feature of Nano composite materials [44].

Nano composites in medical applications must have special and important properties that can be tailored to meet the needs of a medical application. For example, a medical Nano composites must not be harmful to living tissue, non- having the potential to cause cancer, corrosion-resistant, and has low poisoning [45 and 46].

2.7.1 Applications of silicone rubber nano composites

Many lower limb amputated surgeries are performed in Iraq each year, with the major reason being victims of car bombs, peripheral vascular disease, and/or diabetes, and other causes being various accidents, infections, tumors, and the patient can continue out his routine, he commonly utilizes prosthesis [47].

Because of the use of prostheses, soft tissue in the residual limb carries body weight, Liner socket that separates the residual limb from the prosthetic component [48]. Amputees do not use synthetic liners if they are uncomfortable since they help to convey soft tissue loads to the mechanical limb and must be manufactured in a way that affords patient relief. One of the drawbacks of utilizing synthetic liners is the development of skin problems in the amputee stump. The skin of the limb is exposed to many abnormal conditions during weight-bearing. The skin is exposed to shear stress forces, which can cause edema of the stump and blisters due to shear forces and stress that occurs at the end of the stump is exacerbated by a poor nutritional status of the skin, vascular insufficiency, or local pressure from a poorly made prosthesis [49].

Furthermore, sweat cannot drain freely from the skin area where the liner is worn. In addition to abscesses, cellulitis, pyoderma, and sweat gland inflammation, increased moisture that can cause skin inflammation and bacterial infection [50].

Silicone rubber offers a wide range of medical applications. The most essential of these applications include internal or semi internal equipment that make contact with the human body or skin. To be used safely inside the human body, polymers used in biomedical applications must meet particular requirements and regulations. To begin with, they must be biocompatible, non-toxic to the human body, and have high tissue constancy [51].

Polymer biocompatibility is determined by several factors, including its chemical structure. Depending on the placement and movement of the material, as well as the surrounding human environment, the body's response to a polymeric medical device can be accepted or rejected [52]. As a result, for biomedical applications, selecting the proper polymers with high stability against the previously listed conditions is crucial [53].

2.8 Materials

2.8.1 Silicone Rubber

Silicones, one of the most often utilized classes of biomaterials, are renowned for their inherent biocompatibility and resilience. The material's intrinsic chemical and thermal stability, low surface tension, and hydrophobicity are responsible for these fundamental properties [54]. Due to these qualities, silicones have a wide range of applications in medical liner and other items. Silicone elastomer is a thermosetting material that is amenable to diverse molding, dipping, and extrusion processes. Silicones are a class of synthetic polymers whose backbone consists of repeated silicone-oxygen linkages (siloxane bonds), as depicted in figure (2.6) [55].

In addition to forming polymeric chains with oxygen, silicon atoms also create bonds with organic groups, notably methyl groups. This most prevalent form of silicone is known as poly-di-methyl-siloxane or poly-dms for short (PDMS).

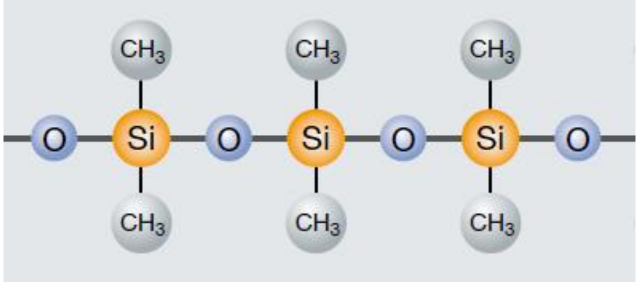


Fig. 2.6: Silicone rubber chemical structure [56]

PDMS is a liquid whose viscosity varies with chain length. Cross-linking processes can turn PDMS polymers into three-dimensional elastomeric networks by forming chemical links between adjacent chains. Silicone rubbers have excellent heat ageing resistance. Although silicones do not demonstrate strong strength at room temperature, they retain their qualities at high temperatures significantly better than other rubbers [56 and 57].

There are two varieties of silicone elastomers available, both with the same basic qualities. Polymers having a high molecular weight and moderately long polymer chains are found in solid silicone rubber. HTV (high temperature vulcanizing) and RTV (room temperature vulcanizing) rubbers are thermosetting rubbers that are vulcanized using heat. RTV silicone rubber is classified as condensation cure catalysed by tin salts or addition cure catalysed by platinum. The silicon-oxygen bond is very resistant to ozone, oxygen, heat (up to 315 ºC), UV light, moisture, and general weathering effects, while the methyl substituents add flexibility [58].

Liquid silicone rubber is made up of polymers with lower molecular weights and thus shorter chains. It has better flow characteristics. Liquid silicone rubber is always addition-curing (catalysed by platinum) [59].

2.8.2 Polyurethanes

Polyurethane is among the most important classes of industrial polymers with the fastest growing global market. This is due to the ability to modify the starting chemicals for a range of polyurethanes with desired properties. The global polyurethane market was valued at more than $65 billion and is expected to increase at a rate of 3.2% until 2027 [60].

The PUs compounds are generally thermoset polymers formed by a addition reaction between a multifunctional alcohol (polyol) and a di- or tri- (isocyanate), resulting in a reticular urethane structure [61 and 62], as seen in the reaction below:-

$$\underset{\text{Polyol}}{(HO - R - OH)n} + \underset{\text{Isocyanate}}{(O = C = N - R0 - N = C = O)n} \longrightarrow \underset{\text{Urethane [62]}}{[-CO – NH- R0 - NH - CO - O - R - O]n}$$

Isocyanates are classified according to their chain structure, with aromatic derivatives (methyldiphenylisocyanate, MDI, and toluendiisocyanate, TDI). In addition to the polyol and isocyanate, a variety of additives like as catalysts, surfactants, antioxidants, pigments, and fillers are used in the synthesis of PUs to adapt the product's properties to its intended purpose [64 and 65].

Polyurethanes are an immensely versatile class of polymers used in insulators, foams, elastomers, synthetic skins, coatings, adhesives, and so forth. Polyurethane was first developed through basic diisocyanate poly addition reactions by Dr. Otto Bayer and partners. In 1937, it reached industrial-scale synthesis and it was established in the market in the 1950s.

Polyurethanes are characterized by the presence of a urethane linkage, and they can be easily synthesized through an addition reaction between alcohol and an isocyanate. However, a functionality of at least two is required in both the starting materials to prepare polyurethane. Polyurethanes are widely explored because of their facile synthesis that can be performed at room temperature and under mild conditions [60].

The modifications in the structure of polyols (soft segments) or isocyanate (rigid segments) can be easily performed using various chemical approaches that provide polyurethanes with a range of properties. For example, an elastic polyurethane can be synthesized by using a polyol with a linear structure and high molecular weight with low functionality. Meanwhile, a rigid polyurethane can be prepared by using a polyol with aromatic groups in the structure, low molecular weight, and higher functionality for cross-linking.

The soft segment is usually a polyether or polyester polyol while the hard segment is composed of a diisocyanate and chain extender. The soft segment provides elasticity, whereas the hard segment contributes strength and rigidity through physical cross-linking points. A balance in chemical structure (hydrophobicity and hydrophilicity) provides water-dispersible polyurethanes for coating applications [60 and 62].

When polyurethane foams are used as a thermal insulator in housing, energy consumption decreases by 75% to 95%, creating positive economic and sustainable effects. Their high electrical resistance allows application for electrical insulation and dielectrics in electronic devices. The fact that polyurethanes are lightweight, accompanied by their high mechanical strength, makes them a key component in the automotive sector for improving efficiency due to less fuel consumption, increased safety, and enhanced comfort of the vehicles.

Flexible foams find a wide range of applications in the automobiles and furniture industries where they are used, such as in beds, couches, and seat cushions. Flexible polyurethanes are also used in the footwear industry as dampers in shoes and in the packing industry to protect shipments from damage. Their chemical inertness and environmental stability make them very suitable for use in adhesives and anticorrosion coatings.

The latter has been receiving great attention, as corrosion is one of the major issues in many countries and is responsible for an average gross domestic product loss of 3%. Some of the novel applications of polyurethanes in areas like biomedical and tissue engineering are possible as a result of their chemical stability, high surface area, and flexibility. They can be used as synthetic scaffolds for the culture of cells or materials to aid in the transport of fluids in the body, such as in synthetic veins or components of a pace maker [60, 61 and 62].

Despite the large number of applications and huge market for polyurethanes, certain issues, such as their high flammability, restrict their use in valuable applications and merit scientific attention.

Additionally, most of the chemicals used in the preparation of polyurethanes are derived from petroleum-based resources, and there are growing concerns about sustainability and toxicity associated with polyurethanes. The instability and degradation of polyurethanes in outdoor applications also need attention [60 and 63].

Polyurethane elastomers outperform silicone elastomers in terms of mechanical qualities, particularly rip and abrasion resistance and flex fatigue life. The chemical composition of these elastomers provides synthetic polymer scientists with numerous chances to customize the structures to satisfy specific requirements. Polyurethanes, in general, have strong compatibility with tissue and blood, as well as good mechanical degradation resistance [66].

The main materials used for the synthesis and formulation of polyurethanes such as polyols, isocyanates, catalysts, blowing agents, surfactants, and additives.

Blowing agents, such as water, are applied during the preparation of polyurethanes to provide foams. They also play an important role in controlling the cellular structure and morphology by forming bubbles within polyurethanes during the foaming process [63].

Surfactants are responsible for improving the dispersion of the polyol and isocyanate to ensure a homogenous system and to provide stable cellular structures by minimizing the collapse of cells during the curing process. Sometimes, additives are incorporated in polyurethanes to reduce the cost and provide specific applications such as flame retardancy, smoke suppression during combustion, color, UV resistance, and mechanical strength, Figure (2.7) shown polyurethane molecule [66].

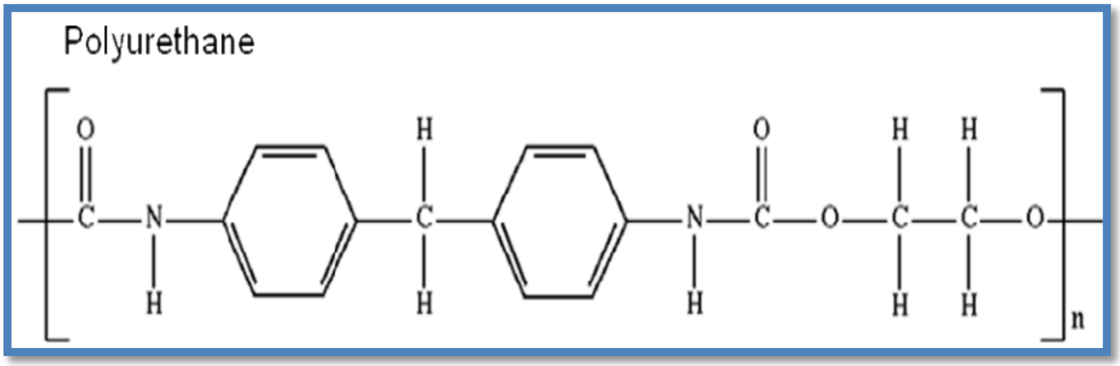


Fig. 2.7: Schematic of polyurethane molecule [65]

2.8.3 Chitosan

Chitin or poly (β-(14)-N-acetyl-D-glucosamine) is a significant natural polysaccharide first recognized in 1884 as demonstrated in figure (2.8). This biopolymer is synthesized by an enormous amount of living organisms and belongs, after cellulose, to the most abundant natural polymers [67].

In the native state, chitin happens as ordered crystalline micro-fibrils that form structural elements in the exoskeleton of arthropods or in the cell walls of fungi and yeast. So far, crab shells and shrimp shells are the primary commercial sources of chitin. In industrial processing, acid therapy extracts chitin to dissolve calcium carbonate, followed by an alkaline solution to dissolve proteins. In addition, a decoloration step is often added to remove pigments and achieve a colorless pure chitin. All these treatments must be adjusted to the source of chitin since variations in the ultrastructure of the original material in order to generate first a high-quality chitin and then chitosan (after partial deacetylation).

During conversion into distinct conformations, chitin is infusible and sparingly soluble. The issue of its solubility is a significant issue in the growth of both chitin processing and utilizing as well as its characterization [68].

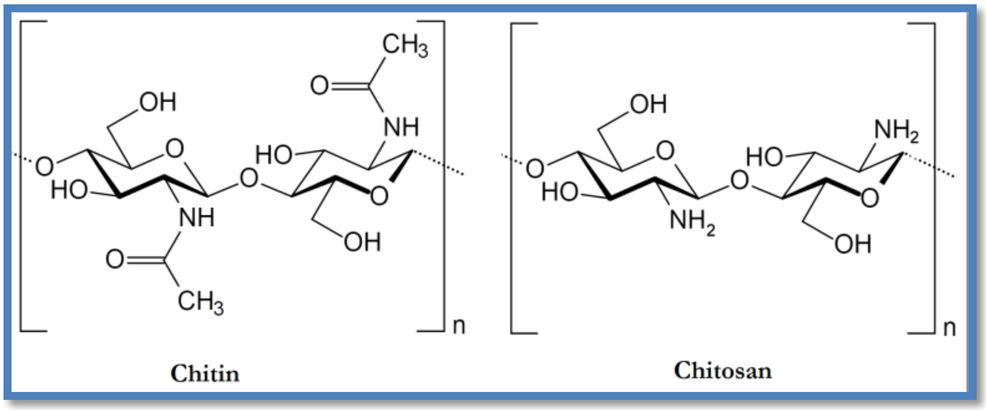


Fig. 2.8: Chemical structure of chitin and chitosan [69]

Chitin becomes more useful when it is converted into chitosan (through partial deacetylation under alkaline circumstances) [69 and 70].

Several applications for chitin and chitosan are outlined, including medication discharge, wound dressing, and biofilms. It is critical to note that chitin is a natural polymer that is both biocompatible and biodegradable in the body, making it popular in biomedical and pharmaceutical applications. Furthermore, the superior film forming properties are beneficial for wound dressing, artificial skin, and packaging [68].

Chitosan is biocompatible, biodegradable and non-toxic, so that it can be used in medical applications such as antimicrobial and wound healing biomaterials. Because of its capacity to bind with cholesterol, lipids, proteins, and metal ions, it is also utilized as a chelating agent [71].

Chitosan's polycationic nature also explains its analgesic properties. To understand chitosan biodegradability, it is important to remember that it is not only a polymer with amino groups, but also a polysaccharide with breakable glycosidic bonds. In fact, several proteases, primarily lysozyme, degrade chitosan in vivo.

Chitosan has many applications due to its many appealing properties such as biodegradability, natural origin, abundance, reactivity, and so on. These include medical, agricultural, food processing, nutritional enhancement, cosmetics, and waste and water treatment [71].

2.8.3.1The relationship between Structure and Properties

Chitosan differs from chitin in that it contains amino groups, which results in its solubility in dilute acids (pH < 6) and the ability to form complexes with metal ions, allowing it to be used for waste water treatment and purification. Chitin, on the other hand, has very few practical applications due to its poor solubility, if any. Interestingly, chitosan's aqueous solubility is pH dependent, allowing for processability under mild conditions [71].

Chitosan with protonated amino groups forms a polycation, which can then form ionic complexes with a wide range of natural or synthetic anionic species, including lipids, proteins, DNA, and some negatively charged synthetic polymers as polymers (acrylic acid). In fact, chitosan is the only naturally occurring positively charged polysaccharide [70].

2.8.3.2 Medical applications of chitosan

Because of chitosan's capacity to act in a variety of ways, it has a wide range of applications in the medical business, including orthopedic and periodontal applications [73]. Tissue engineering [74], drug delivery [71], and wound healing [72] are three examples.

Several biomedical applications include artificial skin, surgical sutures, artificial blood vessels, controlled drug release, contact lenses, eye humor fluid, bandages, sponges, burn dressings, blood cholesterol control, anti-inflammatory, tumor inhibition, anti-viral, dental plaque inhibition, bone healing treatment, wound healing accelerator, hemostatic agent, antibacterial agent, antifungal agent, and weight loss effect [72].

2.9 Surface modification overview

Surface modifications are classified into two types: (i) physicochemical modifications that involve changes to the surface atoms, compounds, or molecules, and (ii) surface coatings that are made of a different material than the underlying structure.

Chemicals reactions (e.g., oxidation, decrease, salinization, and acetylation), etching, and mechanical roughening / polishing and patterning are examples of physicochemical alterations. Grafting (including biomolecule tying), non-covalent and covalent coatings, and thin film deposition are examples of over-coating alterations.

While the specific needs of the surface modification approach vary depending on implementation, many qualities are usually desirable. Thicker coatings frequently have a negative impact on the material's mechanical and functional properties, therefore thin surface modifications are desired for most applications.

Surface alteration should ideally be limited to the outermost molecular layer (10-15), although thicker coatings (10-100 nm) are used in practice to ensure consistency, durability, and functioning. Figure 2.9 represent the surface modification techniques.

Surface stability modification is a fundamental need for proper biological efficiency. Surface stability refers not only to mechanical endurance (cracking strength, delamination, and de-bonding), but also to chemical stability, which is especially important in hostile, chemically active environments like biological media. Following exposure to biological fluids, polymers and ceramics exhibit a variety of surface rearrangements, including translation of surface atoms or molecules in response to environmental variables and mobility of bulk molecules to the surface and vice versa [76].

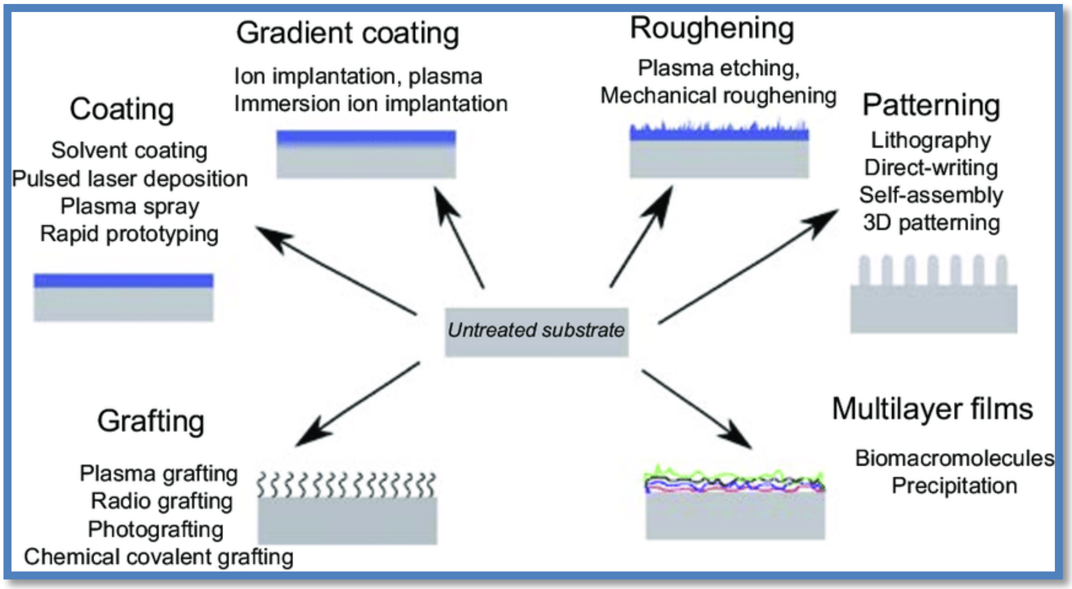


Fig. 2.9: Schematic representation of the surface modification techniques [77]

2.9.1 Physicochemical Surface Modifications

Method of physicochemical analysis Surface modification of polymers via physicochemical processes includes surface coating, polishing, grit blasting, etching, vapor deposition, and self-assembly procedures. As a result, physicochemical methods are further classified as (1) gas phase or radiation methods, (2) liquid and bulk phase methods, and (3) a combination of (1) and (2) methods (2). The polymer surface topography can be adjusted in most of these ways by attaching new molecules/elements/ions via physical interactions such as van der Waals forces, hydrogen bonding, and/or hydrophobic interactions [78].

2.9.2 Mechanical methods

Roughening and micromanipulation are two mechanical methods that can be used to change the surface of biodegradable polymers. In this scenario, mechanical methods, like physicochemical approaches, use a mechanical process to clean the polymer surface and modify the surface chemistry in the absence of chemicals [78].

2.9.3 Biological methods

Immobilizing biomolecules and cells on polymer surfaces can also modify their physiological properties. As a result, a diverse family of polymer-biomolecule hybrids capable of responding well to biological surroundings emerges.

It is crucial to note that "immobilization" refers to the temporary or long-term localisation of biomolecules on or within a polymer. Enzymes, antibodies, affinity proteins, living cells, cell receptor ligands, and medicines have all been immobilized using one of three methods: (1) physical adsorption, (2) physical entrapment, or (3) chemical or covalent attachment.

The biological method, like the physicochemical and mechanical methods, offers benefits and drawbacks. Improved stability, the flexibility to modify the microenvironment of the biomaterials and reuse them, a lower cost and higher purity product, and, most importantly, no immunogenic responses are among the benefits.

As a result, sterilization is highly difficult; there is resistance in mass transfer between the substrate and product, as well as a greater potential for products to obstruct sterilization. Furthermore, biologically modified polymers are typically used in medical applications [79].

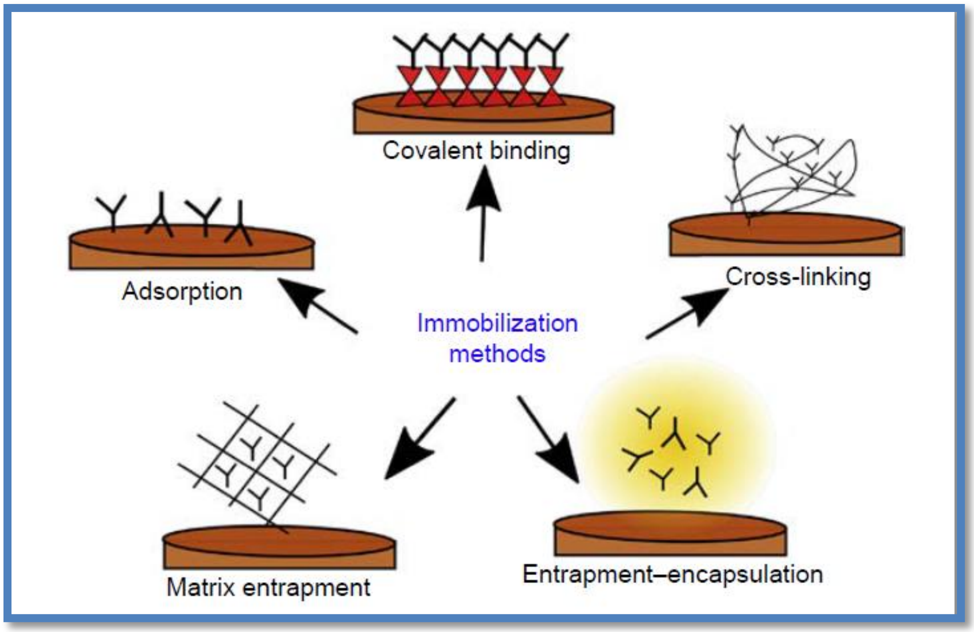


Fig. 2.10: Illustration of different methods by which biomolecules can be immobilized on the surface [79]

2.10 Surface Modification of IPN (SiR/PU)

Outbreaks of foodborne disease and nosocomial infections caused by bacterial contamination and resistance are the two most serious public health issues confronting the food sector and health practitioners today. It is generally known that bacteria can build sessile-structured colonies known as biofilms that can survive for long periods of time by clinging to various surfaces. Furthermore, bacteria within a biofilm may communicate and exchange genetic material associated with pathogenicity and virulence, resulting in significantly increased resistance to antibiotics and therapies [75]. Preventing bacterial formation, spread, and adhesion may thus be part of the solution to limiting bacterial infections, contaminations, and resistance.

Antibacterial coatings may help to reduce the prevalence of nosocomial infections as well as foodborne illnesses by preventing the formation and spread of harmful microorganisms. Antibacterial coatings are now being developed by researchers in the fight against bacterial contamination [70].

The majority of bioactive chemicals used in commercially available antimicrobial coatings are silver, copper (both in the form of nanoparticles), and antibiotics. While the beneficial effects of several bioactive chemicals on pathogenic germs are widely known, their eco-toxicological influence has received less attention [70].

As a result, there is a considerable surge in interest in safer and more environmentally friendly methods of cleaning and controlling microbial infection and/or pollution employing safer antimicrobial coatings. Chitosan is a natural polymer that has potent antibacterial properties against a wide variety of bacteria, yeasts, and molds [76].

2.11 Covalent coating

To improve liner stability and adhesion, covalent coating techniques rely on direct coupling of overcoats to the base material [76].

A common technique for surface modification is polymer coating of medical equipment via noncovalent adsorption. Despite its advantages, such as ease of use and batch production of polymers for coating, the product's efficacy is typically hampered by the slow attrition of the polymer from the device surface, particularly in high-shear stress settings.

Covalent attachment is a more durable means of altering the surface properties of medical devices. However, because of the chemical inertness of the surface, chemical modification of polydimethylsiloxane (PDMS) can be problematic. As a result, the material is irradiated or scratched, resulting in the formation of surface active groups. Alternatively, the surface is changed to give chemical functionalities that may stimulate polymerization, such as bromoester formation, which is essential for atom transfer radical polymerization (ATRP) [80].

Recent study has concentrated on coating the surface of IPN with natural products against bacteria to enhance their antibacterial characteristics and decrease the Biofilm surface formation. The most important of these materials is the natural chitosan, which is abundant in nature, and this is what we will discuss in this research [81].

The IPN surface will be covered with a chitosan as a thin-layer. But before coating the chitosan on the surface's IPN, the IPN surface should be firstly modified to generate free radicals capable of bonding with the material to be coated, As well as a modification of the coating material (Chitosan) in order to form a bond between the surface and Chitosan.

These amendments, which we shall discuss here in this search, are the chemical modifications of both substances (the base material and the coating material) [76].

Recently used APTES and glutaraldehyde are efficient techniques that introduce organic molecular by forming the base of Schiff. Surface analysis findings have shown that chitosan can be immobilized on the surface of IPN using these techniques [82].

This method is considered to be one of the most effective modern methods for coating polymer surfaces in general and special silicone rubber to give a surface coated with the material to be painted according to the properties intended for the surface. It is characterized by its consistency between the base material and the coating material, which gives better stability for the coating layer and its longer use time despite the friction and temperature conditions [76].

The majority of investigations used aminosilanes, namely 3-aminopropyltriethoxysilane (APTES). Other authors, however, have advocated 3-chloropropyltriethoxysilane (CPTES).

Unlike APTES, CPTES does not require activation and has the capacity to immediately engage the biomolecule's nucleophilic groups (e.g. amines, thiols etc.). A recent research, for example, advocated co-immobilization of oligopeptides using a monolayer of 3-chloropropyltriethoxysilane (CPTES) as a cross linker [83].

CPTES contains a chlorine molecule, a surely understand electron pulling out bunch. Subsequently, chlorine draws the electronic thickness from the adjoining C, accordingly yielding an electrophilic (electron inadequate) -CH2-bunch. Peptides and proteins contain free amino gatherings because of the presence of the N end and a few amino corrosive side chains, which have nucleophilic properties and propensity to respond with electrophiles. Thusly, the organo-utilitarian gathering of CPTES will respond with peptides and proteins. The connection between the chlorine and carbon on CPTES is energized because of the distinction of electro-negativities among carbon and chlorine [84].

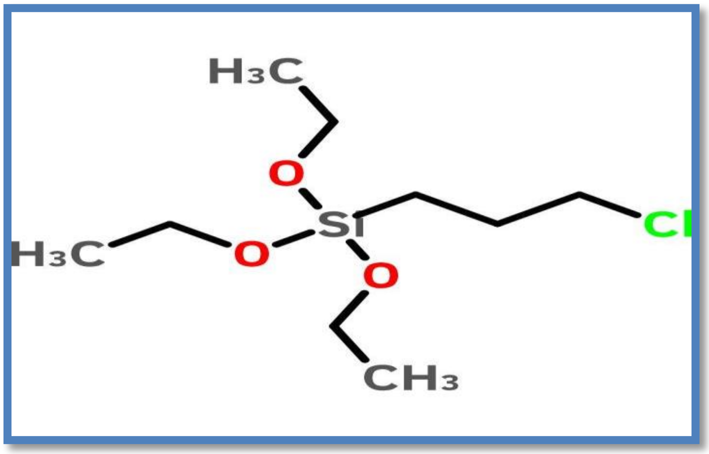


Fig. 2.11: Chemical structure of CPTES [84].

2.12 Literature Reviews

There was limited literature available on the using of IPN of prosthetic liner and of prosthetics liners perspiration control especially above knee prosthesis:-

Joan E. Sanders et al., in 2004, presented 15 elastomer linings' mechanical properties. Prosthetic products were tested under pressure, frictional loading, shear, and tensile situations. The test was performed at equal loading levels for all species, and the results were recorded at the various limb amputation sites. In general, silicone gel liners from the same groups were very similar to one another. When compared to silicone elastomer goods, it had low hardness, shear stress, and tensile strength, indicating light, cross-linked structures with significant fluid content. Silicone rubber products stretched to response groups better than gel bushings, suggesting a greater range of compression, shear, and tensile stiffness values. Urethane is a substance that can be compatible with the skin (a leather-like material) [85].

Erin Boutwell et al., in 2012, presented the impact of prosthetic gel liners on residual limb pressures and gait characteristics have not been extensively explored. This study looked at the impact of gel liner thickness on peak socket pressures and walking patterns in persons with unilateral transtibial amputations. For most people, the thicker liner gave higher comfort within the prosthetic socket, which may be associated to lower fibular head peak pressures. Furthermore, while the thicker liner may have promoted comfort by providing a more compliant limb-socket interface, the higher compliance may have reduced force and vibration input to the residual limb, contributing to the larger vertical GRF loading peaks [86].

Noor H. Aysa et al., in 2015, presented the utilization of alum, which is a potassium-aluminum 38ulphate salt (K_2SO_4). $Al_2(SO_4)_3.12H_2O$ as a bi-functional filler that aids in the production of closed cell composites and the attainment of a more sterilized product. The percentage of alum added to silicone rubber varies (0, 1, 2, 3, 4 and 5)%, with increasing alum percentage, all degrees of alum powder have decreased mechanical properties. The alum powder has little strengthening activity. Due to the production of holes in the material and the weakening of the cohesiveness of the recipe components, the addition of alum reduces all mechanical parameters (tensile strength, tear resistance, modulus, compression, hardness, elongation, and specific gravity) [87].

Noor H. Aysa et al., in 2015, presented disclosed the development of an antibacterial prosthetic liner made from artificial limb-mediated zinc oxide nanoparticles, as well as the research of mechanical qualities and antibacterial activity. As the concentration of both types of ZnO nanoparticles (unmodified and modified) increased, tensile strength, tear resistance, elongation, modulus, hardness, compression, and specific gravity decreased. Composites containing modified ZnO nanoparticles have higher mechanical properties than those containing unmodified ZnO nanoparticles [88].

John C. Cagle and colleagues, in 2018, presented investigated the compressive, shear, tensile, and volumetric elasticity, as well as the coefficients of friction (CoFs) and thermal conductivities of polyurethane, silicone, and thermoplastic elastomer (TPE) liners.

In compression and shear, polyurethane and silicone liners were found to be more rigid than TPE liners. Greater tensile elasticity was largely caused by fabric backings (and thus reduced pistoning). Comparatively, silicone and

TPE liners showed greater CoFs and a wider range than polyurethane liners. All of the investigated materials were nearly incompressible. All materials have heat conductivities that are equivalent and comparable to leather. Polyurethane liners are softer and less tacky than they were sixteen years ago, whereas TPE liners have increased tensile rigidity. A stiff cloth backing can enhance the tensile rigidity by more than 200%. Compressive stiffness can be used to describe the ability of a liner to flow. Heat is virtually entirely moved via conduction in elastomeric liners [89].

Sihama Issa Salih et al., in 2018, presented materials that could be utilized to replace maxillofacial facial components lost due to sickness or accident. Silicone rubbers are thought to be the best materials in this field. As a result, the purpose of this research is to investigate the influence of PMMA material addition on the mechanical properties of SiR/PMMA blends at various loading levels (5%, 10%, 15%, and 20%) of PMMA to silicone rubber. The results revealed that the optimum proportion of PMMA with perfect characteristics is 10%. As a result, this sample could be a viable material for maxillofacial prosthetic applications [90].

Sihama Issa Salih et al., in 2019, presented that the growing occurrence of cases for a maxillofacial due to accidents and cases of disease has made it necessary to concentrate on the manufacture of alternate materials for sites damaged in this area. The goal of this study was to create nano composite materials out of a polymer blend (silicone rubber: 5% PMMA) reinforced with two distinct types of natural nano-powders. Pomegranate Peel Powder (PPP) and Ajwa Date Seed Powder (SPDA) with different loading levels (0.0, 0.1, 0.2, 0.3, and 0.4) %. The results revealed that the optimal percent of both (PPP) and (SPDA) have ideal characteristics [91].

Siti Nur Nabilah Lutfi et al., in 2020, presented research on the newly modified Foam Liner, a combination of two different foams (EVA + PU + EVA) as the newly improved Foam Liner in terms of compressive and tensile qualities compared to PeliteTM, polyurethane (PU) foam, and ethylene-vinyl acetate (EVA) foam. The material with the highest compressive stress (566.63 kPa) and the highest tensile stress was PeliteTM (1145 kPa). Foam Liner measured 551.83 kPa under compression and 715.40 kPa under tension, placing it between EVA and PeliteTM. PU foam has a compressive stress of 2.80 kPa and a tensile stress of 33.93 kPa. Foam Liner has intermediate compressive elasticity but high tensile elasticity compared to EVA and PeliteTM. The compressive and tensile stiffness of PeliteTM remains unparalleled. Although it is advantageous for amputees with bony prominence, persistent pressure can lead to skin breakdown and ulceration. A foam liner would be appropriate for amputees with soft tissues on their remaining limbs [92].

Jin Gyang Xie et al., in 2021, presented laser confocal microscope to assess the surface roughness of the prosthetic socket and liner materials. The silicon rubber fabric's coefficient of friction was found to be much lower than that of the foam liner materials. Frictional energy dissipation is lowest at the liner/acrylic socket interface and highest for 3D-printed socket materials. Meanwhile, temperature rise has a positive relationship with friction coefficient and frictional energy dissipation. And the findings were that three types of 3D-printed materials with high surface roughness have a greater interface coefficient of friction and energy dissipation than acrylic. The stiffness and energy consumption of the prosthetic liner materials have a significant impact on the interface friction characteristics. The friction behaviour of 3D-printed reinforced nylon is affected by the type of reinforcing fiber used [93].

Mohamed et al., in 2021, presented a new polyurethane prosthetic liner for the anterior-distal region of the residual limb as a Pelite replacement and then compare the biomechanical gait analysis of the new modified polyurethane liner to the old Pelite liner. A unilateral transtibial amputee was chosen as the subject. An Ethylene vinyl-acetate- Polyurethane - Ethylene vinyl-acetate sandwich was placed in the anterior-distal region of the residual limb to generate the modified polyurethane foam liner. The sandwich function of Ethylene vinyl-acetate - Polyurethane - Ethylene vinyl-acetate was created to improve the subject's walking motion and reduce pain while wearing the Pelite liner. The original liner exerted somewhat higher force than the Pelite and the modified liner throughout the loading response period. The original liner exerted less Ground Reaction Force on the amputated side at 30% and 50% of the gait cycle than the Pelite liner and the modified liner. According to biomechanical research, the modified polyurethane foam liner improved prosthesis users' gait cycle and walking stride [94].

Boudjemaa Ismail. et al. in 2021, compared the effect of three different types of liners, the first was a gel liner, the second was a flexible polyurethane foam liner, and also suggested a liner made of polyurethane-shape memory polymer foam. The comparison between the effects of each one of this liner on the stresses at the limb-prosthetic interface allows determining which liner it is more comfortable for the patients.

The memory-foam liner achieved the smallest value of stresses at the limb-prosthetic interface between all three cases, the contact pressure was 23 Kpa and shear stress up to 5.1 Kpa, and this indicates that this liner is very comfortable for the patient [95].

Daniel Besnea et al. in 2021, presented some solutions for utilising closed cells constructed of silicon rubber RTV-2 as liners for lower limb prosthetics. The material used might give the mechanical qualities required for this sort of prosthesis. Even though it is employed in a wide variety of temperature values, this material ensures long-term durability and reliability. It is safe for the human body and can be in contact with the skin for an extended period of time. They molded the cell prototype as a molded casting and examined the circumferential stress and strain data. Finally, the acquired results demonstrate the material's suitability for the purpose [96].

Dominik et al., in 2021, presented develop viscoelastic polyurethane foams for use in limb prosthesis. Foams with various isocyanate indexes (0.6-0.9) and water content were developed as part of the experiment (1, 2 and 3 php). The data were investigated in connection to foam formulation changes. The foams' performance qualities, such as recovery time, hardness, resilience, and sweat absorption, indicate that foams with a water content of 2 percent and an isocyanate index of 0.8 to 0.9 will be suitable for prosthetic applications [97].

Ahmed K. and Zohar J., in 2022, presented Silicone rubber liners that are recommended for usage because they can absorb moisture, distribute tension, and are anti-bacterial. The curing time and temperature are important factors in determining crosslink density. It can be seen from the results that the cross-link density has a direct effect on the tensile strength, modulus of elasticity, percentage of elongation, and water absorption, and the cure time (15 min.) produces the best results. As a result, employing it makes the patient's prosthesis more comfortable and acceptable. The effect of cure time on physical attributes was investigated in this research [98].

Xiao jun Xi and et al., in 2022, presented the influence mechanisms of polyurethane soft segments on modified silicone coatings, a series of modified coatings was prepared by introducing different contents of hydroxypropyl-terminated polydimethylsiloxane (PDMS2200) into the soft segment of polyurethane. The results show that PDMS2200 could aggravate the micro-phase separation of the modified coatings, increase the surface-free energy, and reduce its elastic modulus; when the micro-phase separation exceeded a certain degree, increasing PDMS2200 would decrease the tensile properties. The PED-TDI polyurethane-modified silicone coating prepared with the formula of PU-Si17 had the best tensile properties and antifouling properties among all modified coatings [99].

2.12.1 The difference between current study and previous studies

1- In the previous studies, the focus was on the coefficient of friction and the comparison of the different types of bushings in this respect.

2-Polyurethane foam with nano chitosan was not added to IPN previously in order to improve the properties of the silicone lining suitable for the weather conditions in Iraq.

3- In our study, the porosity property was improved in terms of water absorption and sweating that occurs in the amputation area by adding water droplets with isocyanate, which made open cell.

Chapter Three

Experimental Part

3.1 Introduction

This chapter describes the experimental work, particularly, materials selection, properties of the materials, preparation either silicone rubber or poly Urethane from their raw materials, IPN (SiR/PU) with different ratio (100:0, 90:10, 85:15, 80:20, 75:25, 70:30 and 65:35) % and tertiary blend (SiR/PU and chitosan) with 3% ratio.

Also, it contains the surface modification of tertiary blend with methanol, toluene and acetone to remove all oils and filth, then to develop a hydrophilic surface immersed in 3:7 (98% H_2SO_4+ 30% H_2O_2) solution for 5 hours, after that used CPTES and Glutaraldehyde immersed techniques to work as cross-linker between tertiary blend chitosan solution, where chitosan solution acted as coated (after diluted by hexane) on the surface of tertiary blend to improved bacterial growth, immersed for 1 hour in chitosan solution and to increased stability of this coated on the tertiary blend it can be immersed in 0.1 M of NaOH solution. All information reported in figure 3.1.

Many tests were used to characterization IPN and tertiary blend with coated surface such as XRD, FTIR, SEM, TGA and AFM.

Wettability test including contact angle for SiR, IPN and the tertiary blend with chitosan layer, and compared the different between them. Every mechanical test was taken the average of three specimens from the same sample.

Test the prepared tertiary blend against bacteria growth and biofilm formation using two kinds of bacteria Pseudomonas and Staphylococcus aureus, which are gram- negative and gram-positive, respectively

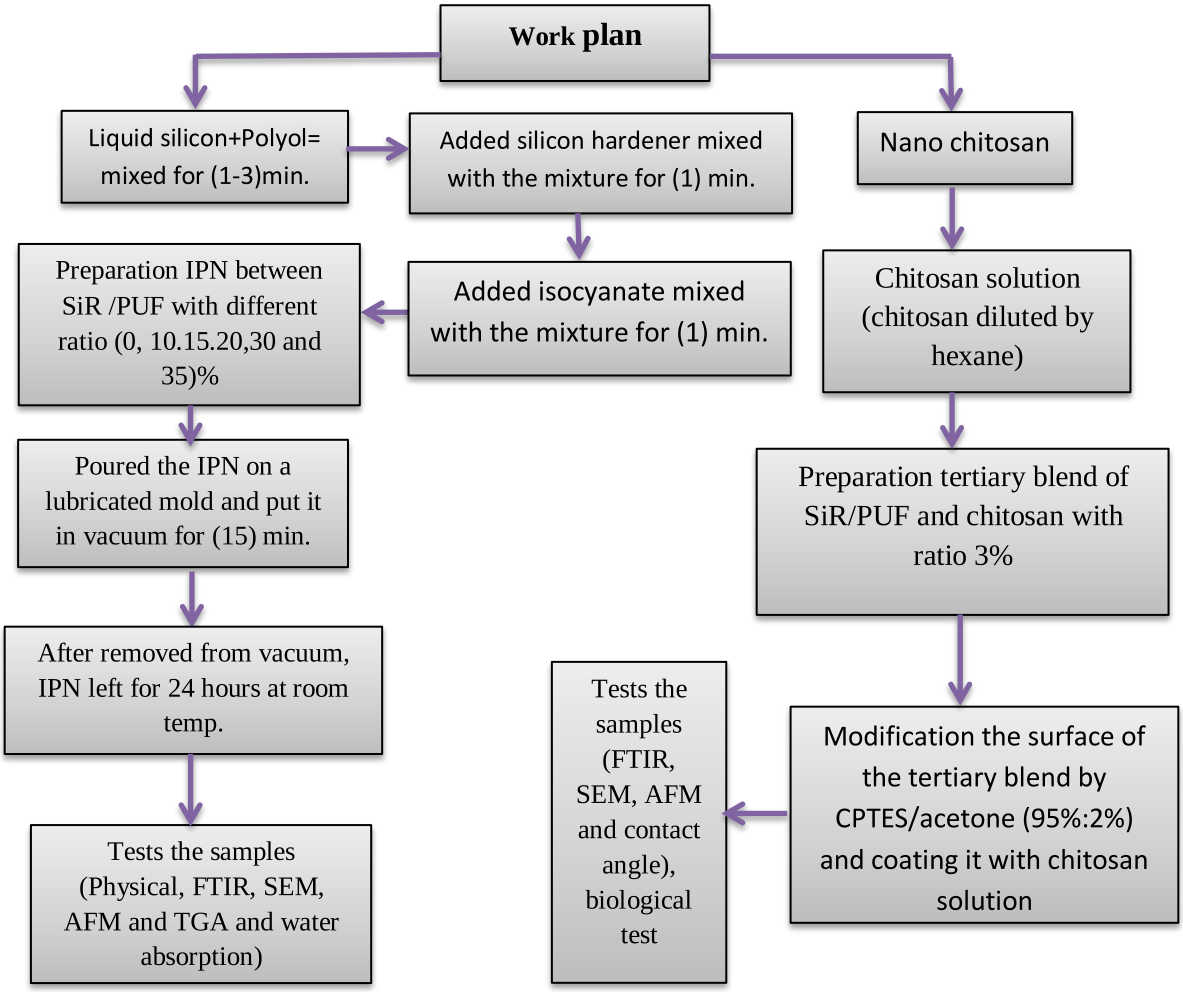


Fig. 3.1: Work plan diagram.

3.2 Materials

3.2.1 Silicon rubber (SiR)

In the current work, imported rubber-silicone from Company of Technology was utilised (Sunny Zhou), RT-800 silicon rubber, platinum hardener used with silicon, selected due to its excellent characteristics such as:

1- High temperature resistance (can reach 0~250 degrees), acid and alkali-resistance and aging resistance.
2- Light viscosity and good flow-ability. Easy for pouring operation.
3- It can be cured both at room temperature or be heated.

4- Low shrinkage. Not releasing low molecular during cross-linking process. So the volume is constant. The shrinkage rate is less than 0.1%.
5- Tasteless, no flammable, safe and reliable.
6- Favorable tensile and tear strength.

Life casting silicone is mainly used to make soft silicone products, such as body organs, breast enhancers, shoulder pads, etc. Specification properties of SiR shown in table (3.1):

Table 3.1: Properties of SiR

Property	**Inspection Method**	**Value**
Product data (Catalyzed A+B)		NP25
Hardness	Shore A	0±1
Colour	/	White
Life time	25 °C (77 ºF)	20-30 min
Curing time	25 °C (77 ºF)	3 hours initially cure 24 hours completely cure
Mixed viscosity	MPa. s	3000±500
Tear-strength	kg/cm	20±2
Tensile-strength	MPa	4±1

3.2.2 Polyurethane

This material was supplied from Henkel polybit Industries company , (UAE). Poly foam I-20 is a two-component, polyol the resin and MDI (isocyanate) the hardener. Cream time: 22-24 second, Gel time: 115-140 second and. The properties of PU components were listed in table 3.2.

Table 3.2: Properties of polyurethane components

Type of Component	Color	Viscosity at 20ºC	Specific gravity
MDI	dark brown	150 - 200 cps	at 20ºC: 1.24
Polyol	brown to yellow	approx.450 cps	at 20°C: 1.16

3.2.3 Chitosan

This material was supplied from Sangherb Company-China, with the properties listed in table (3.3).

Table 3.3: Properties of nano Chitosan

Property	Value
Appearance	white powder
Density	0.03 g/ml
Particle size	≤ 80 nm
Moisture	9.45%
Insoluble	0.10%
Viscosity	25 Cps

3.2.4: 3-Chloropropyltriethoxysilane CPTES

The concentration of the used CPTES was 95%, other properties shown table (3.4):

Table 3.4: Properties of CPTES

Property	Value
Appearance	Liquid
Boiling Point/Range	195 - 196 °C / 383 - 384.8 °F
Specific Gravity	1.070
Solubility	Soluble in water
Molecular Formula	C6 H15 Cl O3 Si
Molecular Weight	198.72

3.2.5 Glutaraldehyde

The specific properties of glutaraldehyde shown in table (3.5):

Table 3.5: Properties of Glutaraldehyde

Property	**Value**
Appearance	Liquid
Color	Colorless
Initial boiling point	101 °C
Water solubility	at 20 °C soluble
Density	1.061 g/cm3
Molecular formula	$(CH_2)_3(CHO)$

3.3 Preparation of SiR, PU and IPN (SiR/PU)

Silicon rubber (SiR) is typically composed of two components: a flowable liquid and a hardener. The second substance in the blend is polyurethane foam, which is composed of two parts: di-isocyanate and polyol.

Pure sample (matrix) have been prepared by combining two parts silicone rubber in 100:1.5 ratios based on laboratory studies, where part A is the base material and part B is the catalyst material as shown in figure (3.2).

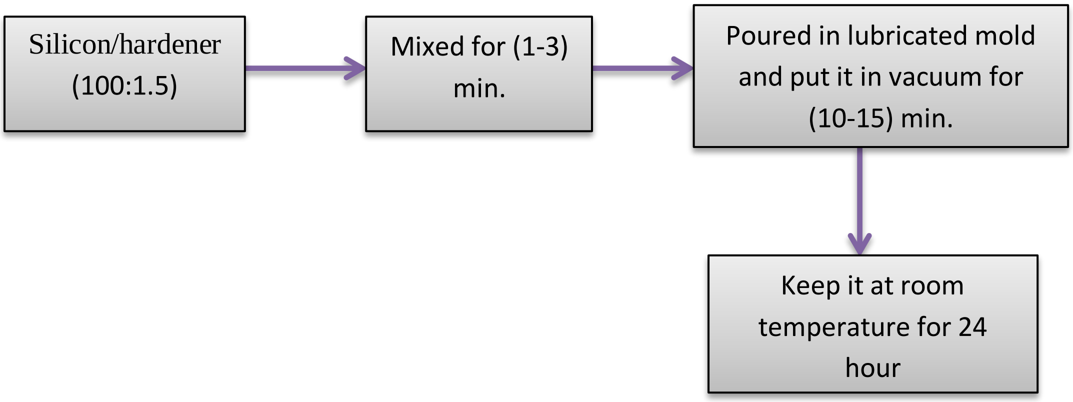


Fig. 3.2: Preparation of SiR

Polyurethane was prepared by mixing polyol /isocyanate (100:70), as shown in figure (3.3).

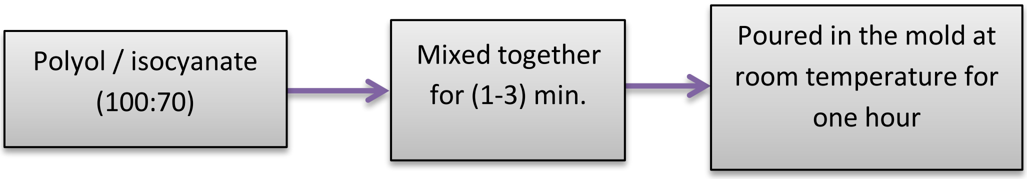


Fig. 3.3: Preparation of PU

Several IPN (SiR/PU) ratio was used, such as (100:0, 90:10, 85:15, 80:20, 75:25, 70:30 and 65:35) %, Initially; part A of silicone rubber in liquid form is mixed with part A of poly Urethane (polyol) for (1-3) minute, and then part B silicone rubber hardener (platinum) was added to the mixture and mixed for (1-3) minute. After that, a part B of poly Urethane liquid hardener (isocyanate) was added to the mixture and thoroughly stirred for (1-3) minute. Then take the IPN and put in the vacuum machine for 15 min. to remove the bubbles. After removing IPN from the vacuum machine, it was poured in the mold that was lubricated before, and then the prepared IPN left for 24 hours at room temperature, as shown in figure (3.4).

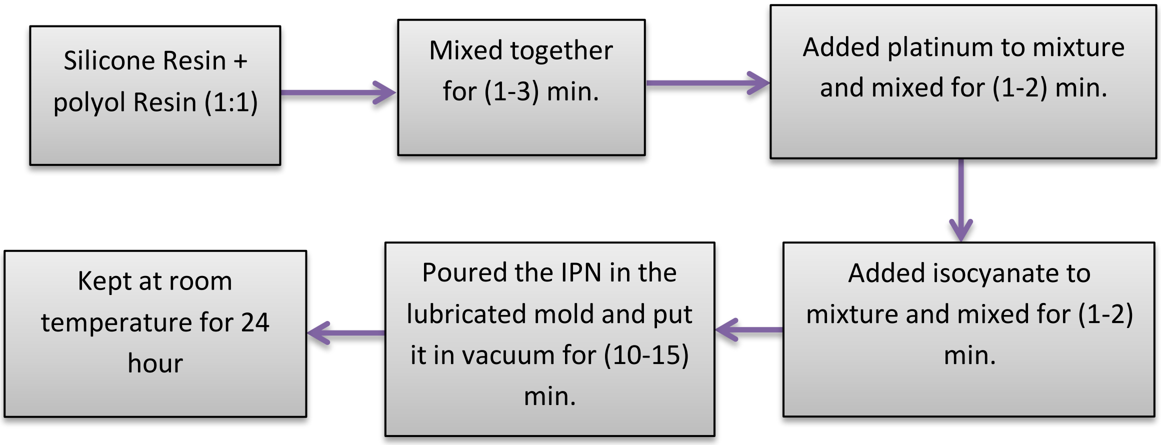


Fig. 3.4: Preparation of IPN (SiR/PU)

During the mixing process to reach the final IPN, the slurry of the first mixture between silicone and polyurethane changed the color of IPN from a bright white color to an off-white color, and with the addition of silicone hardener it turned into a gelatinous mixture. In the last step, when polyurethane hardener was added, a reaction occurred between the two materials, which led to the emission of heat and the color of IPN turned pink.

3.3.1 Preparation IPN (SiR/PU) for water absorbance test

For the purpose of knowing the ability of the mixture to absorb water, two methods were followed in preparing the IPN:

1-The first method:

Adding sodium bicarbonate: Both silicone and polyurethane were mixed, and bicarbonate powder was added in proportions (1, 2, 3) %, then silicone hardener was added, and then polyurethane hardener, and every addition process was done by hand mixing at a period of (1-3) minute for good mixing of the materials, then the samples were placed in the vacuum for (15) minutes.Then the samples were taken out and placed at room temperature for 24 hours.

2-The second method:

Adding drops of water to the isocyanate before mixing: (5, 10 and 15) drops of water added to polyurethane hardener and the best drops additive was mixed with different ratio of isocyanate to show the effect on the ability of absorption water, with rapid shaking for 30-60 seconds and then added to the mixture mentioned previously.

3.4 Sample Preparation

3.4.1 Preparation of Tensile, Elastic Modulus and Elongation

The mold that was used for the preparation samples of tensile, elastic modulus and elongation had the following dimensions (150 mm length, 150 mm width and 3 mm thickness). This mold lubricated and pour the appropriate amount of blend in the mold and then it is left for one day, and then (dumbbell specimen) by hand press as in figure (3.5) to conduct a tensile test on the samples generated. Tensile strength and percentage of elongation tests are accordance with ASTM-D412 [100].

Fig. 3.5: Tensile sample for the blend

Fig. 3.6: Tensile measuring device

3.4.2 Hardness samples

The mold used to prepare these samples has a cylindrical shape with diameter 30 mm and thickness 4 mm as shown in figure (3.7). Test specimens, in accordance with ASTM D2240 for testing Shore A Durometer hardness, were produced. Seven samples were manufactured for this purpose, each one containing a certain proportion of Polyurethane foam (0,10,15,20,25,30,35) wt.% [101].

The test was conducted in the laboratories of the Faculty of Materials Engineering / University of Babylon using handeness devise as shown in figure (3.8).

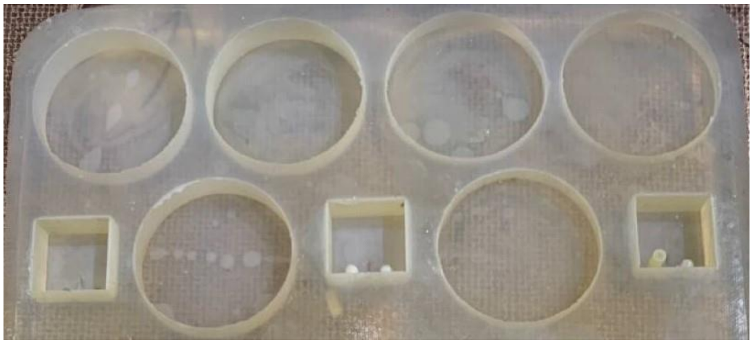


Fig. 3.7: Mold for hardness sample

Fig. 3.8: Hardness device

3.4.3 Specific gravity sample

The mold is the same mold of hardness while specific gravity is checked on density device type GP-120 S (Matsu Haku, Chain) according to the ASTM D792 [115] as shown in figure (3.9).

Fig. 3.9: Specific gravity device

This test is done by examining the weight of the specimen in the air and then check weighting with water. Archimedes' principle, which states that the apparent weight loss of a material submerged in a liquid matches the weight of the liquid displaced, is supported by the finding of specific gravity. The specific gravity, which is defined as the weight of a given volume of material divided by the weight of an equal amount of water, can be computed when the weight of the material and the weight of an equal volume of water are known [102].

3.4.4 Fatigue samples

Flexibility test samples with dimensions include a half circular central notch with a radius of 2.5mm for preparation. The mould is made up of three parts: the central portion with dimensions of 282*222*6mm, six empty spaces with dimensions of (153*62mm), and a circular middle notch with a radius of 2.5mm that divides the part and the six vacant areas. The first section is mounted on a 282*222*10mm base and covered with a cover for thickness adjustment ASTM D430, as shown in figure (3.10).

The device was located in State Company for Rubber and Tires Industries, using the (Wallace-Dematta Flexing Machine) which counts the number of cycles at which the crack and examination are performed inside the device and is fixed by hooks) The device operates at a constant speed (300 rpm).

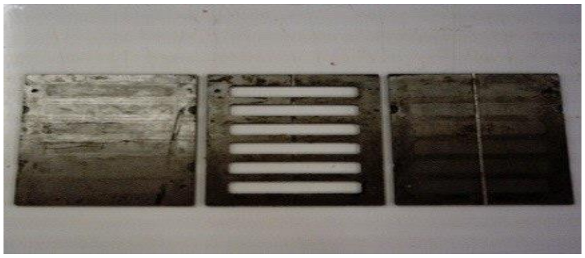


Fig. 3.10: Mold for flexibility test sample

3.4.5 Preparation the tertiary blend

The chitosan nanoparticles (0.1 g/cm^3) were added to the IPN was dissolved individually in hexane (30 ml hexane for each 8 g) as shown in figure (3.11), [76].

According to [76], which included the best percentage of addition of Chitosan was 3%, this percentage was directly worked out, as it was added to IPN (SiR/PU) as follow:

The nanoparticles Chitosan that diluted by hexane placed on the Ultrasonic device for one hour and then mixed with IPN which diluted with hexane and placed on the magnetic stirrer for one hour at 60ºC, so that the hexane evaporates during continuous mixing of the components.

Fig. 3.11: Chitosan and the blend dissolve in hexane

After the full evaporation of hexane, the cure agent (hardener) was placed on the mixture at a rate of 1.5% of silicone resin and 70% of polyurethane resin. Then take the tertiary blend and put it in vacuum machine for 10 min to remove the bubbles as shown in figure (3.12).

After that, the tertiary blend was poured in the mold that was lubricated before. Finally the mold left at room temperature for one day.

Fig. 3.12: Vacuum device

3.4.6 Modifying the Surface of tertiary blend

The surface of the tertiary blend was chemically changed to coat it with chitosan solution, and a thin layer of chitosan inhibits the formation of biofilm bacteria. The following procedures were as followed:

1- Clean the surface for 10 minutes each in methanol, toluene, and acetone before drying it in N_2, to remove all oils and the dust.

2- To develop a hydrophilic surface, immerse the clean surface in a 3:7 (98% H_2SO_4 and 30% H_2O_2) solution for 5 hours, rinsed with deionized water, and dried in N2.

3- Immerse the substrate for 30 and 60 minutes in a 2% CPTES + 95% acetone solution before washing three times with acetone.

4- The surface layer was submerged in a 2% glutaraldehyde / H_2O solution for 1 hour after drying. The substrate was removed and air dried after being washed with deionized water.

5- Preparation of chitosan solution (already prepared): 3 g chitosan was mixed in 100 ml of 2% acetic acid solution and agitated for 30 minutes to produce a homogeneous chitosan solution.

6- Immerse the substrate for 1 hour in a 3% chitosan solution.

7- Finally, the substrate was treated for 1 hour with a 0.1 M NaOH solution, washed with deionized water until the waste water pH reached 7, then dried at 80° C.

3.5 Characterization of SiR, PU, IPN and tertiary blend

3.5.1 Fourier Transform Infrared Spectroscopy (FTIR)

The samples for FTIR analysis are prepared by mixing small piece of each sample with KBr powder and then compressed to form a tablet. Then Fourier transform infrared spectroscopic measurements were carried on using 8400S

–FTIR-Perkin-Elmer spectrophotometer in the College of Material at University of Babylon, as shown in figure (3.13). This test was carried out on the pure silicon, pure Polyurethane, IPN and tertiary blend

Fig. 3.13: FTIR device

3.5.2 X-Ray Diffraction (XRD)

The X-Ray diffraction method gives interference effects with structures close in size to the radiation wavelength, for investigating orderly arrangements of atoms or molecules though the interaction of' electromagnetic radiation [101]. The particles crystallinity of the blend was determined by XRD using the sophisticated X-ray diffractometer SHIMADZU–XRD 6000 as shown in figure (3.14). Crystalline extent was determined by diameters (D) where gained from the peaks of XRD depending on the Debye-Scherer's equation [102].

$$D=K \lambda / \beta \cos\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

Whereas:

K is 0.89 as a constant

λ is the incident X-ray beam wavelength (Cu Kα=1.5406 A°),

θ is the angle of diffraction of Bragg, and

β is the full X-ray pattern line width at half peak radius height.

The samples were prepared by placing small piece of each sample in a 200 mesh sieve. The sample was taken out from the sieve and placed in the sample holder, which consists of a circle of 20mm diameter and depth of 2 mm, then press well so that the powder is at the surface level of the sample holder.

Fig. 3.14: XRD device

3.5.3 Scanning Electron Microscopy (SEM)

This test was conducted in the Islamic Republic of Iran at Tescan Mira3 Company, where it was conducted Scanning Electron Microscopy scans a surface to project an image by electron beam focusing, as shown in Figure (3.15). Multiple signals, producing which could be utilized to gain the information about the composition and the topography of the surface when the electrons in the beam interact with the sample [103].

Fig. 3.15: SEM device

3.5.4 Thermo Gravimetric Analysis (TGA)

In a controlled environment, a thermo gravimetric analysis (TGA) device analyses the amount and rate of change in the mass of a sample as a function of temperature and time. The method is used to characterize materials that exhibit mass loss or gain due to volatile loss, breakdown, and oxidation.

The sample were heated at a rate 30 to 950 ºC under nitrogen atmosphere, This test was conducted in the Islamic Republic of Iran at Taban Lab and the device is Universal V4.5A TA Instruments as shown in figure (3.16).

Fig. 3.16: TGA device

3.5.5 Atomic Force Microscopy (AFM)

AFM is an amazing instrument for measuring nanometer dimension's features, it has several characteristics that make it unique, such as creating a highly magnified 3-D image of a nanoparticle surface, a monitoring, motion of atomically sharp probe as it is scanned across a surface generated magnified image for few nanometers-sized dimensions including single atoms and molecules on a surface. This gives scientists and engineers an ability to visualize nanometer-sized objects and to measure the dimensions of the surface feature [104]. This analysis is made in the Islamic Republic of Iran at Taban lab.

3.6 Water absorption

Water absorption is used to determine the amount of water absorbed under specified conditions, as a guide to the effects of exposure to water or humid conditions on liner properties according to the ASTM 570-98 [106]. Factors affecting water absorption include: type of plastic, additives used, temperature and duration of exposure. In this test, the samples were immersed in water at room temperature at varying intervals of (10, 20, 30 and 60) minutes to determine the extent of the material’s ability to absorb water and according to the need that is used in the work of liner socket.

The percentage of water absorption in the sample is calculated by the weight change with the following equation:

$$WAC= (W_2-W_1/W_1)\ \% \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3.2)$$

Where W_1 is the initial weight of the specimen, W_2 the weight of the specimen after immersion in water for different time [106].

3.7 Rebound Resilience test

The ratio of the inventor's energy after the impact of its energy before impact is described as rebound resilience (expressed as a percentage). The test piece is subjected to one half cycle of deformation only. In these test methods, a strain is applied to a rubber test sample by a free-falling indentor. It shows the ability of a rubber vulcanizate to absorb and return the impact energy which depends on rubber type, vulcanization conditions, curing ingredients, application temperature, and fillers amounts. That is a very important characteristic to predict the damping of vibration in specific applications [107, 108]. The device was located in State Company for Rubber and Tires Industries.

3.8 Wettability

As shown in Figure (3.17), a contact angle device (optical contact angle & intention interface meter) was used to evaluate wettability (Powreach, ST200KS, China). The goal of this experiment is to examine the wettability angles of tertiary blend coating with chitosan layer and the tertiary blend without coating.

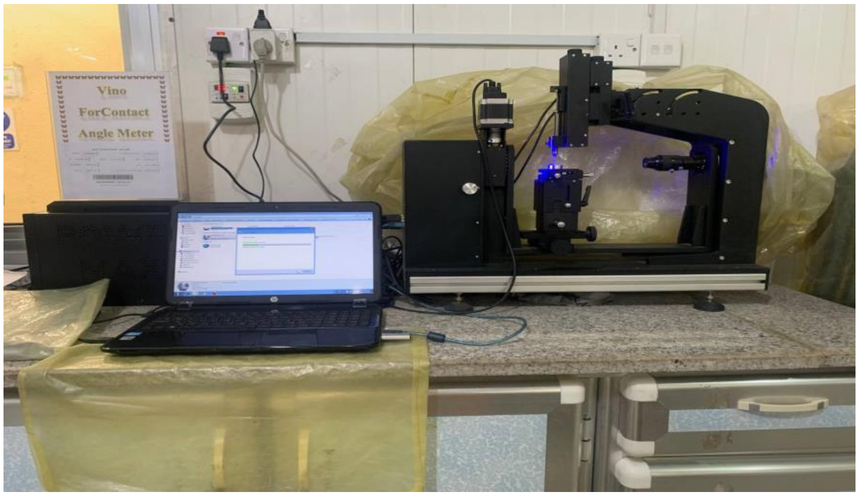


Fig. 3.17: Contact angle device

3.9 Biological Tests

3.9.1 Antibacterial test

The antimicrobial properties were evaluated against Staphylococcus aureus Gram-positive bacterium and Pseudomonas Gram-negative one. The kinetic of bacteria growth rate was determined by Agar Well Diffusion Method, five sample have been test (SiR, IPN, tertiary blend with and without coated).

A sterile swab was used on a Muller-Hinton agar tray to achieve an inoculum from the bacterial suspension and spreader small filter paper disks containing antibiotics are placed onto a plate upon which bacteria are growing.

The antibiotic diffuses from the disk into the agar. If the bacteria are sensitive to the antibiotic, a clear ring, or zone of inhibition, is seen around the disk indicating poor growth. Using special comparators that interpret the diameter of the zones of inhibition, consequently the sample can be described as resistant, intermediate, or sensitive. Tables are used to determine the breakpoint for each sample; the plates were incubated at 37 ° C for 24 hrs. The inhibition zone was then evaluated in millimeter.

3.9.2 Biofilm formation test

In the current study, 6 clinical isolates(Staphylococcus and Pseudomonas) were screened for their capability to form biofilm via micro titration plate's method as stated by Zhang et al., (2016) with some modification.

1- isolates from fresh agar plates were inoculated in 5 mL of nutrient broth with 2% sucrose, the broth was incubated for 24 h at 37 ºC (Mathur et al., 2006).

2- Twenty microliter of bacterial suspension from each isolates (equivalent to 0.5 McFarland standard) was add and used to inoculate micro titer wells containing 180 µl from the nutrient broth, Broth to each well of the micro plate, which was cover and incubated at 37 °C for 24 hours.

3- After incubation, the plate was washed three times with normal saline to eliminate non-adherent cells.

4- To fix the adhered cells, 200 µl of 99% methanol per well was add for 15 minutes. The plate was dried for 30 minutes at room temperature .

5- Then 200 µl of 1% crystal violet was added for 15 minutes.

6- After eliminating the dye solution and washing with sterile distill water, the attached dye was solubilized with 96% ethanol, and the optical density was appointed in a micro-titer plate reader at 630 nm. The biofilm formation was evaluated as described in Table (3.6).

Table 3.6: Evaluation of biofilm formation by microtiter plate method

Optical density at 630 nm	Adherence
OD ≤ 0.120	Non–adherent
0.120 > OD > 0.240	Moderate
OD > 0.240	Strong

Chapter Four

Results and Discussion

4.1 Introduction

In this chapter, the practical results obtained in the laboratory of the materials, for this part whether these tests are for neat materials of silicone rubber and polyurethane, as well as IPN and the tertiary blend that was manufactured and the products of these materials were compared. Also the changes in the physical (hardness, tensile, elastic modulus, elongation, fatigue, rebound, specific gravity and water absorption), characterization (XRD, FTIR, SEM, AFM and TGA), and biological properties of SiR, PU, IPN and tertiary blend were calculated.

In addition to the examination of wettability of samples and the antimicrobial properties were evaluated against Staphylococcus aureus Gram-positive bacterium and Pseudomonas Gram-negative one by agar well diffusion, as well as the biofilm formation were determined for same type of bacteria by using micro titration plate’s method.

4.2 Mechanical Results

4.2.1 Hardness

From the figure (4.1), it can be noticed an increased in the hardness rate with the increased in the percentages of polyurethane foam for the samples, , the hardness of silicone rubber about (18-80) shore A instrument while the hardness of polyurethane is between (45-75). Therefore, this increase is a scientific result of mixing these two polymers. This result corresponds with XRD results and [75].

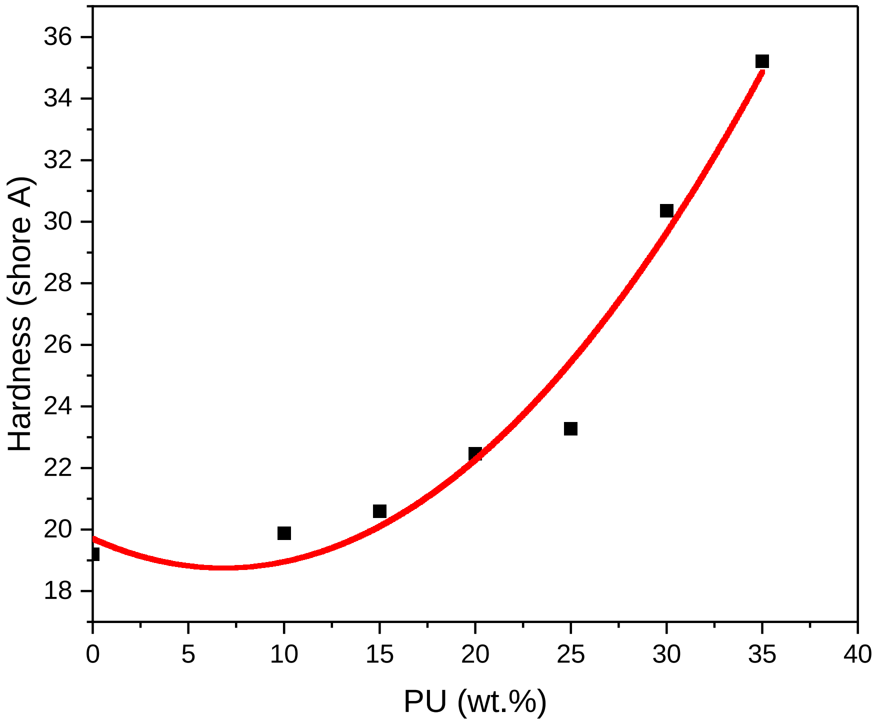


Fig. 4.1: PU content as a function of IPN hardness

4.2.2 Tensile

From figure (4.2) the curve shows that there is a decrease in the tensile strength applied to the samples with the increase in the proportions of polyurethane.

Noting that there is a relative discrepancy between the ratios often due to the presence of impurities or bubbles in some samples.

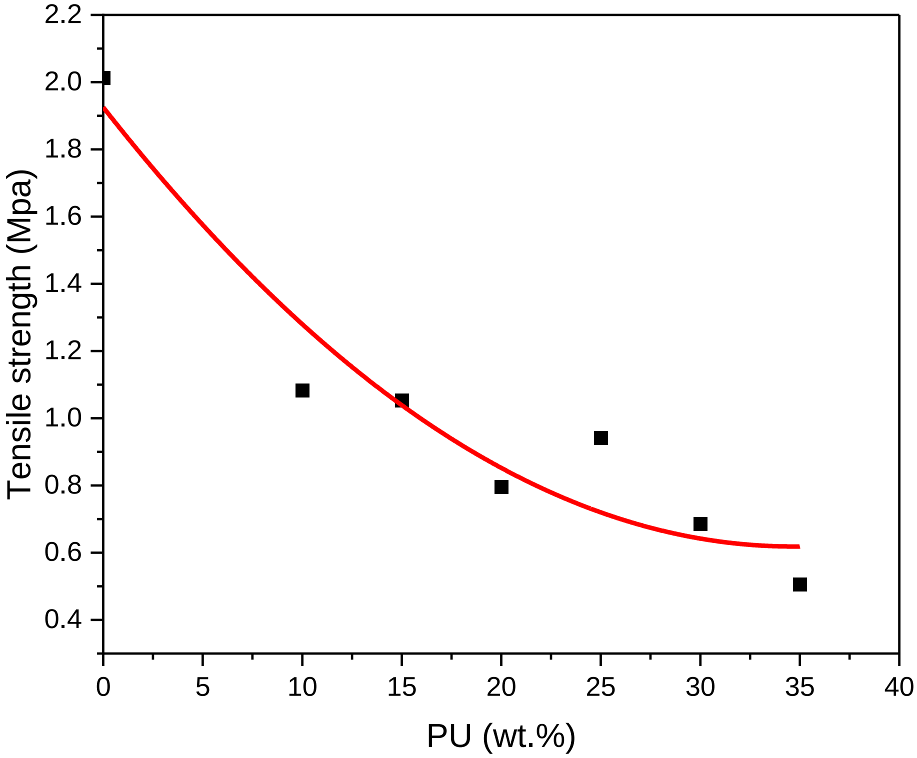


Fig. 4.2: PU content as a function of IPN tensile strength

In general, a gradual decrease occurs and appears clearly in the last sample, where the percentage of polyurethane increased to 35%, and this decrease is due to the restriction of the chain that occurs within the mixture, which in turn hinders the smooth movement of the chains, since the aromatic rings of polyurethane, as in figure (2.7) in chapter two, restrict the movement and tighten IPN so that it becomes less flexible.

4.2.3 Elastic Modulus

The elastic modulus for a neat silicone rubber increases significantly with aging time. When PU added to the silicone rubber and made IPN, elastic modulus increase as shown in figure (4. 3).

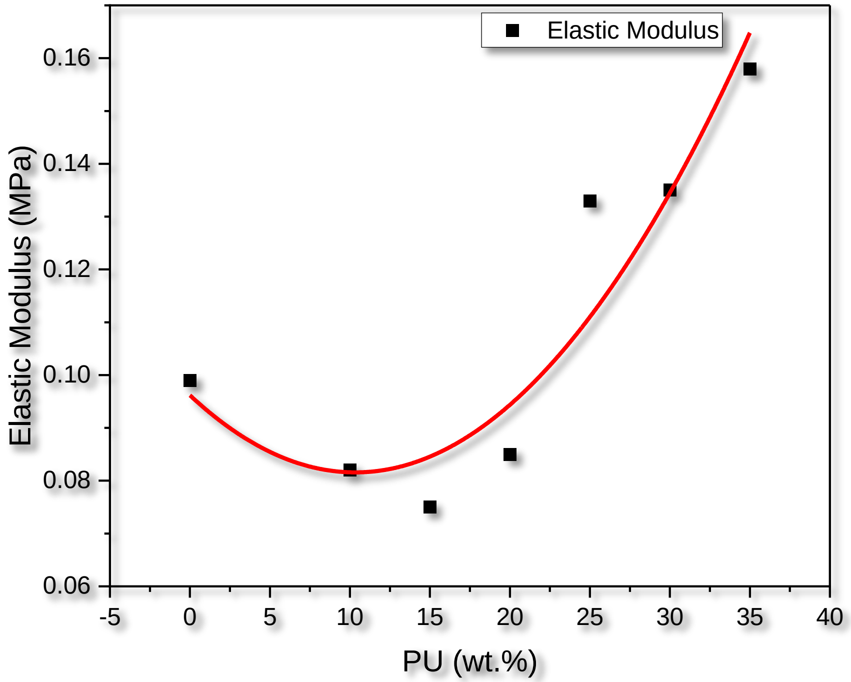


Fig. 4.3: PU content as a function of IPN elastic modulus

At PU 20% and increasing continuously until 35%, due to the effect of urethane group in density and structure on IPN and this consistent with hardness result. In general, elastic modulus increases with an increase in polyurethane percentage.

4.2.4 Elongation

The elongation percentage at breaking was also affected by the PU addition as shown in figure (4.4). It can be notice a decrease in the rate of elongation of the samples whenever the percentage of polyurethane increases, due to the presence of the aromatic ring in the chemical composition of PU, which hinders the process of elongation of the samples and restricts the movement of the chains within IPN.

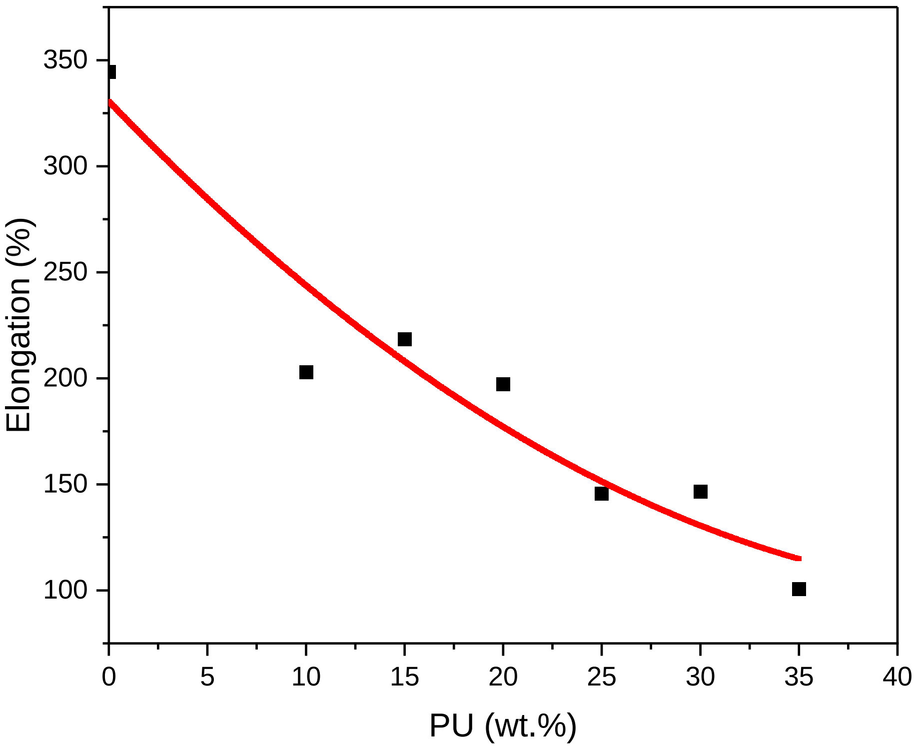


Fig. 4.4: Effect of PU foam on elongation of SiR

Where the elongation started at (344.4%) and went in the last sample to about (100.7%) when the percentage of polyurethane increased to 35%, this result corresponds with [86].

4.2.5 Fatigue

It can see from table (4.1) that fatigue life decreases with increase the percentage of PU in IPN (SiR/PU) because of the chemical structure of polyurethane which contain hard segments that impede the movement of the silicone chains and restrict their movement, which facilitates the crack growth process, and the resulting gaps cause a kind of crack. The result is consistent with the research [109].

Table 4.1: Fatigue results

Sample	Fatigue result(S-N)
SiR (100%)	6418
IPN (80:20)	4514
IPN (65:35)	1300

4.2.6 Rebound Resilience

The results shown in table (4.2) that the damping ability of the material increased with the increased of the proportion of polyurethane in IPN as a result of the presence of pores in the structure that help in damping.

Table 4.2: Resilience results

Sample	Resilience (%)
SiR (100%)	11.11
IPN (80:20)	8.33
IPN (65:35)	7.12

4.2.7 Specific Gravity

From table (4.3), it can be noticed that with the increased in the content of PU, the specific gravity of IPN increased as a result of the physical interaction between the molecules of PU and SiR, which gives it more density.

Table 4.3: Specific gravity for the samples

Sample	Specific volume
SiR 100%	23.26
IPN (80:20)	16.38
IPN (65:35)	9.65

4.3 Water Absorption

Adding sodium bicarbonate to IPN have no effected on this property, where by adding drops of water to the isocyanate (water content 7% of isocyanate), best additives gives increased about 2% after 10 min. and this ratio added to different ratio of isocyanate which can be noticed an increased in the absorbance of water was observed for several samples with the stability of the absorbance ratio after a period of 30m, as in the table (4.4)**:**

Table 4.4: Effect the amount of isocyanate on absorbing water

Water content	**Isocyanate of PU**	**Absorption Average after 10 min.**	**Absorption Average after 30 min.**
7%	1 ml	2%	5%
	2 ml	5%	6.8%
	3 ml	4%	6%
	4 ml	4%	5%

After 30 minutes, there was saturation of the samples so that the absorbability is proven at that limit and according to what is shown in the table 4.4.

The performance features of polyurethane are dependent on the PU material's chemical structure and its pore structure. Introduction of hydroxyl groups (–OH) from water prioritizes reaction of isocyanate group (–NCO) with H_2O faster than –OH from the polyol due to –NCO mobility and accessibility of –NCO to H_2O.

The best sample is the second where isocyanate was (2 ml) and where the absorbability of the mixture became about 6.8% after 30 minutes; the results consistent with the research [97].

4.4 IPN characterization

4.4.1 XRD Analysis

As shown in figures (4.5 - 4.7), which represent XRD for silicon rubber, polyurethane and the prepared IPN, respectively.

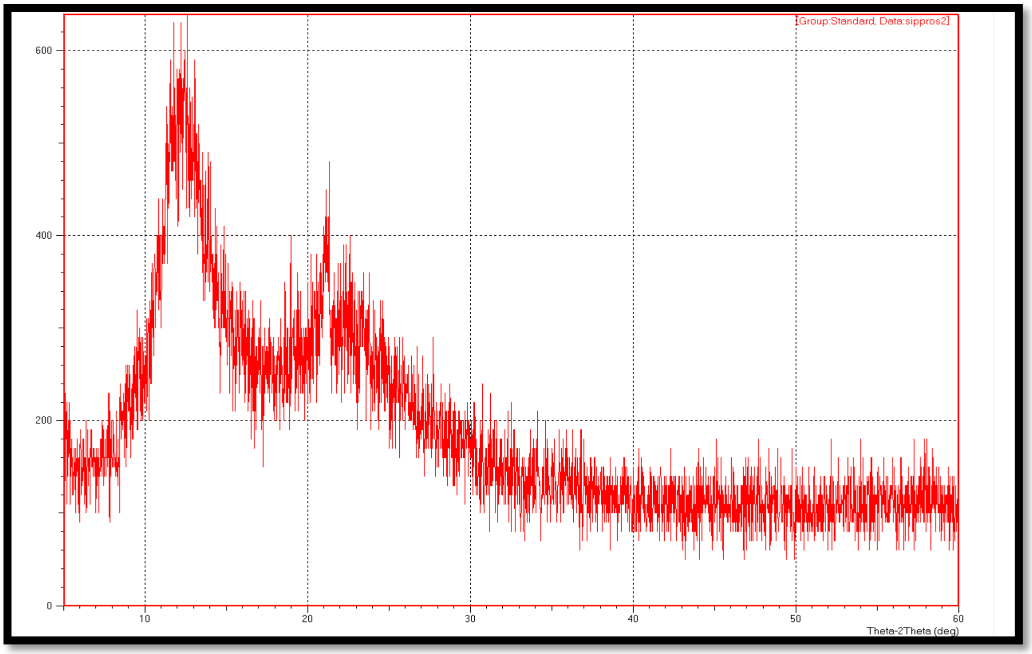


Fig. 4.5: XRD of SiR

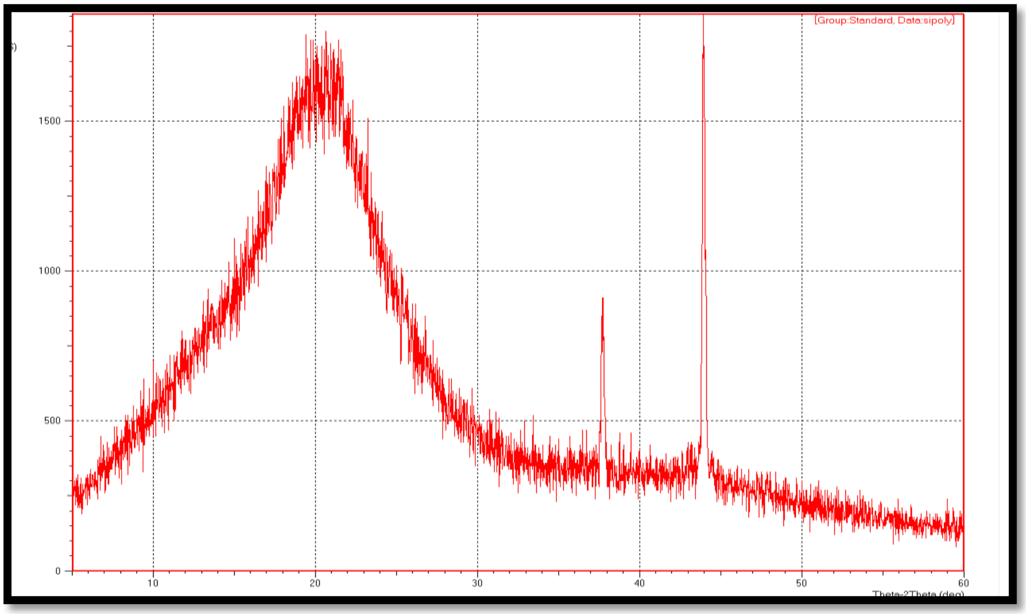


Fig. 4.6: XRD of PU

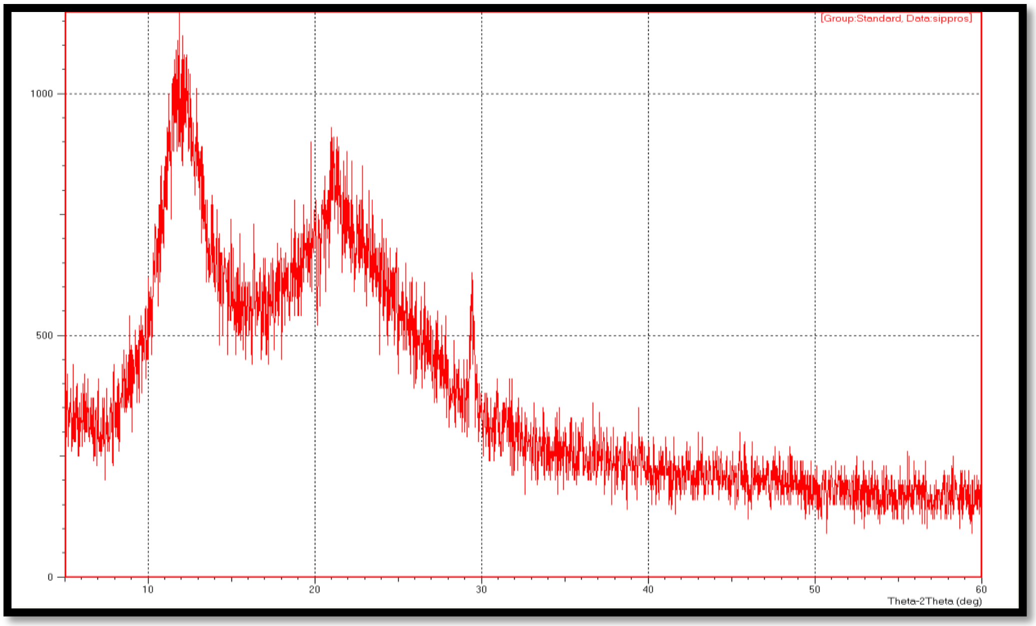


Fig. 4.7: XRD of IPN

It can be noticed that silicone rubber in general had semi-crystallization structure towards randomness, where crystallization was very little and appears at 12° θ and 21° θ, while polyurethane shown abroad peak around 2θ=20°, but it had a narrow peak around 2θ= 38° and 43° .

The resulting IPN of these two polymers tends to the crystalline structure of silicone, which was semi-crystalline, where crystallization appears at 12° θ and 21.5° θ with higher intensity, but polyurethane peaks had shifting and low crystallinity degree appears at 29° θ, and then it behaves randomly.

This was due to the fact that the amount of silicone used in the mixture was the base material (the largest) compared to with the amount of polyurethane.

These new crystalline structure will affect the behaviors and properties of the PU such as density and so on.

From Scherer equation, the crystallite size (D), increased from 20.06 (for the neat SiR) up to 26.51at 2θ=12º with 20 wt.% PU addition. These results compatibles with this research [110].

4.4.2 FTIR Analysis

The results obtained by FTIR test for silicone rubber, polyurethane and the blend are shown in figure (4.8).

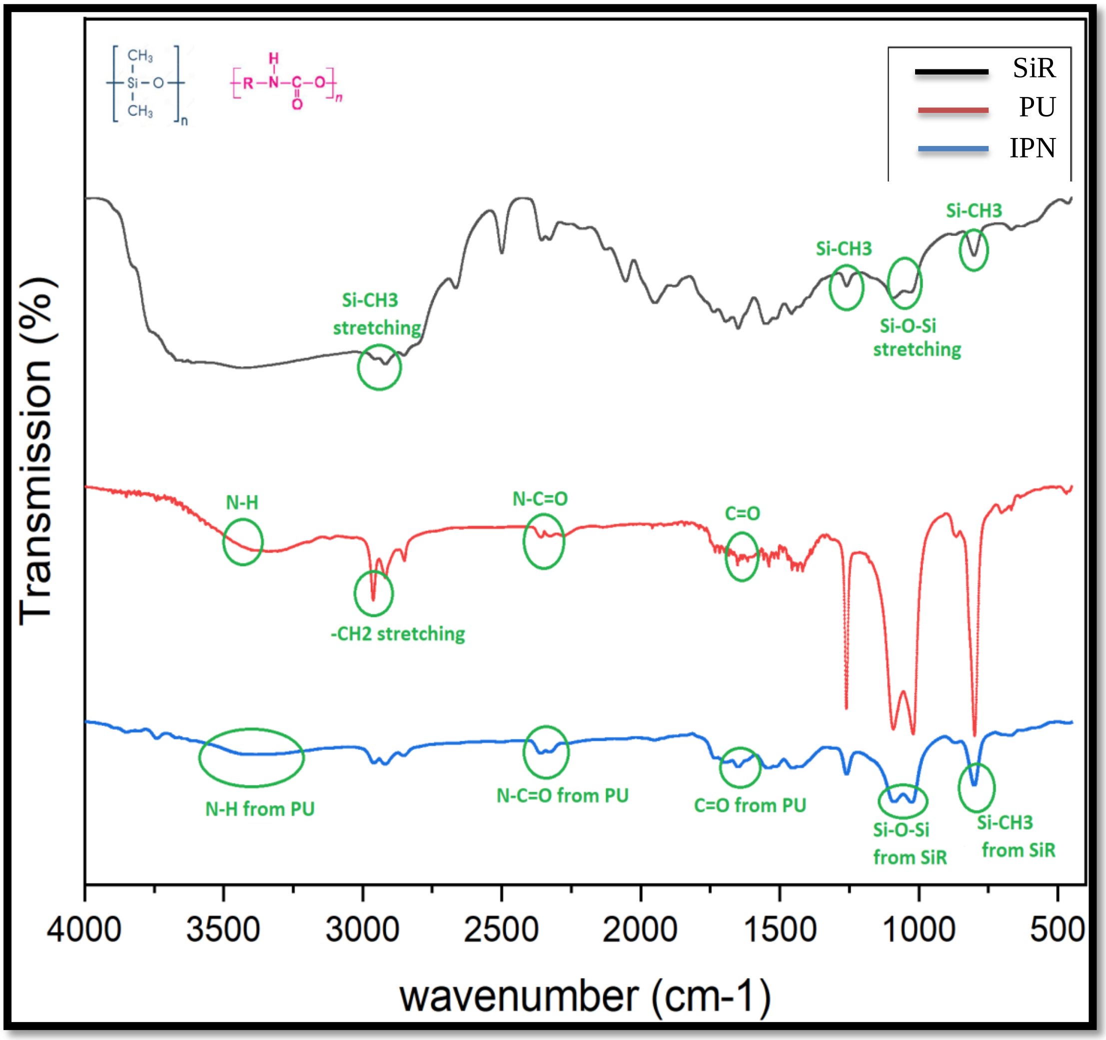


Fig. 4.8: FTIR for SiR, PU and IPN between them

FTIR spectra are used to analyze the existing forms of certain groups [94]. The major component of SiR is (Si-O-Si) and ($Si-CH_{3)}$ bond and the major component of PU foam is (C=O), (C-O) and (N-H) bond.

For silicone rubber the ($Si-CH_{3)}$ bond reaches 810 cm^{-1} and 2900 cm^{-1}, while (Si-O-Si) bond found at 1090 cm^{-1} and this bond is featured for silicone rubber.

For polyurethane the carboxyl group (C=O) found at 1650 cm^{-1}, which it is special group for PU. Around 3300 cm^{-1} (N-H) bond found, at 2900 cm^{-1} ($–CH_2$) stretching , and around 2300 cm^{-1} (N-C=O) bond found.

The FTIR spectra of IPN (SiR: X% PU) with different ratios of PU (0, 10, 15, 20, 25, 30, and 35%) are shown in figure (4.8). It can be seen from the infrared spectrum of these groups of polymeric blend specimens; these spectra are quite similar to the FTIR spectrum of silicone rubbers and PU, no other new peak or peak shifts were observed for the IPN (SiR/PU) specimens with the addition of PU.

All the bonds that appeared at both silicone and polyurethane appeared clearly in the final IPN between them, where at 3350 cm^{1-} the bond of (N-H) appeared, but with less intensity than what it is in polyurethane because the mixture contains only 20% of polyurethane and the rest is silicone and the pulse was not intensified in this region, which proves that there is no (O-H) bond in silicone rubber, and at 1090 cm^{-1}, the special bond (Si-O-Si) from silicone appeared in the final IPN.

This is due to the found physical interaction and absence of any crosslinking and chemical reaction between constituents of IPN [89].

The results obtained by FTIR test for uncoated tertiary blend, coated tertiary blend with immersion for (30 and 60) minute in CPTES/acetone, are shown in figure (4.9).

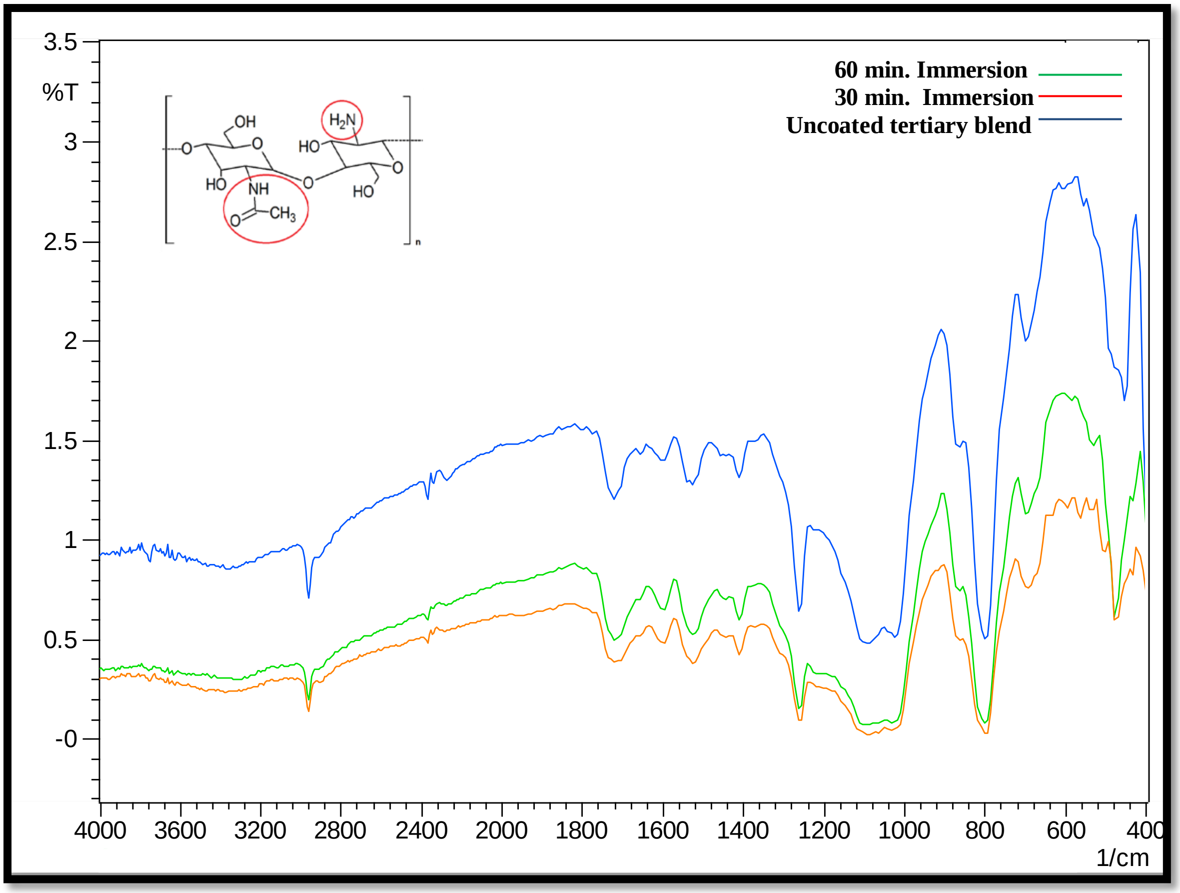


Fig. 4.9: FTIR for tertiary blend samples coated and uncoated

From this figure, if the wavelengths of each of the final IPN before adding Nano chitosan are compared with the tertiary blend after the addition. it can be noticed an increase in the pulse intensity at 800 cm^{-1}, 1100 cm^{-1}, 1650 cm^{-1}, 2945 cm^{-1} and 3300 cm^{-1}, due to the presence of bonds ($Si-CH_3$), (Si-O-Si), (C=O), ($-CH_2$ stretching) and (N-H) from IPN, while from chitosan are (C-N stretching), (-C-O stretching), (N-H bending), (C=O), ($-CH_2$ stretching), (O-H) and main amines (NH_2) at 1420 cm^{-1}, 1100 cm^{-1}, 1550 cm^{-1}, 1692 cm^{-1}, 3750 cm^{-1} and 2890 cm^{-1}; respectively.

The spectra of all the samples the tertiary blend without coating and the coated samples who immersed for (30, 60 minute), it can be noticed that there is not any new peak in the 30m sample ,only shifting of the peaks in the 60m sample.

This prove that the occurrence of physical interaction between the original material and the coating material, and this may be due to the effect of the immersion time of the sample in the CPTES/acetone solution, in addition to the effect of temperatures and other conditions. This is consistent with the results of the researchers in [89, 111].

4.4.3 SEM Analysis

In the SEM examination several samples are examined including silicone rubber only, polyurethane and IPN as shown in figure (4.10 - 4.12).

The photographic imaging for fracture surface morphology of silicone rubber and polyurethane were showed in Figures 4.10-4.12, (A and B) at magnifications (2.00 kx, 500x, 200x). This images micrographs clearly illustrate homogeneous structural morphology was observed and there is no any new phase or phase separated dominants in silicone rubber and polyurethane structure.

The fracture surface morphology of the prepared IPN (80% SiR: 20% PU) was shown at magnification (2.00 kx, 500x, 200x) in Figures [(4.10), (4.11), (4.12) C], this photographic imaging clearly illustrates the apparition of two distinct phases.

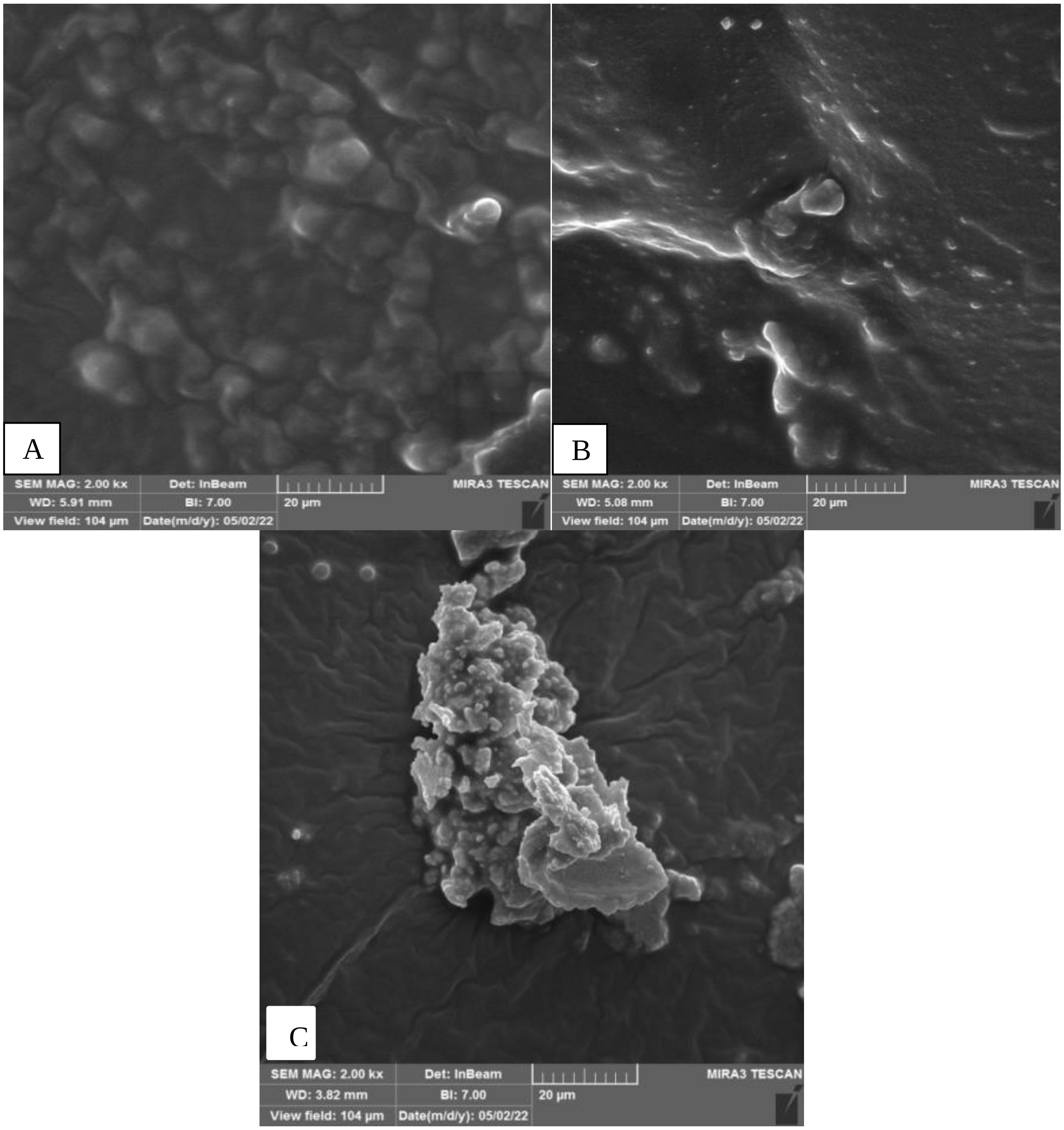


Fig. 4.10: SEM image at (2.00) kx for: (A) silicone rubber, (B) polyurethane and (C) IPN.

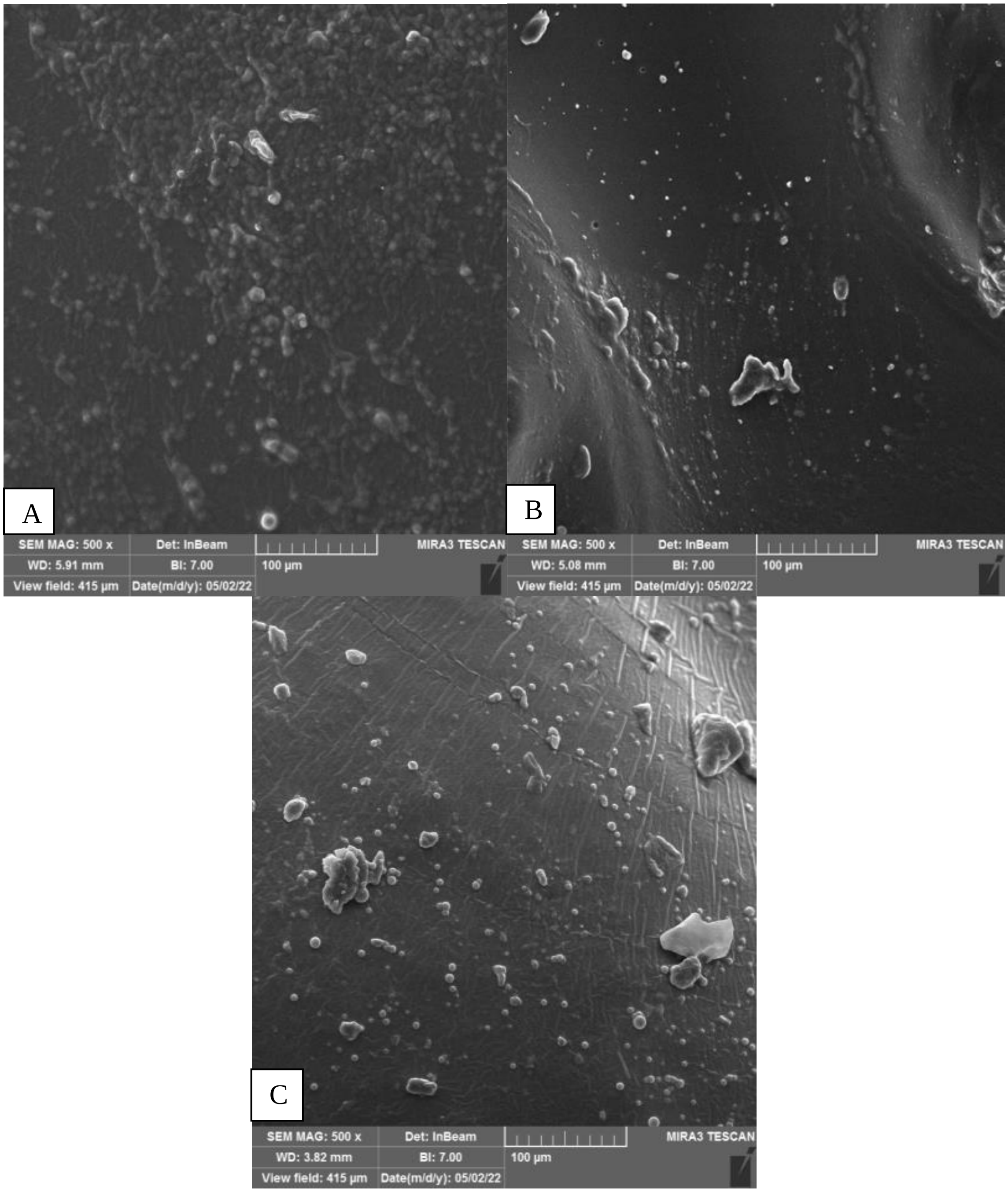


Fig. 4.11: SEM image at (500) x for: (A) silicone rubber, (B) polyurethane and (C) IPN

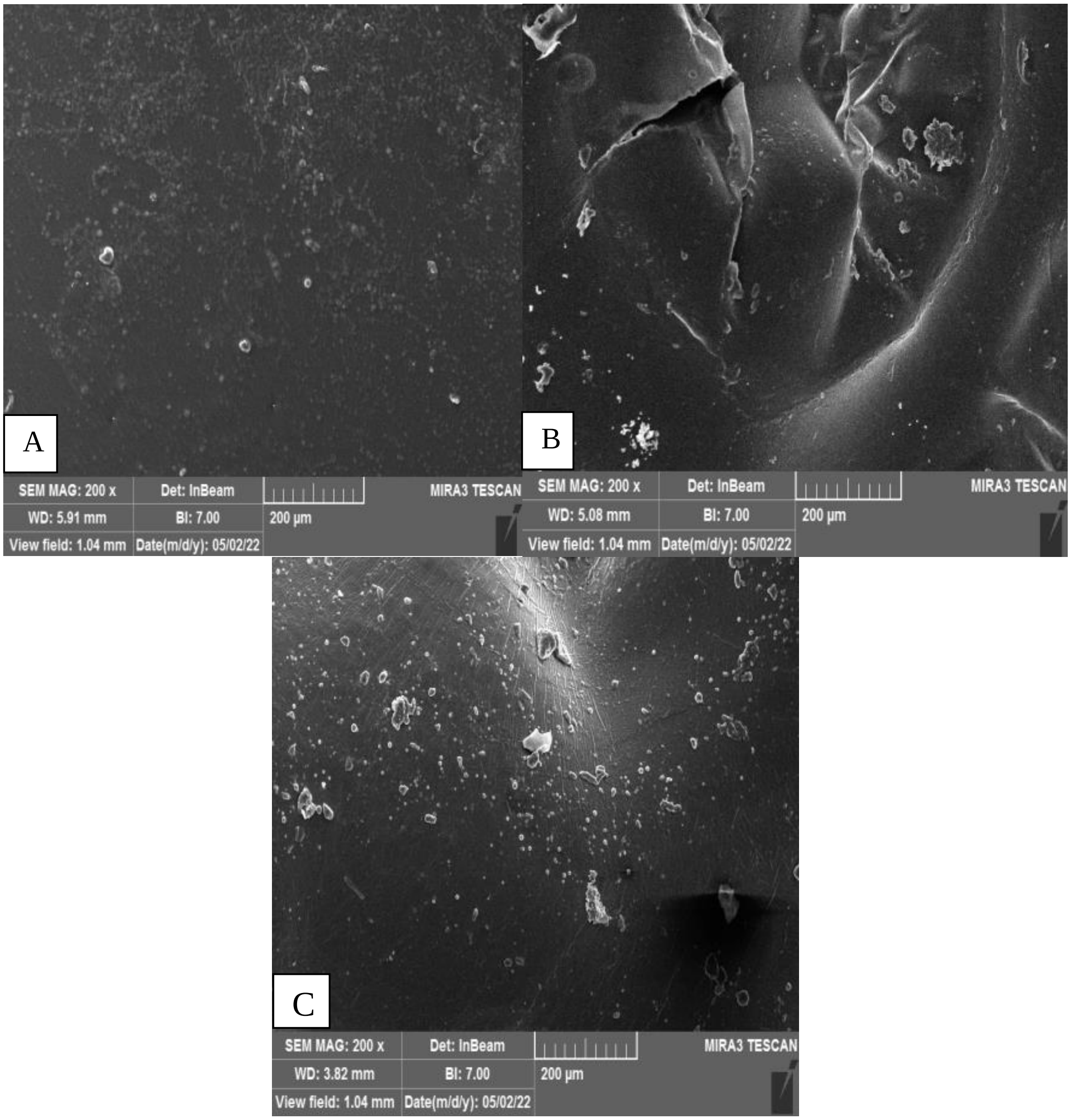


Fig. 4.12: SEM image at (200) x for: (A) silicone rubber, (B) polyurethane and (C) IPN

This image showed that the IPN has a continuous and homogenous morphology of silicone rubber phase with a random distribution of PU phase, which is embedded in matrix material and dispersed as a globule’s shapes in to the silicone rubber matrixes which give heterogonous morphology to IPN.

Furthermore, it can be observed that different sizes of these spherical shapes from PU material dispersed randomly in this matrix, there is a group of polyurethane agglomerates that differ in size and distribution in the matrix due the presence of organic polymers polyurethane and inorganic silicone rubber, mixed did not occurred between them due to the absence of physical interaction.

The results of this examination are consistent with the results of the FTIR examination.

It can be noticed from Figure (4.13) FTIR for three samples, the first sample of the tertiary blend, and the second tertiary blend coated with immersed in CPTES/acetone solution for 30 minutes and the third and was tertiary blend coated immersion for 60 minutes.

Nano chitosan has clearly interfered with IPN which consisting of silicone and polyurethane, so that all the open pores in it have been closed with the concentration of Nano chitosan particles in them, and it also found that the crosslinking strong and clearly homogeneous for the tertiary blend structure, indicating to better interfacial adhesion between constituents of composite material. And this indicated to a good compatibility between the component of IPN and the nanoparticles, which enhances the mechanical properties, this may be due to the dilution, this corresponds to research that studies this property [75, 91, and 113].

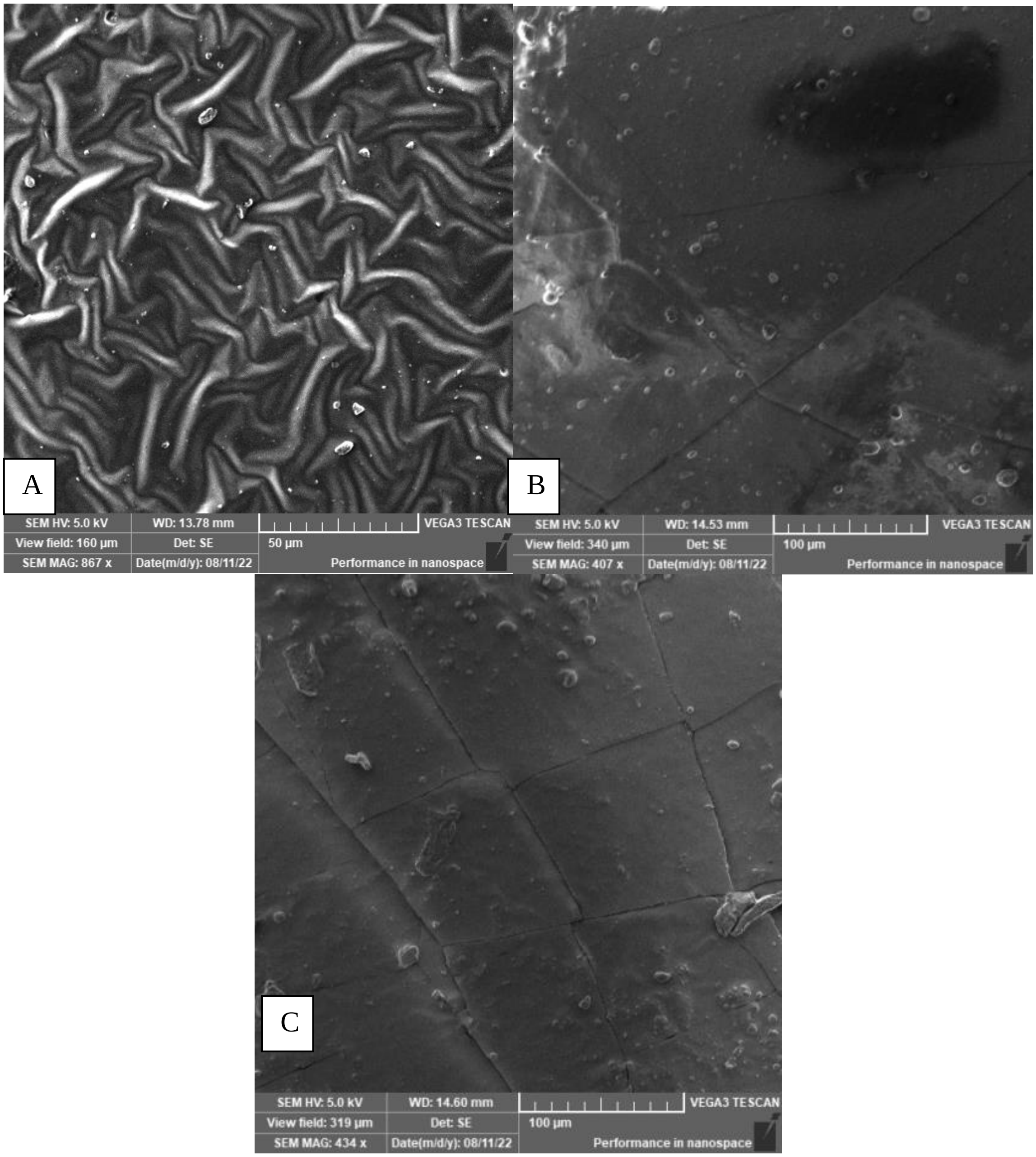


Fig. 4.13: SEM image of: (A) Uncoated tertiary blend with chitosan 3%, (B) tertiary blend coated by chitosan (immersed for 30 min in CPTES/acetone), (C) tertiary blend coated by chitosan (immersed for 60 min in CPTES/acetone)

4.4.4 AFM Analysis

Figure (4.14) represents the (3-D) AFM images of SiR and IPN (SiR/PU), and table below shown the difference in average diameter and roughness.

Table 4.5: AFM parameter for SiR and the IPN

Sample	**Average Diameter nm**	**Root Mean Square(S_q) nm**
SiR	1302.07	89.1
IPN	1353.00	35.8

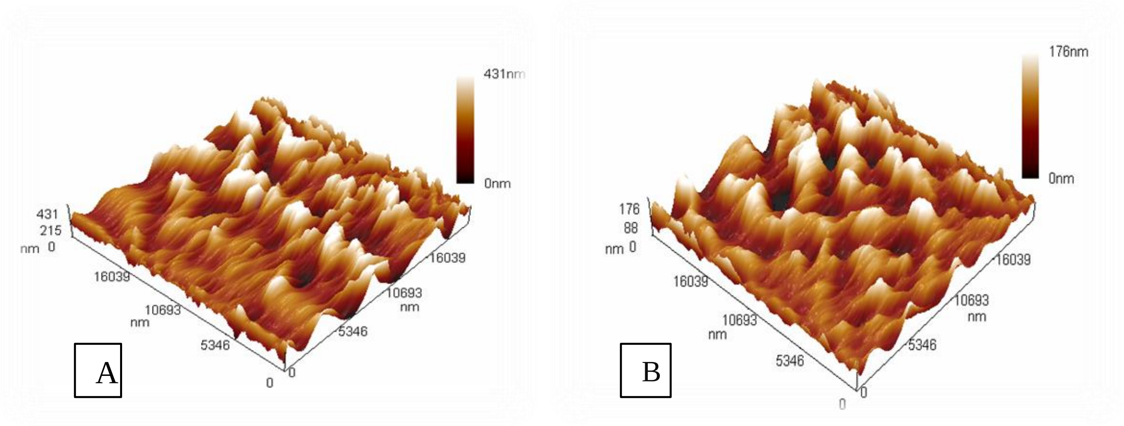


Fig. 4.14: AFM image 3D of: (A) SiR and (B) IPN

With the addition of polyurethane to silicone, it can be noticed from table (4.5); there was an increased in the average diameter as the indicator for porosity, where it was 1302.7nm and reached to 1353.00 nm, and the surface roughness has decreased relatively.

This may be due to the overlap of the liquid silicone material and its penetration between the cavities of the polyurethane, and this corresponds to researchers at [92].

AFM examination was conducted for the three samples for the purpose of knowing the surface roughness of each sample and the average diameter in addition to the size distribution on the surface as shown in the table (4.6).

It can be noticed that average diameter was (1076.29) nm for tertiary blend, increased to (1229.86) nm when tertiary blend coating with 30 minutes immersed in a 2% CPTES + 95 % acetone solution, noting a clear increased in the third sample, where the immersion was lasted for 60 minutes compared to the first sample, but the percentage of increase is less than in the second sample.

Tab. 4.6: AFM parameter for Tertiary blend uncoted and coated

Sample	**Average Diameter nm**	**Root Mean Square(S_q) nm**
Tertiary blend	1076.29	24.3
Tertiary blend with coating for 30 min	1229.86	40.7
Tertiary blend with coating for 60 min	1119.06	45

On other hand (S_q) which represents roughness for each samples increased from 24.3 nm for Tertiary blend to 40.7 nm for sample two until sample three it became 45 nm.

This increase in the surface roughness of the samples can be attributed to its effect on the surface treatment through the acids to which it was exposed, and the more time the sample was exposed to acid or immersion in CPTES and acetone solution leads to a roughness in the surface as shown in figure (4.15).

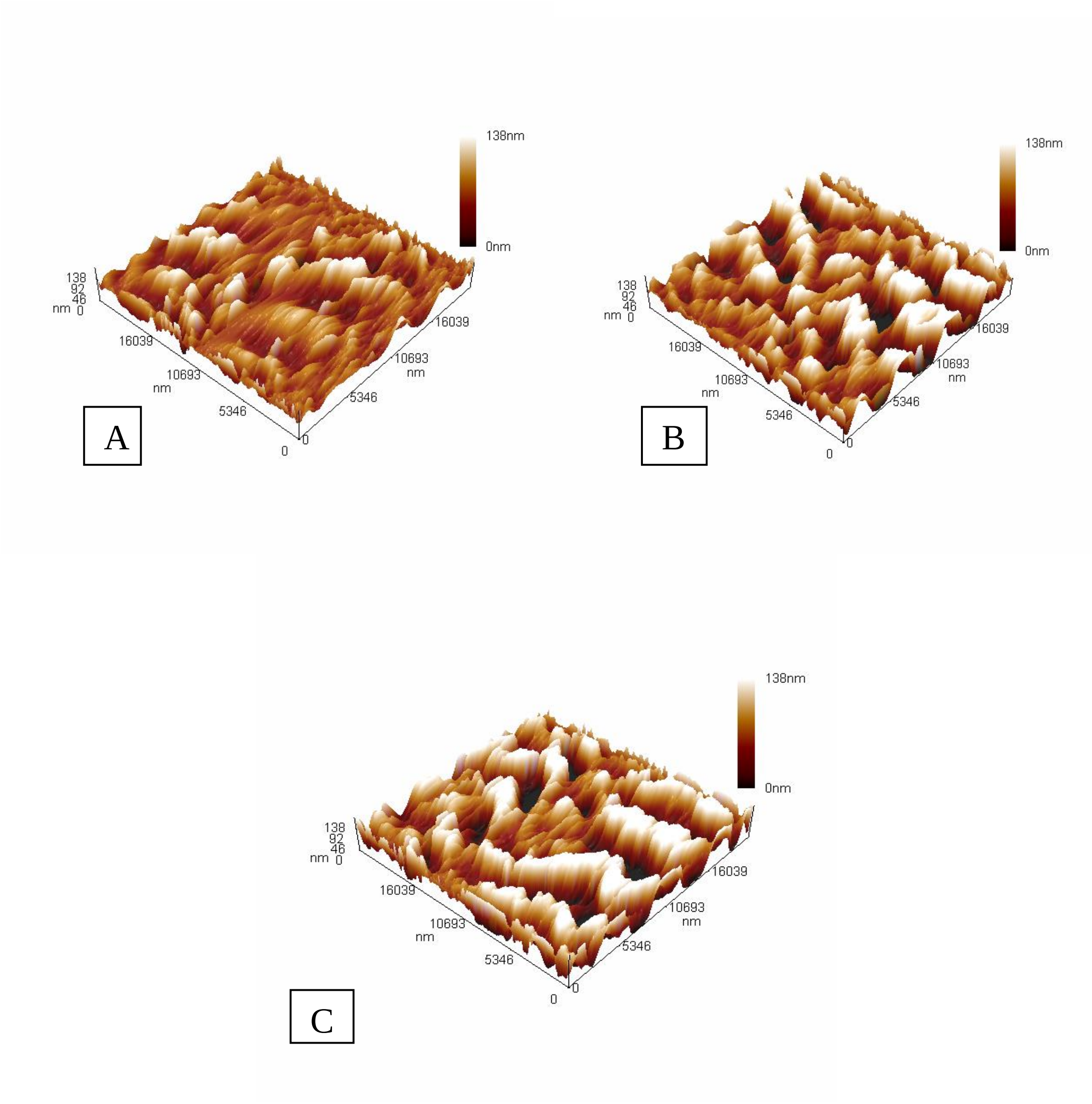


Fig. 4.15: AFM parameter and analysis of: (A) Tertiary blend, (B) Tertiary blend coated (30 min) and (C) Tertiary blend coated (60 min)

The slight decrease in porosity that occurred in the second sample after 60 minutes may be attributed to the increase in the density of the coated on the surface, which allows more chitosan solution penetration between the pores and helps to close them.

4.4.5 TGA Analysis

Figure (4.16) gave TGA/DTG curve of silicone rubber. It is clear that SiR had high thermal stability than PU foam, here, three stages $T_{-5.34\%}$, $T_{-71.28\%}$, and $T_{-16.14\%}$ at 250ºC ,590ºC and 975ºC, respectively.

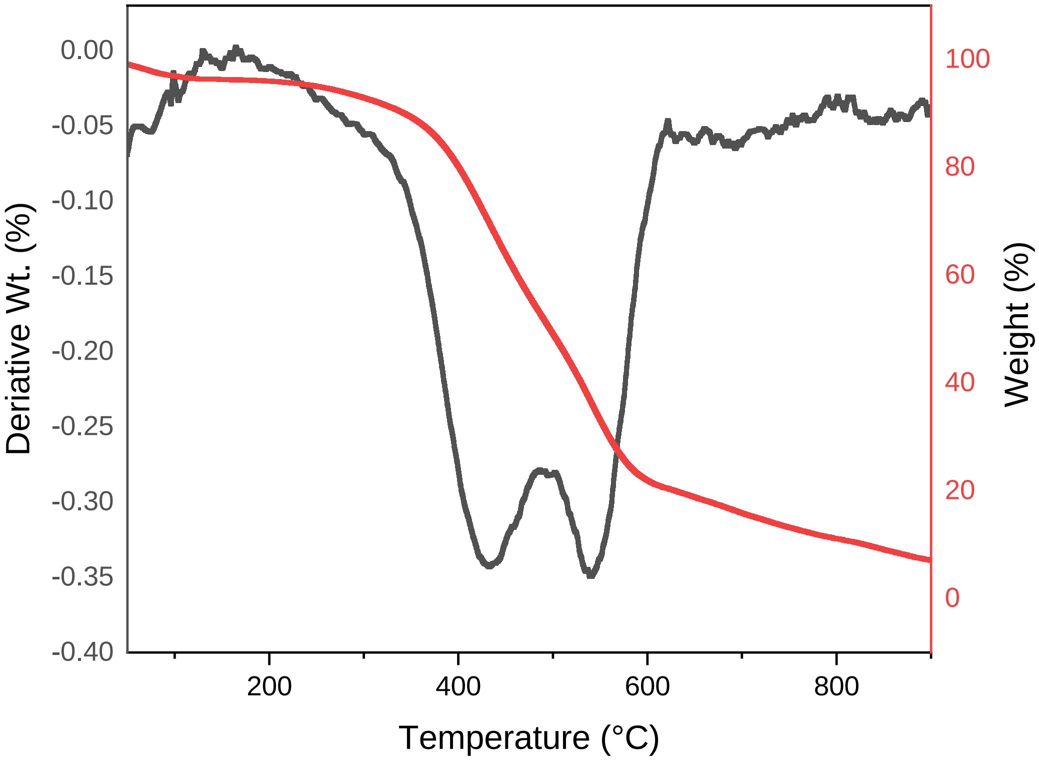


Fig. 4.16: Results of DTG, TGA analysis and parameters description for SiR

First stage was dehydration, started at 30º to 250º which represents the lowest weight loss about 5.34% due to moisture evaporation in the silicone matrix, second stage was decomposition structure of silicone rubber bond in nitrogen atmosphere, where a weight loss about 71.28% began at just above 250ºC and finished above 570ºC, this is due to the lack of high-energy chemical bonds, because the silicone rubber only possesses the Si-O-Si bonds in its molecular backbone.

Finally, third stage was degradation of silicon rubber with weight loss about 16.14%. Residual weight was about 7.28%.

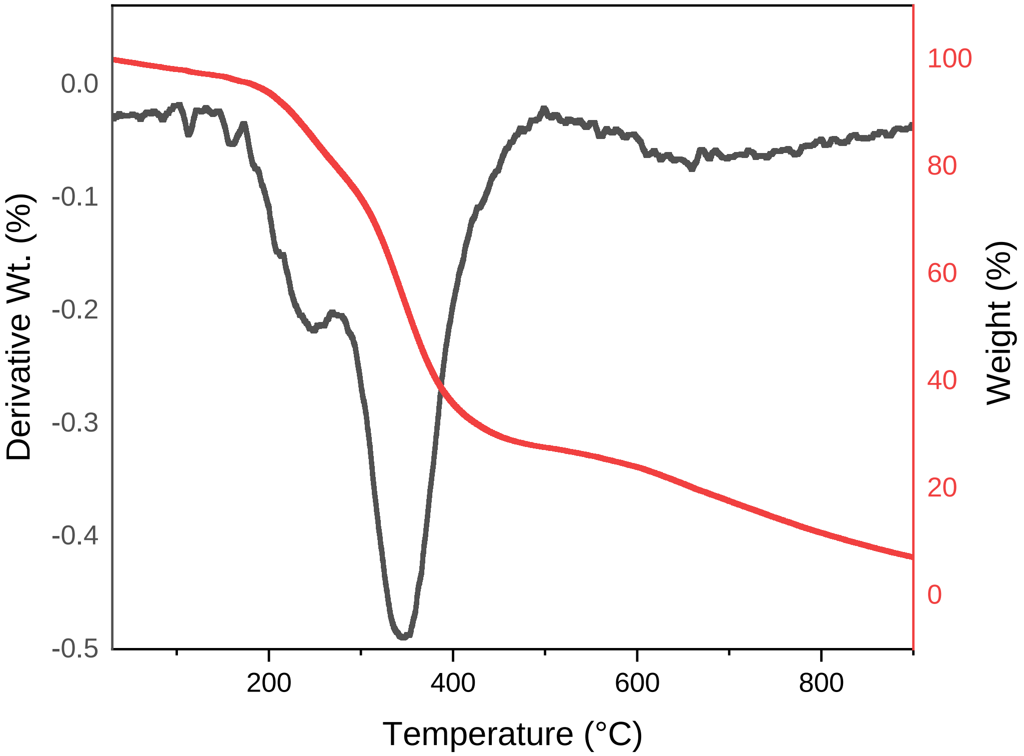


Fig. 4.17: Results of DTG, TGA analysis and parameters description for PU

The samples were heated in the N2 atmosphere from room temperature to the maximum of 950ºC. The weight loss percentage and temperature relationships were obtained for the PU sample.

From figure (4.17) notice that PU had four stages $T_{-4.32\%}$, $T_{-57.62\%}$, $T_{10.74\%}$ and $T_{20.42\%}$ at 190ºC, 387ºC, 500ºC and 900ºC.

The highest weight loss was 57.62% at 190ºC to 387ºC, This part should be the breaking of C-O bond in hard segment, which is decomposed into isocyanate and polyol. Residual weight was 6.9%.

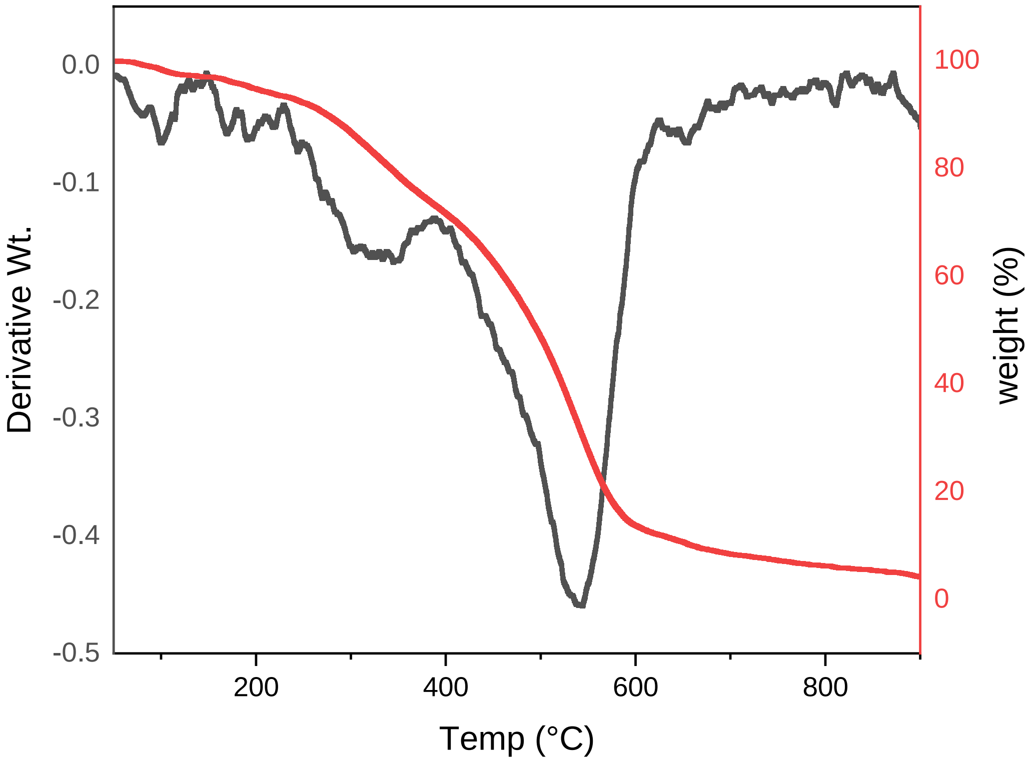


Fig. 4.18: Results of DTG, TGA analysis and parameters description for IPN

In the case of IPN, the results exhibit five stages and the first one represent hydration for IPN due to moisture evaporation at 180ºC a weight loss about 2.55% in IPN.

Second, third parameters about 275ºC, and 420ºC, with weight loss about 5.65% and 24.06%, represent initial decomposition temperature (IDT) for urethane group respectively as shown in figure (4.18).

There was no major degradation until 230ºC, significant degradation was seen between 420ºC to 570ºC, which represent fourth parameter and the biggest weight loss about 46.29%, due to the increase of PU content compered to silicone rubber. Residual weight was about 5.02%, these results agreed with [113, 114].

4.5 Wettability Results

It can be noted that from figure (4.19 - 4.22) the water contact angle markedly decreases from 80.959◦ of IPN (80%SiR+20%PU) surface to 68.118◦ of the tertiary blend surface, and decreases to 65.219º, 63.523º of the modified surface of tertiary blend after the chitosan coating for 30 min and 60 min, respectively.

Chitosan is hydrophilic polymers. The increased hydrophilicity implies that chitosan was successfully coating onto tertiary blend surface. Silicone rubber is hydrophobic as well as rigid polyurethane and this is a feature that needs to be modified and relative improvement if we want to introduce these materials into the manufacture of the internal storage of the socket, and this correspond to research that study this property [76].

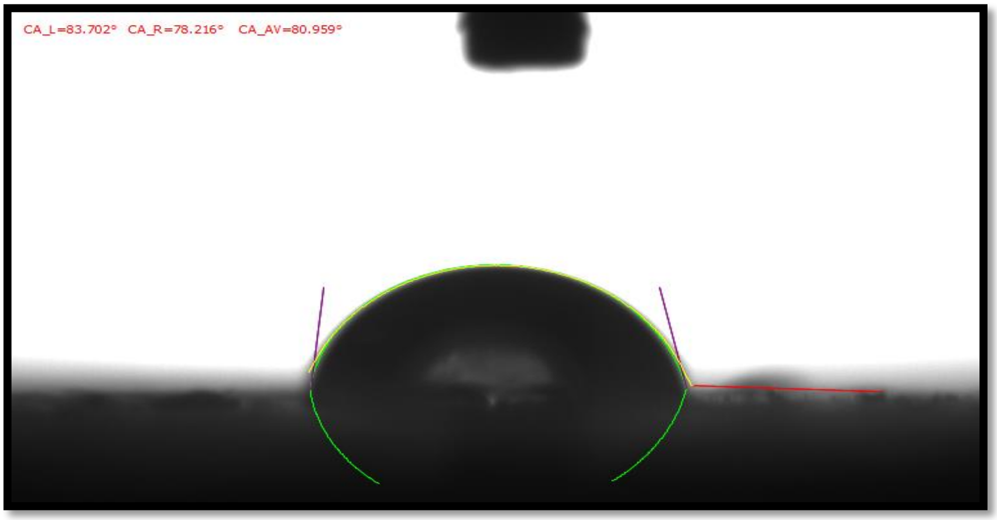


Fig. 4.19: Contacting angle of IPN surface

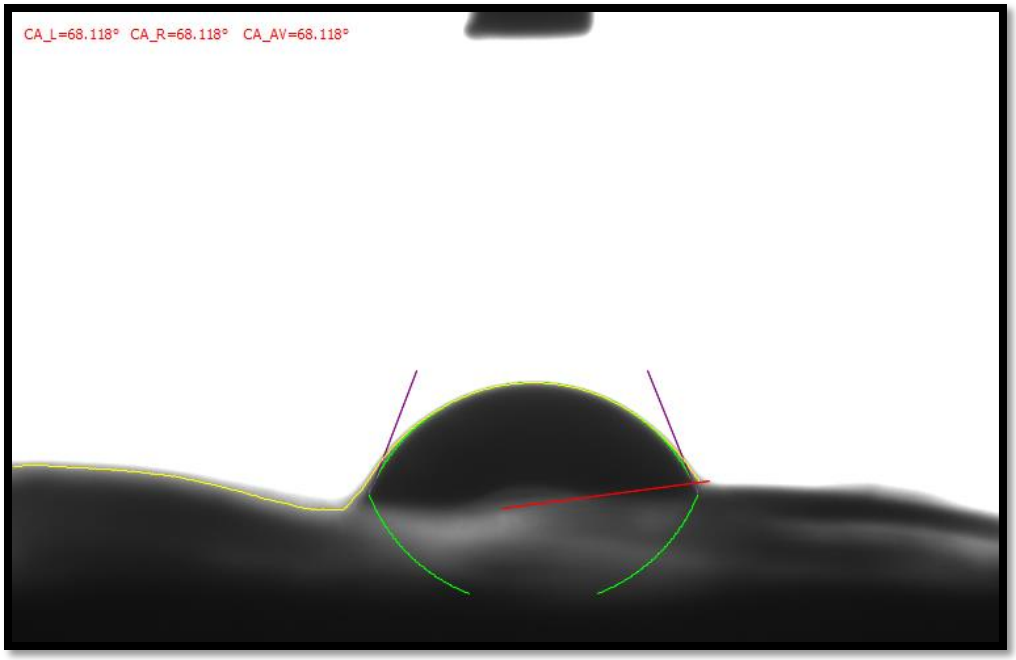


Fig. 4.20: Contact angle of tertiary blend surface

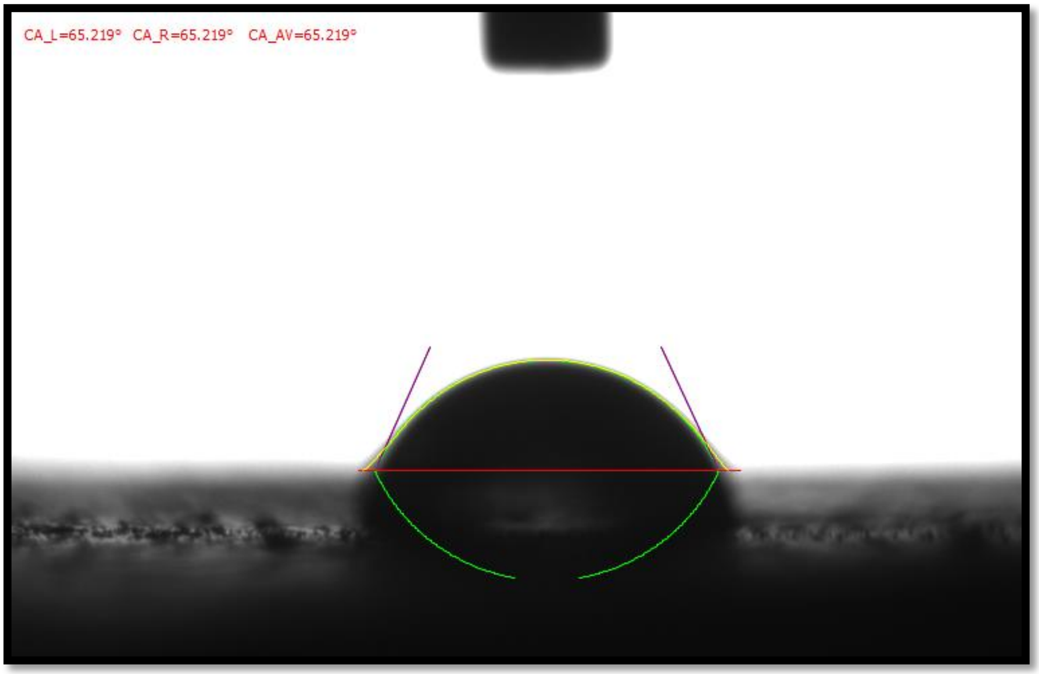


Fig. 4.21: Contact angle of the modified tertiary blend (30 min) surface

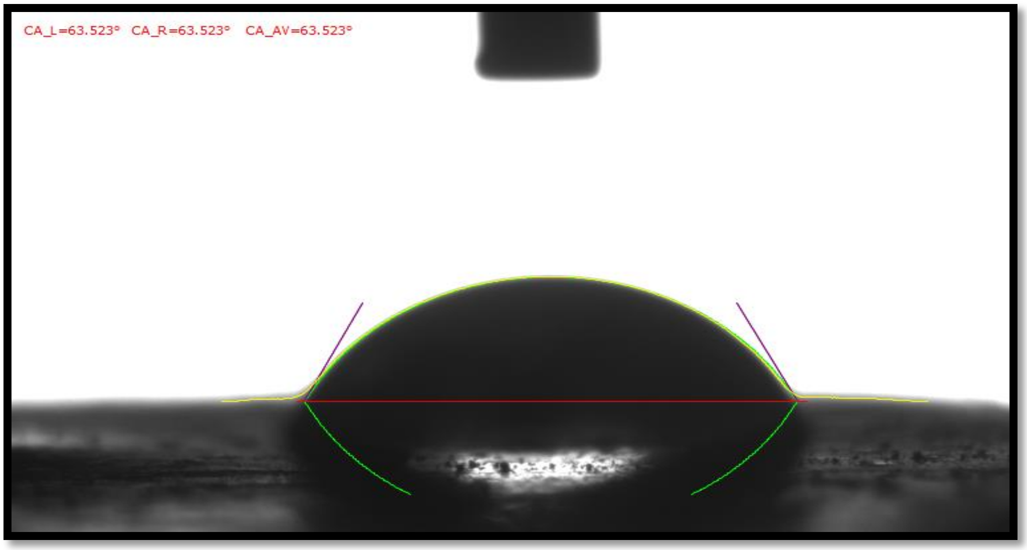


Fig. 4.22: Contact angle the modified tertiary blend (60 min) surface

4.6 Biological Results

4.6.1 Antibacterial Result

Figures 4.23 and 4.24 as well as table 4.7 represent the antibacterial activities of SiR, IPN, tertiary blend (uncoated), tertiary blend coated with 30 min and 60 min against Staphylococcus aureus and Pseudomonas, which are gram-positive and gram-negative, respectively.

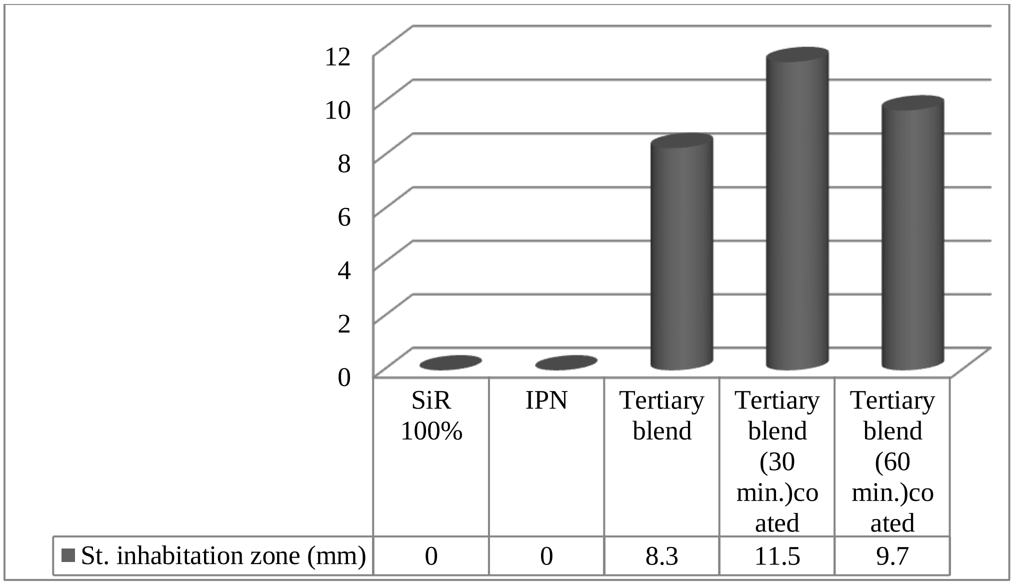


Fig. 4.23: Antibacterial activity against Staphylococcus

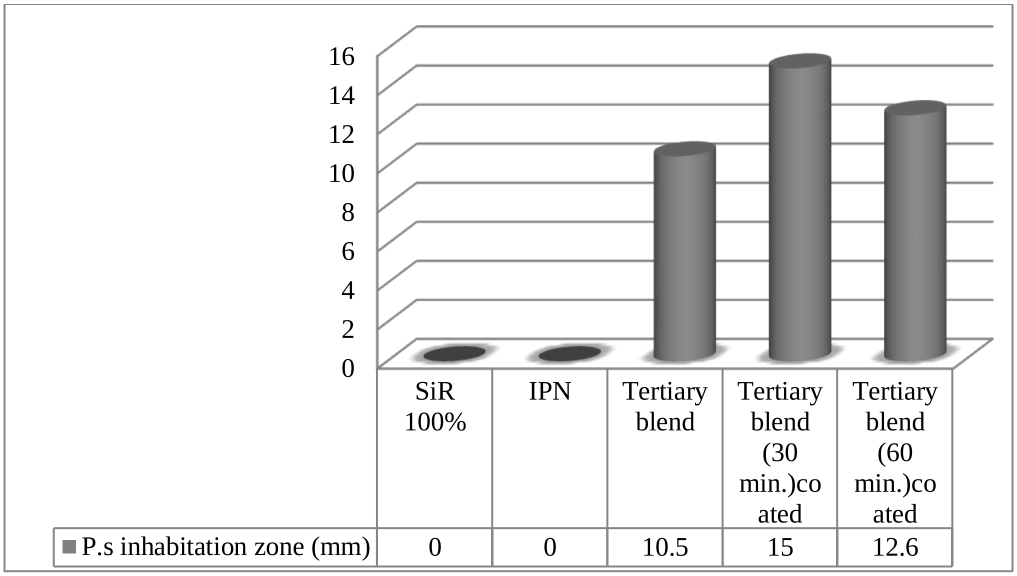


Fig. 4.24: Antibacterial activity against Pseudomonas

Table 4.7: inhibition zone of Pseudomonas and Staphylococcus aureus results

Sample	**Inhibition Zone Diameter (mm)**	
	Pseudomonas	Staphylococcus aureus
SiR 100%	0	0
IPN	0	0
Tertiary blend	10.5	8.3
Tertiary blend (30 min) coated	15	11.5
Tertiary blend (60 min) coated	12.6	9.7

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

$$IE = \frac{I\ Zone\ at\ high\ concentration - I\ Zone\ at\ low\ concentration}{I\ Zone\ at\ low\ concentration} * 100\%$$

The following findings can be concluded:

1. Both neat SiR and the IPN have no antibacterial activity.

2. Because of chitosan present, the tertiary blend has good antibacterial activity especially against Pseudomonas microorganism.
3. The 30 min coating duration gave best results (10.5 mm) than the 60 min duration time (8.3 mm). These results coincide with the inhibition efficiency (IE) results; 42.8% vs. 38% respectively.
4. These results agreed with AFM, contact angle, and SEM results.

4.4.2 Biofilm Formation test

Biofilm formation is regulated by a variety of environmental factors, such as pH, the availability of nutrients and oxygen, and the concentration of bacterial metabolites. The microtiter plate biofilm assay is a useful method for assessing bacterial attachment by measuring the staining of the adherent biomass. Because it utilizes a 96-well plate format, it is suitable as a tool for screening large numbers of bacterial strains or species. The results obtained are shown in Table (4.8).

Table 4.8: Results of bacterial formation's biofilm and adherence by microtiter plate method

Type of bacteria	Type of sample	OD value at 630 nm	Adherence	Biofilm formation
Pseudomonas (G^{-ve})	Uncoated tertiary blend	≥ 0.287	Strong	High
	Tertiary blend coated (30min.) immersed at CPTES/acetone	≥ 0.089	Non	Non
	Tertiary blend coated (60min.) immersed at CPTES/acetone	≥ 0.092	Non	Non
Staphylococcus (G^{+ve})	Uncoated tertiary blend	≥ 0.291	Strong	High
	Tertiary blend coated (30min.) immersed at CPTES/acetone	≥ 0.091	Non	Non
	Tertiary blend coated (60min.) immersed at CPTES/acetone	≥ 0.097	Non	Non

It shows the non- adherence by the bacteria on the surface of tertiary blend which coated by chitosan and the non-formation of the biofilm layer; while, they form at the surface without the presence of chitosan as a coating.

The following findings can be concluded:

1. The uncoated tertiary blend gave strong adherent against both Pseudomonas and Staphylococcus microorganisms, since their Optical Density (OD) are more than 0.24 nm.
2. Pseudomonas (G^{-ve}) gave less Optical Density (OD) than Staphylococcus (G^{+ve}) in both coating duration times.
3. The best sample in privation biofilm formation is the coated sample which immersed for 3o min, since its OD is 0.089 nm. As shown in table (4.8), these correspond with antibacterial result.

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

1. Through physical tests, the following was observed: an increased in hardness and modulus of elasticity at 20% PU in IPN, as well as an increased in the rebound ratio.

2. Through structural tests, the following were observed: the tendency of the resulted IPN to crystallize with an increase in the crystallite size, physical interaction between SiR and PU, and an increase in roughness and porosity.

By examining the water absorption, an increased the absorption ratio was obtained, and the contact angle decreased at tertiary blend.

3. Light weight: adding 20% of polyurethane to silicone rubber gives the required specifications for making the liner in terms of light weight and porosity.

4- CPTES can be used as cross-linker between tertiary blend and chitosan solution and used glutaraldehyde as a fixing agent.

5. At biological tests: Both neat SiR and the IPN have no antibacterial activity, while the tertiary blend has good activity especially against Pseudomonas microorganism and the 30 min coating duration gave the best results than the 30 min in terms of inhibition zone diameter (IZ) and inhibition efficiency (IE).

6. Pseudomonas microorganism have less bacterial adherent than Staphylococcus ; less Biofilm formation tendency and the best sample was the coated one which immersed for 30 min. .

5.2 Recommendations

1- Using more than one method to increase the porosity (physical, chemical and mechanical) to achieve the best porosity.

2- Conducting a study for manufacturing superabsorbent blend by adding different proportions of water/isocyanate.

3- Study coating layer thickness and adhesion strength tests for samples after coating.

4- Make numerical part for this project.

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الخلاصة:

تكون الأطراف الصناعية السفلية على ثلاثة أنواع: فوق الركبة ، من خلال الركبة وتحت الركبة. يتكون طرف فوق الركبة من عدة أجزاء ويعتبر المقبس (التجويف) من أهم هذه الأجزاء والذي يحتاج بدوره إلى بطانة داخلية تعمل على تثبيته بالجزء المبتور وتمنع الاحتكاك المباشر بينه وبين الجلد مما يحول بالتالي من نمو العفن في هذه المنطقة. للقيام بوظائفها الحساسة هذه, فتحتاج البطانة إلى تحسين خصائصها البيولوجية والميكانيكية, لذا يهدف العمل الحالي الى تحسين هذه الخواص وجعلها مناسبة للظروف المناخية القاسية في العراق والتي تتسبب بتعرق الطرف الصناعي مصحوبا بروائح كريهة.

تم تكوين شبكات بوليمرية متداخلة (Interpenetrating Polymer Network; IPN) وذلك بإضافة سائل البولي يوريثان (PU resin) الى سائل مطاط السليكون (SiR resin) وبوجود المصلدات المناسبة لكل منهما. أضيف البولي يوريثان بعدة نسب وزنية (10 ، 15 ، 20 ، 25 ، 30 و35٪) وبعد اختيار الخليط الافضل, تم اضافة مسحوق الشيتوزان النانوي بنسب 3% وزناً بغية اكسابه خواص مقاومة للبكتريا. امعاناً في زيادة كفاءة مقاومة البكتريا لأسطح الشبكات البوليمرية هذه, فقد تم طلاءها بطبقة من الشيتوزان واستخدمت مادة CPTES لربط الطلاء.

تم إجراء العديد من الاختبارات مثل مطيافية فورييه بالأشعة تحت الحمراء (FTIR) , تحليل حيود الأشعة السينية (XRD) , مجهر المسح الإلكتروني (SEM) , مجهر القوى الذرية (AFM) والتحليل الحراري الوزني (TGA) اضافة الى الاختبارات الميكانيكية (الشد, الكلال, الارتدادية , معامل المرونة و الاستطالة), كما تم حساب الوزن النوعي وامتصاصية الماء. لرصد مدى تغير خصائص السطح بعد الطلاء, فقد اجريت اختبارات زاوية التلامس والمقاومة المايكروبية لنوعين من البكتيريا وهما Staphylococcus و Pseudomonas كما وظفت تقنية Microtiter Plate Assay لدراسة تكون الاغشية الحيوية.

أظهرت النتائج الـ FTIR عدم وجود تفاعل كيميائي بين SiR وPU فيما أظهرت نتائج الـ XRD حصول زياده في الـ crystallite size من 20.06 الى 26.51 عند ($2\theta=12^{o}$) , كما ان نتائج الـ SEM أظهرت عدم امتزاجية الخلائط البوليمرية هذه. أوضحت نتائج الـ AFM زيادة في المسامية وانخفاضاً في الخشونة ، في حين بين اختبار ال TGA (مع DTG) ان الشبكات البوليمرية تتحلل عند 420 درجة مئوية مصحوبة بفقدان وزني يصل الى 46.29٪.

بينت النتائج ان طبقة طلاء الشيتوزان قد قللت من قيمة زاوية التلامس من 80.989^{o} الى 63.523^{o} ومنعت تكوين نوعي البكتريا المذكورين انفاً فيما زادت قابلية امتصاص الماء بنسبة 6.8٪ مما يعني زيادة امتصاص التعرق والحد من ظهور الروائح المحرجة للمرضى في اشهر الصيف اللاهبة.

أظهرت الاختبارات الميكانيكية حصول زيادة في الصلابة بمقدار 60%, بينما الزيادة حاصلة لمعامل المرونة بنسبة 40% مع زيادة نسبة البولي يوريثان في شبكة البوليمر المتداخلة، وعند نسبة

20٪ بولي يوريثان زادت قدرة التخميد و قلت الخواص الميكانيكية من حيث إجهاد الشد, الاستطالة والكلال .

أظهرت نتائج الفحص المضادة للبكتيريا أن كلا من SiR و IPN ليس لهما قدرات على مقاومة نمو البكتريا، في حين أن الخليط الثلاثي المغطى بمحلول الشيتوزان لديه قدرة جيدة خاصة ضد الكائنات الحية الدقيقة Pseudomonas ومدة الغمرفي محلول (CPTES/acetone) لمدة 30 دقيقة أعطت أفضل النتائج (منطقة تثبيط 10.5 مم وكفاءة تثبيط 42.8٪ مقابل 8.3. مم و 38٪ على التوالي).

أظهرت نتائج تكوين الأغشية الحيوية أن الكائنات الدقيقة الزائفة (G^{-ve}) لديها ميل أقل (أفضل) من المكورات العنقودية (G^{+ve}) لتشكيل هذا الفيلم. وكانت أكفأ عينة في تكوين الأغشية الحيوية هي العينة المطلية التي تم غمرها لمدة 30 دقيقة ، حيث أن Optical Density (OD) يبلغ 0.089 نانومتر.

وزارة التعليم العالي والبحث العلمي

جامعة بابل

كلية هندسة المواد

قسم البوليمر والصناعات البتروكيمياوية

تحضير وتقييم البطانة اللينة لتعويضات مقبس فوق الركبة للاطراف الصناعية

الرسالة مقدمة إلى

كلية هندسة المواد/ جامعة بابل وهي جزء من متطلبات الحصول على درجة الماجستير في هندسة المواد / البوليمر

من قبل

هاجر عبد الصمد محمد علي مهدي

بكلوريوس هندسة المواد/ بوليمر 2014

إشراف

أ .د محمد حمزة المعموري **أ.م.د اسراء علي حسين**

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