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Preparation and Evaluation of Polymeric Coatings for Dental Applications

A Thesis
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I certify that this thesis entitled "**Preparation and Evaluation of Polymeric Coatings for Dental Applications"** had been carried out under my supervision at the University of Babylon/ College of Material's Engineering/ Department of Polymer in partial fulfillment of the requirements for the degree of Master in Material's Engineering/Polymer.

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Abstract

The most common problems in dental implants are cracked, broken teeth, gum disease, root infection, tooth decay and biofilm formation. To overcome that, the proposed act to solve this problem is to select a base material with good mechanical properties, high thermal stability and corrosion resistance consideration should be given to bacteriostatic surface. Titanium and Poly(methylmethacrylate) as Biomaterials used for this purpose because of its unique characteristics and coated by Biopolymer coating to get anti-bacterial surface and non- Biofilm formation.

In this study, two types of substrates, commercial pure Titanium (Ti) and Poly(methylmethacrylate) (PMMA) are used as dental implants and coated by pure Chitosan and polycabrolactine (PCL)mixed with different weight percentage of nano Hydroxyapatite (0.1, 0.5, 1)wt% after by dispersing ultra-sonication to enhanced the adhesive strength using two coating techniques Layer by layer (LBL) and Spin coating (SP)

Many of the properties are studied in this research, such as thermal, mechanical and biologics properties.

Fourier Transforms Infrared (FTIR) is tested to the coating (PCL+nHA) to identify the existing bonds and chemical reactions for the coating. The test show the addition of nHA to the PCL matrix did not result in any chemical bonds.

The wettability of the substrate is studied using the contact angle test where the contact angle was 82.45◦ and 101.281◦ for Ti and PMMA substrates respectively before applying the coating reduce to 35.871◦ and 55.7◦due to the coating with (Chitosan, PCL).

Optical microscope (OM) is carried out to determine the coating's homogeneity within the coating.

The bacterial activity was studied using the Agar well Diffusion Method. The results showed that PCL/nHA has bacterial activity as the inhibition area reaches about 20mm for both gram-positive bacterial(Enterococcus fecalis) and gram-negative bacterial(Escherichia coli).

The results of adhesive strength are also studied by Pull-off test, where they increase with increasing the concentration of the nHA reach to 14%.

The corrosion test of the coating was studied and the results show that the corrosion current for base Ti substrate1.895e-4. After applying coating the corrosion resistance decrease and reach to 4.02e-7.

Contents

Abbreviations

AFM	Atomic force microscope
APTES	Aminopropyltriethoxysilane
CA	Contact angle
CA	Contact angle
CVD	Chemical vapor deposition
CVD	Chemical vapor deposition
DSC	Differential scanning calorimetry
E.corr	Corrosion potential
FTIR	infrared Fourier spectroscopy
G+ve bacteria	Gram- positive bacteria
G-ve bacteria	Gram-negative bacteria
LBL	Layer by Layer
O.D	The optical density

Symbol

µA	Micro ampere
µm	Micro meter
HA	Hydroxyapatite
NP	Nanoparticles
PCL	Polycabrolactone
PMMA	Polymethylmethacrylate
ppm	Partial per million
SP	Spin coating
Ti	Titanium

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Chapter One

1.1 Introduction

For the purpose of resolving the issue of tooth loss, dental implants have grown in popularity recently [1]. Due to their superior mechanical qualities, low specific weight, great corrosion resistance, and good biocompatibility, titanium and its alloys have been widely employed as the raw material for dental implants [2]. Titanium dental implants have a high success rate, but there are still a considerable number of failures due to a variety of issues, such as a lack of implant osseointegration, low bone quality, smoking, or infection. In particular, it is believed that infection is a major contributor to the mid- to long-term failure of dental implants [3]. In order to secure various types of prostheses, dental implants are now a trusted therapeutic option for individuals who are partially or completely edentulous. Dental implants are now a common surgery for replacing a single tooth in the cosmetic zone, offering many benefits but also difficulties for sophisticated individuals. Particularly in the dental implant sector, surface treatments are typically used to change substrate materials while maintaining desirable qualities. Mechanical, chemical, or physical approaches can all be used to treat surfaces. Surface treatment is utilized in dental implants to change the surface topography and surface energy, which improves wettability [3][4], boosts cell development proliferation [5], and speeds up the osseointegration process [6]. The characteristics of the surface affect how well a dental implant performs. The biocompatibility of the materials and the surface abrasion played a crucial part in ensuring optimal tissue and osseointegration contact. Increased roughness can concurrently increase the surface area of the implant, facilitate cell migration and adhesion to the implant, and boost the osseointegration process, according to research by Goyal and colleagues [7]. The majority of surface treatments can benefit the dental implant, according to earlier studies. Over 45 years ago, Bra nemark et al.

published the first description of the osseointegration process [1][2]. Their research on the forms and materials of dental implants helped to usher in a new era of study. The osteoinductive potential of implant surfaces, however, has only recently come to the forefront of biomedical research, replacing the earlier focus on implant shape. There are currently about 1300 distinct implant systems that vary in size, shape, mass, and surface materials. Considerations include surface topography, surface chemistry, wettability, and surface modification [3]. There are currently about 1300 distinct implant systems that vary in size, shape, mass, and surface materials. Considerations include surface topography, surface chemistry, wettability, and surface modification [3]. The most common implant forms are cylindrical or tapered [4]. Because they enable direct interactions with host osteoblasts during bone formation, surface characteristics like topography, wettability, and coatings have an impact on biological processes during osseointegration [5]. Dental implants have excellent long-term survival rates in general. However, a very small proportion of people do have implant failure. Poor osseointegration causes primary implant failure in 1-2% of patients within the first few months [6]. Pre-implantities are the most frequent reason for secondary implant failure, which happens in about 5% of patients several years after successful osseointegration [6][7]. The number of those living in poverty is rising as a result of the demographic trend in industrialized nations. Clinical problems such low bone density or quality, as well as other challenging comorbidities Osteointegration issues can occur in patients with diabetes mellitus, osteoporosis, bisphosphonate medication, or following radiation [8]. In order to expedite osseointegration after implant implantation, these patients continue to provide a substantial challenge in dental implantology [8]. New bioactive surface features are also being created with the intention of accelerating osseointegration to support

early loading techniques. In order to improve early osseointegration and long-term bone-to-implant contact while minimizing severe marginal bone loss, scientific research on surface modifications must first identify the underlying causes of these effects.

1.2 Literature Review

R. Marguerite in 2006 [9]. In their research determined that chitin is a biodegradable, renewable polymer that forms films and possesses antibacterial and antifungistatic characteristics. Chitosan has an advantage over other polysaccharides like cellulose, starch, galactomannans, etc. because its chemical structure makes it easy to make complicated alterations at the C-2 position, allowing for the development of polymers with specific functions.

Morshed Khandaker, 2007 [10]. In their work, due to the enhanced PMMA cement surface roughness, In contrast to untreated PMMA samples, Polycaprolactone PCL-treated PMMA samples showed statistically significant improvements in osteoblast cytocompatibility. These results show that the PMMA's PCL coating had no negative effects on the material's mechanical characteristics when it was bent. Since the physico- and biocompatibility of PMMA was improved by the PCL coating method established in this work, it can be concluded that PCL coating on PMMA alters the surface, promoting in vivo bone formation, which improves implant with bone.

Xiaojun Yu in 2008 [11]. A promising technique to increase titanium implant biocompatibility is biomimetic surface modification. Layer by layer (LBL) self-assembly was used to cover pure titanium with a multilayer of chitosan and heparin (Hep). The NaOH treated Titanium substrate (negatively charged surface) was initially painted with a single layer of positively charged Poly-L-lysine (PLL), then alternate layers of negatively and positively charged Hep, and then a final layer of positively

charged Ch. To examine the in vitro cytocompatibility of the modified titanium and untreated titanium surfaces, osteoblasts were cocultured with each. The multilayer was characterised by DR-FTIR, SEM, and AFM. The outcomes supported the stepwise fabrication of the Hep-Ch multilayer on the Titanium surface. The Titanium with Hep-Ch multilayer coating was enhanced.

Z. Abdul Amer et al. in 2014[12]. In their study, Chitosan is combined with PMMA, a polymer with great biocompatibility, to achieve various degrees of breakdown for drug release. In this study, various experiments were carried out, including flexural strength, biodegradability, tensile strength, Fourier Transform Spectroscopy (FTIR), and sample morphological testing.Mechanical evidence shows that adding 10% chitosan increased the flexural modulus by (59.77%), enhanced peak tensile strength by (46.15%), and increased the young modulus by (53.84%), which decreased by 10% when samples were immersed in synthetic body fluid (SBF) solution. The morphological test showed that samples had formed vacancies and pits after being submerged in the (SBF) solution. The process of degradation is also evidently demonstrated by the weight loss, swelling, porosity, and water absorption.

I. Younes, M. Rinaudo in 2015 [13]. This study described the most widely used methods for extracting chitin from marine species. As a result, the manufacturing conditions for chitosan are reviewed since they have a significant impact on the synthesis of chitosan at various levels of acetylation (DA) and molecular weight (MW).The biological processes that include antioxidants, anticancer, antifungal, and antibacterial effects are also discussed. Interestingly, the homogenous distribution of the acetyl groups, DA, and MW offers the link between chemical structure

and biological activity for the first time in chitosan molecules. X-ray diffraction, IR spectroscopy, and NMR are all used for characterization.

Giovanna Orsini, 2016 [14]. in the study of dental implants The Self-assembling LBL methodology offers a new method for achieving Enhancing the implant's biocompatibility, achieving effective osseointegration with the surrounding bone tissues, and forming a strong soft tissue closure prevent infections around the implant, protect soft tissue, and it's crucial to increase the success rate of implants. For these objectives LBL widely applied, as was previously indicated.

Mani Karthega 2016 [15]. Using the electrospinning approach, Polycaprolactone (PCL) and Polycaprolactone/Ti (PCL/Ti) composite nanofiber were created and coated with various weight percentage compositions of Ti (2 %, 4 %, and 6 % wt). The surface morphology and elemental composition results show that electrospinning the PCL/Ti composite nanofiber fiber on the alloy's surface was successful. According to electrochemical and cell proliferation experiments, PCL and PCL 6% wt Ti composite nanofiber showed good support for cell proliferation along with improved alloy anticorrosion.

Farzad Soleymani 2017 [16].To increase its corrosion resistance, bioactivity, and biocompatibility, an anodized alloy was coated with polymer composite consisting of polycaprolactone/chitosan (PCL/Ch) with various percentage of baghdadite. It was assessed how varying baghdadite concentrations (0, 1, 3, and 5 % wt) influenced the microstructure, wettability, roughness, and corrosion resistance of the surface. The applied nano-polymer-ceramic coating with 3 % wt baghdadite content was found to be hydrophobic, boosting corrosion resistance and lowering the corrosion current density in the surrounding environment.

Rashid Mad Jin 2018 [17]. In order to create porosity scaffolds for tissue engineering purposes, two semicrystalline polymers were combined. nHA/PCL/chitosan, and PCL/chitosan. The scaffolds' appropriate pore diameters were crucial for cell spreading, adhesion, and penetration. There were scaffolds. When tested on human skin fibroblasts it is harmless. The addition of nHA following the mixing of chitosan with The scaffolds' wettability, or hydrophilicity, was improved by PCL. Tetracycline HCL medication was added to the scaffolds' antimicrobial qualities. There were scaffolds created with appropriate characteristics for tissue engineering applications.

F. Causa, P 2019 [18]. Within this paper Hydroxyapatite (HAP) particles were added to the PCL matrix to improve mechanical properties and encourage osteoconductivity; three PCL-based composites with varied volume ratios of HAP (13%, 20%, and 32%) were examined. Biocompatibility and osteoconductivity were examined together with the mechanical properties and structure. The mechanical performance of the scaffold (such as elastic modulus) significantly improved with the inclusion of HAP particles, especially between 20% and 32%. After examining the viability, proliferation, morphology, it was discovered that HA-loaded PCL improved osteoconduction compared to PCL alone. The findings suggest that by carefully balancing the structural and mechanical properties of the polymer and biological activities, PCL represents a possible candidate as an effective substrate for bone replacement.

1.3 Summary of Literatures Review

The previous paragraphs cover some of the previous work of many types of research who studied the use of Chitosan and PCL with nanoHydroxyapatite to produce nanocomposite coating to use in nonBiofilm formation and corrosion resistance application. The difference between the current work and these works may be in the

number of coating layers, weight percentage of nanoparticles that were used, the technique of applied or the application of applied.

1.4 Literature Research Perspective

In previous research, both Chitosan and nHA were not used as coating agents to improve the mechanical properties of the coat as well as to prevent the formation of the biofilm and prevent the emergence of bacteria on the surface of Titanium.

1.5 Study Aims

The main purpose of this study is to modify dental implants which have mechanical and antibacterial properties by using two types of substrates, Poly Methyl Methacrylate and Titanium. These substrates coated with five layers of Nano Chitosan solutions and Polycaprolactone with different percentage (0.1,0.5.1wt%) of nanohydroxyapatite to produce bacteriostatic surface and good wettability. Using layer by layer and spin coating technologies.

Chapter Two

2.1 Introduction

Humans have historically relied largely on biological substances such as leather, wool, chitosan, silk and cellulose. Natural polymers can now be customized to fit specific requirements. The introduction of contemporary biotechnology has also changed scientists' perceptions of organisms and the compounds they create. Genetic engineering of numerous plant species, for example, could result in a new supply of structural polymers to replace traditional commercial plastics [5].

By harnessing natural enzymes or changing agricultural or marine feed supplies, a new class of biodegradable, renewable and biocompatible materials is on the rise. Polymers have a significant role in both modern industrial and natural economies. Other biological polymers, such as proteins and biomolecules, take and utilize biological information that is required, whereas biological polymers, such as proteins and biomolecules, take and exploit biological information that is not required. Other polymers, such as the polysaccharide family of natural sugars, continue to provide cell activity fuel and serve as structural elements in biological systems. With developments in chemistry and equipment during the last century, a wide range of innovative synthetic polymers have been introduced. Polyurethane, polyethylene and nylon are examples of synthetic polymers that have revolutionized daily living. Man-made polymers can be found in practically every area of modern civilization, from car bodywork to packaging, compact disks to food and clothing additives and pharmaceuticals [19].

The majority of plastic materials are non-biodegradable and derived from non-renewable resources. These materials' strength and endurance, which make them so useful, also assure their persistence in use and make

their disposal more difficult. Furthermore, the synthesis of some polymeric materials necessitates the use of hazardous substances or the creation of by-products. These concerns had already focused increased emphasis on polymers produced from biological precursors or made using modern biotechnology processes. These biopolymers can provide a variety of environmental benefits. Potential uses include truly biodegradable thermoplastics derived from agriculture or microbes, new biocompatible medical goods, and water therapy chemicals that prevent corrosion and mineral buildup [20].

Polymers are used in a variety of medical applications, including medical supplies, assisting or replacing failing bodily parts, and serving as a drug reservoir with a local therapeutic impact. The biological industrial revolution is currently focusing on developing equipment and devices that are totally compatible with the human body and internal intestines, in order to eliminate all faults and complications that humans are exposed to on a regular basis or as a result of medical treatment. As a result, bio-polymer materials with natural degradation and excellent compatibility with the human body were utilized. Because most of these materials have poor mechanical capabilities, the researchers had to resort to painting materials or tools utilized for biodegradable materials with compatibility properties[21][22].

Catheters are commonly used in medicine to drain liquids from the body and to allow access to the body's interior. Almost all catheters are produced of organic rubber, thermoplastic resins, or metal. When catheters contact the body's living tissues, there is a high probability that irritation will happen. In addition, in the event of catheters placed in incisions, body components such as clotted blood and lymph, and in the

case of urinary tract catheters, bladder stones tend to stick to catheters. Therefore, frequent replacement of most catheters is needed [23].

2.2 Biomaterials

Material applications become increasingly important in the biomedical industry in recent years. Nonetheless, the term "biomaterials" could be interpreted in a variety of ways in both clinical medicine and materials research. A biomaterial is also defined as a synthetic material used to remove portions of a biological system or to work in close proximity to human tissue. A biomaterial made by a living system is not the same as a biological material, such as cartilage. Biomaterials are classified according to their biological, chemical, and structural features, such as polymers, glasses, and ceramics, all of which have varied degrees of bioactivity [24].

2.2.1 Surface Characteristics of Biological Control

The basic parameters governing biocompatibility with biomaterials are not completely known. No single test can adequately explain a material's biocompatibility. A variety of tests are necessary to determine the biocompatibility level. These tests vary based on the surface feature being researched, the implant's class, the application, and, most importantly, the infected cells interacting with the biomaterial. The host biomaterial's response is not reciprocal. It's important to remember that the routine of this conceptual model isn't exclusive to any one application. Biomaterial and host interactions cause a wide range of natural phenomena. As a result, a number of in vitro and in vivo assays have been developed to characterize the disease. Surface features and chemical structures of polymers have an impact on biocompatibility and are commonly implanted. The most important surface features of

polymers that can be changed to influence biological compatibility are listed below [25].

2.2.1.1 Toxicity

Toxic behavior studies are required to analyze every material that may be used in biomedical engineering applications. The toxicity experiments determine whether the item is hazardous when used in conjunction with specific or general cell lines. The test is usually done in a lab with relevant/standard cell lines, and the cells are then seeded on the materials. In terms of biocompatibility experiment evaluation, toxicity experiments are commonly dismissed as the primary biocompatibility assessment [26].

2.2.1.2 Adhesion

Adhesion is an important factor to consider when designing biomaterials for suitable cell-material interactions. As a result, improving cell proliferation on implant surfaces is critical for classifying biomaterials for biocompatibility [23]. In biology, "bioadhesion" refers to both cell adhesion and bacterial adhesion. Bacterial adherence to the surfaces of biomaterials can be lethal because it prevents or inhibits the host's immunological response. Nonetheless, implant cell attachment requires both dependent application and dependent cell-kind. In vascular grafts, improved adhesion is desired for better cell attachment, proliferation, and dissemination [24].Furthermore, for medical applications, polymer metallization necessitates a high level of adhesion between the metal and the polymer. As an indirect paradigm, the interior surface of a vascular prosthesis is directly exposed to endothelial cells and hence must be appealing to these cells. Protein is applied to the polymer surfaces to achieve this [27]. Nonetheless, significant adhesion is

required to preserve the protein coating on the polymer surfaces. On the other hand, platelet adhesion with implanted polymer should be mitigated for some applications in order to prevent the formation of thrombuses. Thromboembolism is the influential side effect that hosts experience with artificial heart valves, which eventually leads to blockage of blood flow. Implants must be treated to mitigate regeneration of thrombosis in order to increase the uptime of these prothetics [28][29].

2.2.1.3 Functional Grouping and Chemical Structures

By making the biomaterial appealing to endothelial cells, the host's adverse responses, such as irritants or damaged cells, which lead to homogenization and inflammation, could be avoided (enhanced endothelialization). Cell adhesion and proliferation to specific host cell types are also required for various purposes. The appealing polymer surfaces of biomaterials are sometimes manganese oxide by doping or trapping reactive molecules on the surface. There could be a surface that is available for a specific cell type. As a result, it's critical to recognize the presence of externally created groups that are useful for specific applications, as well as any harmful chemical (compound or element) that may be present in the material [30][31]**.**

2.2.1.4 Wettability

It is undeniable that the wettability of polymer surfaces is quite low. The ability of a liquid to wet a surface is influenced by its roughness. In practice, both the chemical (heterogeneity) and physical (roughness of the surface, particle size, and shape) features of the surface have been shown to influence its wetting behavior. The wettability of a biomaterial could be engineered to reduce the amount of friction between the implant and the host. The parameters of biocontact and protein adsorption are

influenced by wettability regulation. Wettability was also related to the energy of the surface. Low surface energy polymers exhibit poor wettability. Some biomaterials require good wettability to deposit functional groups on the surface. These highly tailored polymers could be used as substrate materials in cell cultures [32][33].

2.2.1.5 Morphology of the Surface

Morphology of biomaterial surface defines the interactions which happen at the biomaterial site and at the host interface. Crystallinity is a significant morphological feature of the materials which impact the host's response. In addition, minimal refractive index, minimal dielectric constant, and great optical transparency combined with good thermal and mechanical stabilization are essential characteristics needed for blood-contact devices, bio-MEMS (micro electro mechanical systems) , and cell culture substrates [20].

2.2.2 Classification of Biomaterials

Classification of biomaterials into two main kinds (1) Biological Biomaterials (2) Synthetic Biomaterials. Biological biomaterials divided into hard and soft tissue types. Synthetic divided into (a) polymers metal (b) ceramics (c) composite biomaterials [9].

a- Metallic Biomaterials

For several biomedical load-bearing systems, the mechanical characteristics of metals and their alloys including strength, coefficient of elasticity and fatigue life that makes them appealing materials. Metallic materials decay in corrosion process and even as the corrosion reactions release specific side products, for example, ions, chemical substances, and insoluble components. Corrosion has two impacts: it damages the

implant by destroying the implanted material, and it has negative effects on the organs and tissues around it [23].

b- Polymeric Biomaterials

Polymeric Reusable medical papers, dental materials, prothetic materials, dressings, implants, encapsulating agents, extracorporeal equipment, tissue-engineered materials, polymeric transdermal systems and orthodoses such as ceramic and metal substituents were all made with synthetic materials. Polymeric biomaterials have several advantages over ceramic metal or materials, including ease of manufacture for various forms (fibers, foil, film, latex, etc.), simplicity of secondary processing, and reasonable prices. The features of polymers are determined by the composition, structure and organization of macromolecules [34][35].

c- Ceramic Biomaterials

Metal oxides, silicates, carbides and sulfides, as well as various hydrides and selenides, are examples of metastatic, polycrystalline ceramics. Non-metallic and metallic oxides such as Al O_3, MgO, SiO_2, and ZrO_2 are formed from ionic salts such as NaCl, CsCl, and Zn. Covalently bound ceramics, such as carbonaceous structures and diamonds like pyrolic carbon and graphite, are exceptions [36]. Some ceramic goods are candidate materials in bio-medical applications because they are non-carcinogenic, non-toxic, non-inflammatory, non-allergic, functional and biocompatible [37].

d- Composite Biomaterial

In engineering, a composite is a micro to macro, each with its own interface. These composites typically consist of one or more discontinuity stages incorporated into a continuous phase. As compared to the

continuous phase, the discontinuous phase is generally stronger and tougher, and it is referred to as a material for strengthening or reinforcing, whereas the continuous phase refers to it as a matrix. Hard fillers, are sometimes used with brittle matrixes to produce products with increased toughness and impact resistance. In other cases, "strengthening" could be aimed at achieving specific functional features, such as Bioactivity in biomedical composites compounds such as the extracellular matrix (ECM), ligaments, tendons, bones, skin, and other human tissues have extra complexity due to their hierarchical composition [38].

Due to the annual growth in global population, the rise in the number of elderly people and the high functional needs of younger people, there is a significant increase in the demand for safe and effective materials in the biomedical engineering field [39].

2.3 Surface Treatment

Surface treatment of biomaterials allows for modifications in the material's surface chemistry, topography, energy and charge to optimize material and biological responses while retaining the implant's bulk properties. Surface alterations can be divided into three groups:

(1) The addition of the functional materials to the surface.

(2) The conversion of the current surface into a more functional surface.

(3) Unique topographies are created on an existing surface by removing material from the required compositions and/or topographies.

Particularly in the dental implant sector, surface treatments are typically carried out to change while maintaining acceptable attributes of the substrate materials. Using the right modification techniques, whether

by addition or subtraction, it is possible to significantly increase the surface area [41][42].

Additionally, there are three categories for surface treatments: mechanical, chemical, and physical treatment.

2.4 Coating Technology

As shown in Figure (2.1) coating strategies are based on the deposition of a surface layer with a separate structure from the underlying foundation material. Surface modification techniques include non-covalent and covalent coatings.

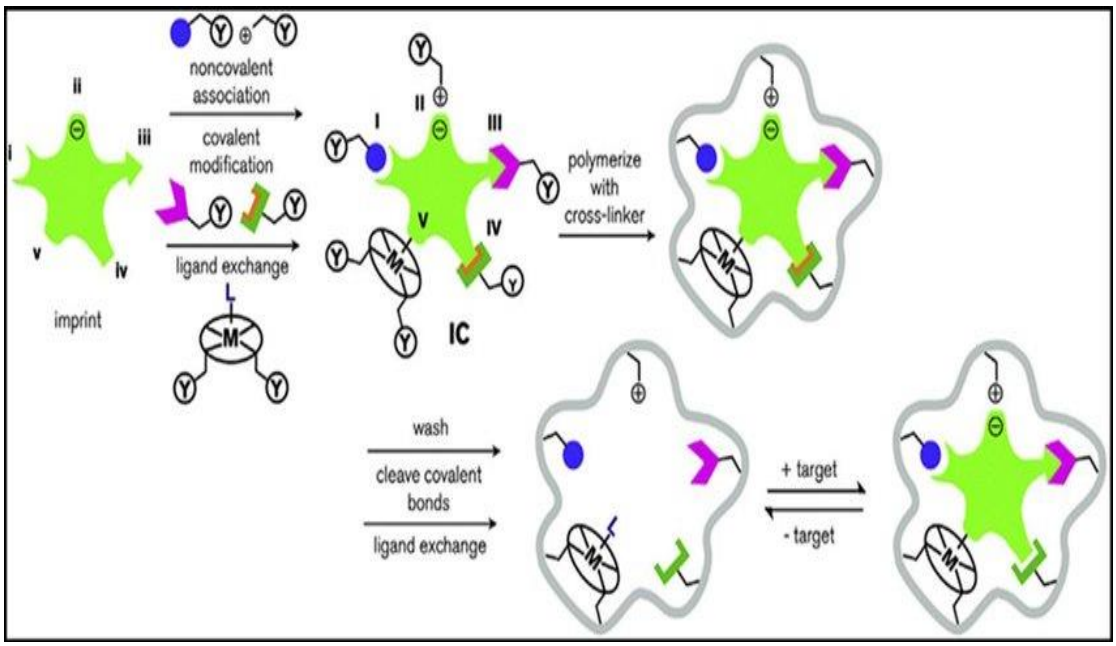


Figure (2.1) Schematic representations of coating strategies [43].

2.4.1Covalent Coating

To improve film durability and adhesion, covalent coating methods rely on direct coupling of overcoats to the substrate material. To incorporate chemically reactive groups into inert hydrophobic polymers and polymerize overcoats on the foundation support, radiation grafting,

both with ionizing radiation and high-energy electron beams, and photography have been intensively pursued [44]. The radiation, in theory, breaks down chemical bonds in the base material, resulting in free radicals and other reactive species, which are subsequently exposed to a monomer. As a free radical chain reaction, the monomer connects on the surface with the reactive species and propagates into a surface grafted polymer. These approaches allow for the creation of a wide range of surface chemistries, as well as the creation of unique graft co-polymers by combining different monomers [45]. Radio frequency glow discharge (RFGD) plasma deposition, in particular, has gotten a lot of attention because it can provide permanent (quite free of pin holes and voids) conformal coatings that can be applied to a variety of supports (metals, ceramics, and polymers) with complex geometries [46].

2.4.2 Non-covalent Coating

Non-covalent coatings have a number of advantages, including ease of application and the ability to cover a variety of different base materials. Solvent casting and metal, parylene, and carbon vapor deposition are examples of popular non-covalent coating processes. One or more extremely organized layers of surfactant molecules are deposited in the Langmuir – Blodgett deposition process Surfactant molecules are compressed and assembled at the air–water contact to deposit phospholipids and amphiphiles on the base material surface. Langmuir – Blodgett films have a high level of order and uniformity, as well as the ability to accommodate a wide range of chemistries [47].

After film production, cross-linking or internally polymerizing the surfactant molecules could improve the stability of these films. Deposition of multilayer polyelectrolytes (e.g. poly

(styrenesulfonate)/poly (allamine), hyaluronic acid / chitosan) is another surface modification technique that takes use of intermolecular interactions. A loaded surface is sequentially plunged into alternating aqueous solutions of opposite-charge polyelectrolytes to deposit multilayers of a polyelectrolyte complex in this simple layer-by-layer process [47].

The use of surface-modifying compounds is another elegant surface modification technique. These molecules are intermingled in the bulk material during fabrication, but due to the driving power to decrease interfacial energy, they will spontaneously rise and focus on the surface [47].

2.4.3 Coating Technologies

In this research there are two basic methods for coating: Layer by Layer and Spin Coating.

2.4.3.1 Layer by Layer (LBL)

The layer-by-layer (LBL) method creates polyelectrolyte multilayer (PEM) films by depositing self-assembling and self-organizing polyelectrolytes in alternating layers on the surface of the material [47]. This method is based on the electrostatic interactions that lead to the sequential adsorption of polyanions and polycations. It seems like a good decision to use the electrostatic interaction between positively and negatively charged molecules as the primary mechanism for multilayer formation. The process works with a number of substrates. The effective fabrication of a variety of films containing charged species has included biological materials (polypeptides, polysaccharides, DNA, proteins, and viruses) and numerous nanoparticle types (clay platelets, carbon

nanotubes, etc.). As previously indicated in [48], electrostatic interactions between components with opposing charge cause LBL multilayers to form. The content, morphology, and structure of the movie may all be accurately controlled by the buildup. The LBL self-assembly is illustrated in Figure (2.2). The initial monolayer is formed through absorption when a charged substrate is submerged in a mixture of polyelectrolytes that have opposing charges. After this phase, the weakly bound or unbound species are removed by washing. Additionally, this wash step can stop the cross-contamination of polyelectrolytes with opposing charges. The second monolayer is then formed via absorption when the monolayer-coated substrate is submerged in a different solution of polyelectrolytes with opposing charges. Until the necessary multilayers are created, this procedure is repeated [49]. Electrostatic attraction is the major factor at work during assembly. Additionally, biological interactions, covalent contacts, hydrophobic interactions, and hydrogen bonding all contribute [50]. Without substantially changing the physical and mechanical characteristics of the substrate, a range of materials (such as titanium, glass, and silicon wafers) can be employed as the substrate materials in the assembly [51]. Assembling can also be done under normal circumstances as opposed to special ones that require high temperatures and pressure. The multilayers may be created using a variety of polyelectrolytes, including as proteins, nucleic acids, medicines, and inorganic nanoparticles [52]. The shape, thickness, and other biological properties of the formed film will be impacted by The polyelectrolyte solution's concentration and ionic strength, pH, temperature, assembly time, molecular weight, and size. These variables are only a few of the numerous variables that can alter the self-assembly process [53].

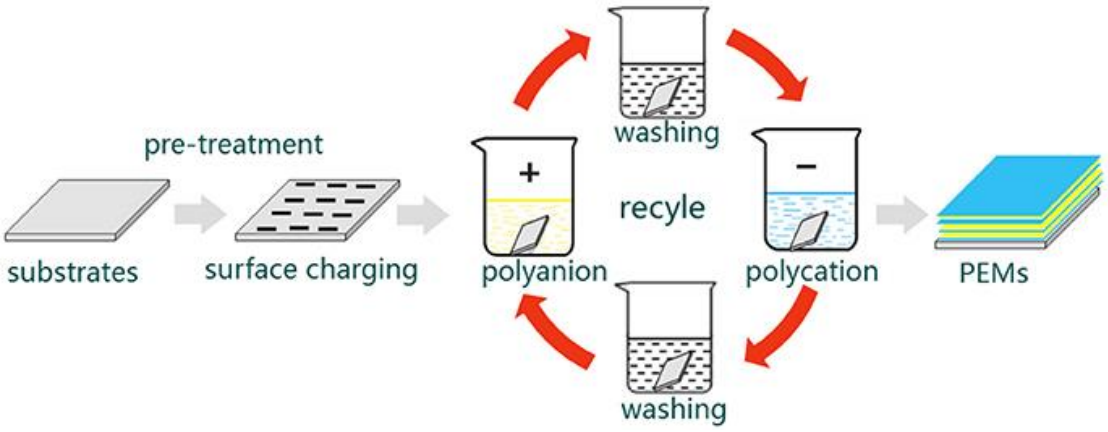


Figure (2.2) A schematic illustration of LBL self-assembly process [51].

The first monolayer is created by absorbing a charged substrate into a solution of polyelectrolytes that have opposing charges. The weakly attached or unbound species are then removed, and a washing step is then included to stop the cross-contamination of polyelectrolytes with opposing charges. After that, a second solution of polyelectrolytes with opposing charges is added to the monolayer-coated substrate, causing a second monolayer to develop through absorption. Until the desired multilayers are created, this process is repeated. Create polyelectrolyte multilayers (PEMs) [52].

2.4.3.2 Spin Coating

The easiest way to create a film on a substrate is by spin coating. Thin-resist layers for photolithography are coated with this approach. The substance to be deposited is diluted in a solvent before being spun onto a surface. The solution is then applied to the substrate's surface. After that, the wafer is quickly spun. The solution's viscosity, surface tension, and spinning rate all affect how thick the film will be. Spinning causes some of the solvent to evaporate, and subsequent baking at high temperatures removes some of it as well. A substantially flat surface is produced via spin coating. For planarization purposes, this method is frequently

employed. Sol-gels can be deposited via spin coating. Solid components are used in this technique. Spin coating is done over disjointed substrates like small flat disks (like glass, steel, etc.) for thin films [54]. The forces required for this coating are centrifugal, viscous and surface tension forces. This coating technique can be used for the formation of layers in a thickness range of nanometers (nm) to micrometers (μm) [55]. The process of spin coating includes the following steps:

1. Deposition.

2. Spin off.

3. Spin away.

4. Evaporation.

Figure (2.3) when doing spin coating, it's necessary to keep in mind a number of crucial elements, including the concentration, film thickness, solution viscosity, and spinning speed and time. Some of the key benefits of the spin coating technology are controlled film thickness, homogeneity, low operation costs, speed, etc.

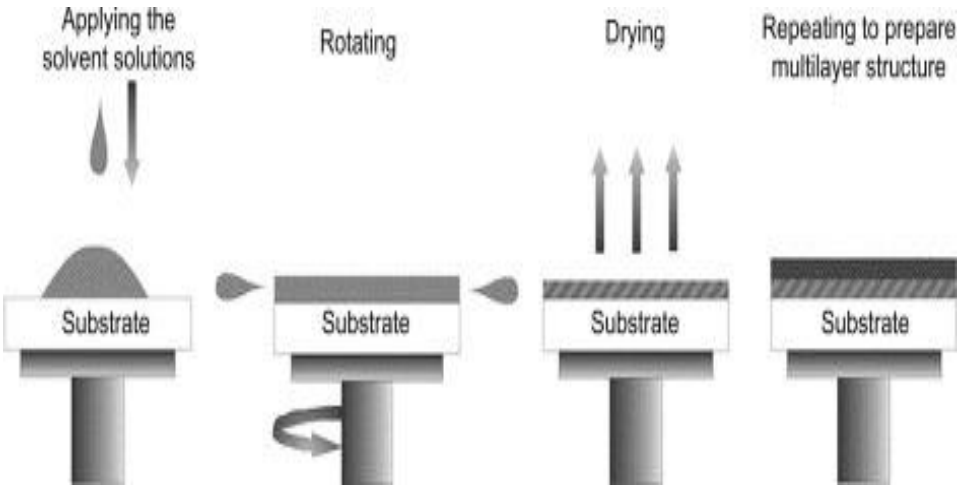


Figure (2.3) Spin Coating stages [54].

2.5 Chitosan

Chitosan has been widely employed in the field of tissue engineering. Because of biodegradable, biocompatible, and nontoxic in addition to having antimicrobial qualities, The most reactive functional groups in chitosan are hydroxyls, acetamides, and amines [56]. Chitosan reportedly increased PCL cell recognition sites, expedited PCL hydrolytic breakdown, and improved wettability and permeability [57]. Tetracycline usage for bone tissue engineering is still not well understood. Tetracycline has been used successfully in recent studies to treat osteoporotic bone loss [58][59].

Chitosan is a naturally occurring amino polysaccharide formed as a deacetylated variant of chitin and is the second most prevalent amino polysaccharide after cellulose. Its non-toxic, Significant research has been conducted in biomedical and pharmaceutical applications such drug delivery, tissue engineering, and wound-healing dressings as a result of biocompatible, antibacterial, and biodegradable qualities among others [60][61].

Chitosan nanoparticles are gaining popularity in nanomedicine, biomedical engineering, and the development of new therapies with improved bioavailability, sensitivity, and specificity, as well as lower toxicity [62].

Chitosan nanoparticles are typically dispersed in a suitable dispersion and placed in an ultrasonic device for dispersion. It is then mixed with the basic material for an adequate amount of time to improve its biological and mechanical properties, and then dried using heat or at ambient temperature, as directed in the article and using this will made a suitable material [63][64].

2.5.1 Chitin and Chitosan preparation, Structure, Characteristics, and Applications

Chitin, also known as poly (-(14)-N-acetyl-D-glucosamine), is a major natural polysaccharide that was first discovered in 1884. This biopolymer is produced by a large number of living creatures and is one of the most a bundant natural polymers, second only to cellulose. Chitin is found as organized crystalline microfibris in the exoskeleton of arthropods and in the cell walls of fungi and yeast in their natural state. Crab shells and shrimp shells have been the most popular commercial items thus far. Chitin can be found in a variety of places. Acid therapy removes chitin to dissolve calcium carbonate in industrial processing, then an alkaline solution dissolves proteins. A decolorization procedure is frequently used to remove colors and produce colorless pure chitin. All of these treatments must be tailored to the chitin source because changes in the ultrastructure of the original material must be taken into account in order to produce high-quality chitin and later chitosan (after partial deacetylation). Chitin is insoluble and sparingly soluble when it is converted into different conformations. The solubility of chitin is a major challenge in the development of both chitin processing and utilization, as well as its characterization [65].

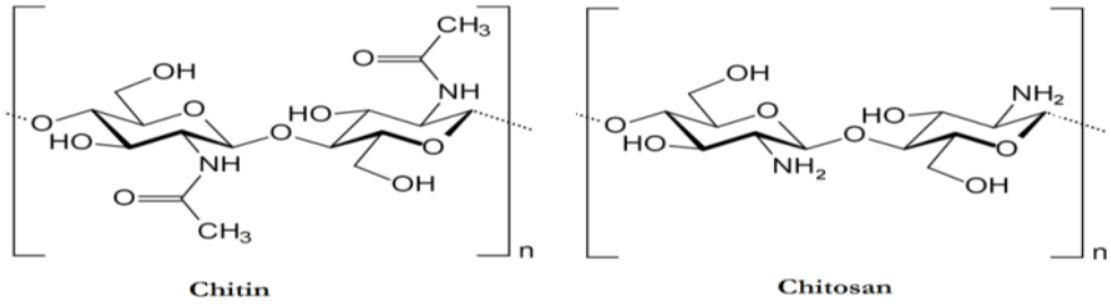


Figure (2.4).Chemical Structure of Chitin and Chitosan [65].

When chitin is converted to chitosan (by partial deacetylation under alkaline circumstances), it has more applications [66]. Chitosan is a random copolymer with a molar fraction (1-DA) of -(14)-N-acetyl-D-glucosamine and a molar fraction DA (degree of acetylation) of -(14)-N-acetyl-D-glucosamine, as shown in Figure (2.4). The molar amount of N-acetylated units (DA) or the proportion of acetylation describes the degree of chitosan acetylation (DA percent).

For chitin and chitosan uses, several examples are defined, including medication discharge, wound dressing and biofilms. It's important to understand that chitin is a natural polymer that's also biocompatible and biodegradable in the body, making it a popular biomedical and pharmaceutical ingredient. Furthermore, superior film forming properties are beneficial for wound dressing, artificial skin and packaging [62][67].

2.5.2 Chemical Deacetylation

Deacetylation of chitin with acids or alkalis, depending on the chemical. However, because glycosidic linkages are very susceptible to acid, alkali deacetylation is more commonly used. Chitin N-deacetylation can be done in a heterogeneous or homogeneous manner. Chitin is frequently processed for a few hours in the heterogeneous approach with a hot concentrated solution of NaOH, and chitosan is generated as an insoluble residue deacetylated up to 85%–99%. After dispersion of chitin in concentrated and dissolving in crushed ice about 0 C°, alkali chitin is made using the homogeneous technique at 25 C° for 3 h or longer. This method yields a soluble chitosan with a degree of acetylation ranging from 48 to 55 percent. Deacetylation with uniformly distributed acetyl

groups along the chains is produced by this process, as seen in chitosan with DA = 10% at 25 C° after 580 hours [69].

Chitosan solubility can be determined not only by the fraction of 2-acetamidemolecule's -2-deoxy-D-glucose units, as well as by the arrangement of N-acetyl groups. Under heterogeneous conditions, this deacetylation reactions results, N-acetyl-D-glucosamine and D-glucosamine residues are distributed unevenly, and certain acetyl groups are distributed block wise along polymeric chains. The outcome is, the solubility and degree of aggregation of chitosan in aqueous solutions may alter, resulting in changes in their average properties [70].

Differences in chitosan preparation may also result in changes in DA, acetyl group distribution along chains, MW, and solution viscosity.

2.6 Polycaprolactone

A biodegradable and biocompatible polymer with a slow rate of breakdown is polycaprolactone (PCL). PCL in Figure (2.5) can be combined with other polymers to enhance cell adhesion, hydrophilicity, and stress fracture resistance. Numerous investigations have demonstrated that PCL mixed with other polymers, including cellulose propionate and cellulose acetate-butyrate, may be used to control the rate at which drugs are released from microcapsules [71].

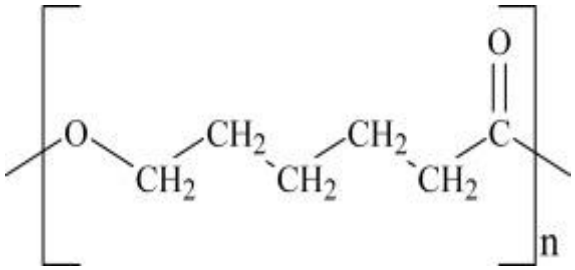


Figure (2.5) Polycaprolactone structure [71].

2.7 Hydroxyapatite

Since Nanohydroxyapatite is one of the bioceramics with characteristics like the mineral elements of real bone, it is frequently employed as a synthetic bone substitute, a drug delivery system, and a covering for metal prosthetics. In reality, because bioactive substances like nHA are able to make direct linkages with the surrounding tissues, the addition of nHA to the scaffolds will actually increase the material's performance [72].

Hydroxyapatite (HA) $Ca_{10}(PO_4)6(OH)_2$), a key component of bone, is both in vitro and in vivo biocompatible with bones, teeth, skin, and muscles. HAP enables direct bonding and quicker bone regeneration to repair bone without the need for intermediate connective tissue, displaying strong bioactivity and osteoconductivity, allowing for a wide range of orthopedic and dental applications [73]. HAs, both natural and synthetic, are currently used in biological and therapeutic applications. Chemicals containing calcium and phosphate ions can be used to make HA [74]. Natural materials, on the other hand, have been proven to be an appealing source of HA in the previous decade, Figure (2.6). Nanohydroxyapatite has also been manufactured to better imitate the mineral component and microstructure of natural bone. However, the intrinsic brittleness and difficulty of processing of HA ceramics were the fundamental limitations to their application [75]. By directly combining calcium phosphates' osteoconductivity with polyesters' high biodegradability or through a biomimetic approach, polymer/ceramic composite scaffolds for bone tissue engineering have been created [74][75].

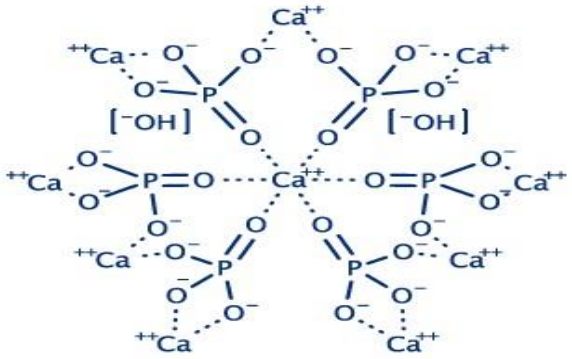


Figure (2.6) Hydroxyapatite structure [75].

2.8 Titanium Ti

Titanium (Ti) and Titanium alloys have been widely employed as implants in the dental and orthopaedic field because of its biocompatibility, low density, and good mechanical qualities,. Unmodified Ti, on the other hand, may harbor bacterial infections after implantation [78]. Implant failure, implant removal, higher treatment expenses, and increased patient morbidity or, in some circumstances, perioperative mortality are all common outcomes of these infections. Antimicrobial drugs must be used with caution for treating infections. Titanium is the most desirable and widely utilized dental implant material in oral medicine. Due to its effective and comfortable restorative effects, dental implants are now being used in an increasing number of patients with dentition defects or edentulous individuals [79].

2.9 Polymethylmethacrylate (PMMA)

Polymethylmethacrylate (PMMA), a lightweight synthetic polymer, can replace polycarbonate when extraordinarily high strength is not required. The advantage of PMMA is that it does not include potentially harmful substances like bisphenol-A, which is included in polycarbonate.

In addition, the synthetic polymer is more reasonably priced. easier to handle, and process as opposed to polycarbonate. PMMA is frequently utilized in practice to treat abnormalities in craniofacial tissue, including skin and dentures [80].

PMMA has excellent mechanical prperties and is not harmful. PMMA exhibits delayed disintegration, but is often used for hip-joint transplants due to its inert qualities. Polycaprolactone and PMMA can thus be blended to create a polymer that is better suitable for biomaterial application Figure (2.7).

PMMA is utilized in a variety of biomaterials, including medicine delivery devices, lenses, bone replacements, and bone cement. It is used to remove scars and wrinkles from skin tissue permanently. PMMA is a polymer that is used in dental implants to replace missing tooth roots.

PMMA exhibits excellent porosity, a low modulus of elasticity, and physical and mechanical properties that are comparable to those of human dentine [80].

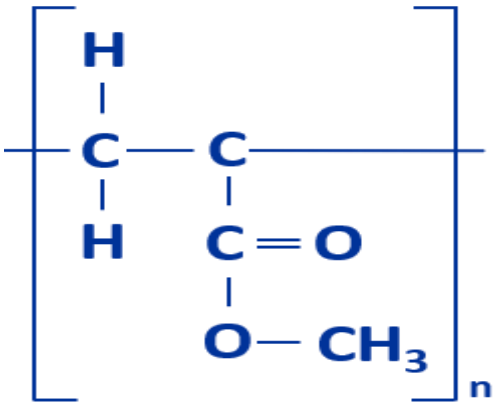


Figure (2.7) PMMA structure [80].

2.10 (3-Aminopropyl)triethoxysilane (APTES)

Is a type of aminosilane that is often employed in the silanization process, which involves functionalizing surfaces with alkoxysilanemolecules. Additionally, it can be utilized to covalently link organic films to metal oxides like Titania and Silica Figure (2.8).

It has been demonstrated that in vitro tests on embryonic rat cardiomyocytes show APTES-functionalized surfaces to be harmless toxicology of different cell types in extended culture needs to be investigated further [81].

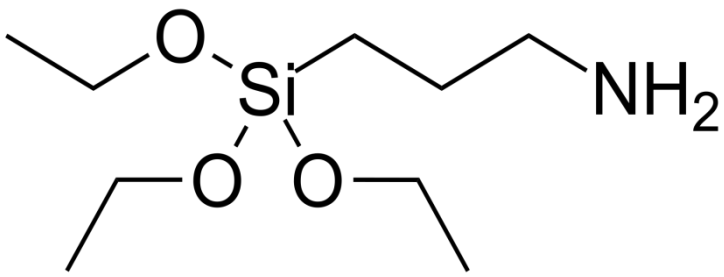


Figure (2.8) APTES Structure [81].

Chapter Three

3.1 Introduction

The preparation of (Chitosan and Polycaprolactone PCL) coats is the focus of this experimental chapter, the properties of the base material are described and modification the substrate (PMMA and Ti), and the required tests conducted. Modified Chitosan and PCL are used to coat the substrate (PMMA, Ti) material, resulting chemically obtaining a surface resistant to bacteria. according to the following steps shown in figure (3.1). Many tests are used to characterization coated surface like FTIR, OM, DSC, contact angle, biologics test, pull-off, corrosion test.

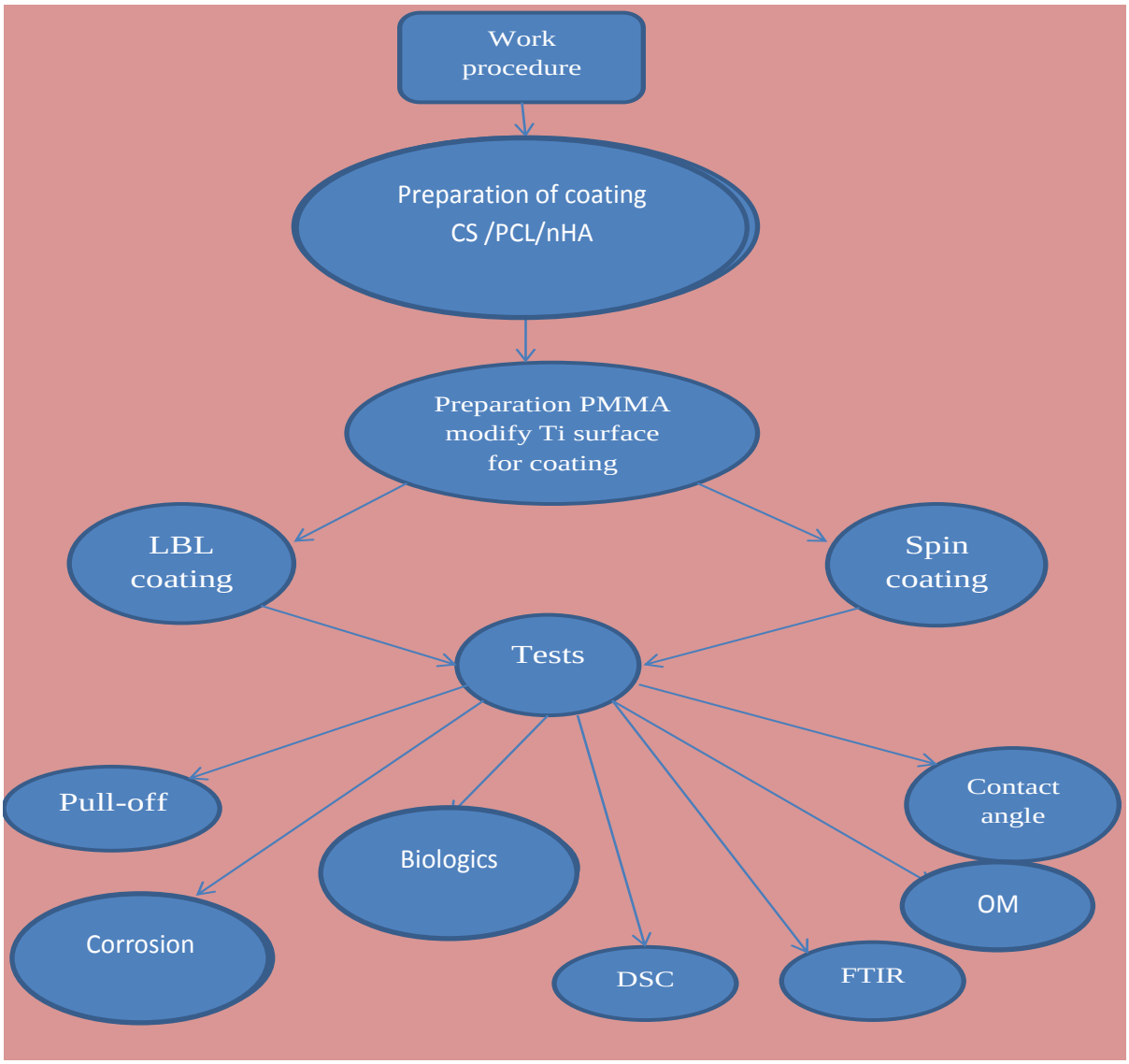


Figure (3.1) Plain of Work.

3.2 Materials Used

3.2.1 Chitosan

Chitosan was purchased from the Iraqi market Importer of (SHAANXI SANGHERB BIO-TECH INC) from China in nanoscale form, and chitosan is modified and converted to a solution for Titanium and PMMA coating. The purchased Chitosan information is shown in Table (3.1).

Table (3.1) The properties of purchased Chitosan [82][83].

Items		Specifications
D.A.C	%	≥95
Viscosity	cpc	≤100
Insoluble	%	≤1
Ash	%	≤1
Moisture	%	≤10
Fineness	nm	≤80 nm
Heavy Metals	ppm	≤10
Ppm		≤0.5
Density	g/ml	0.28
Appearance		White Powder

3.2.2 Polycabrolactone PCL

PCL bought from the Iraqi market in particles form, and PCL is modified and converted to a solution for Titanium and PMMA coating. The purchased PCL information is shown in Table (3.2).

Table (3.2) PCL properties [82].

Chemical formula	$(C_6H_{10}O_2)n$
Density	1.145 g/cm^3
Melting point Tm	60 C°
Thermal conductivity	1.42 W m^{-1} K^{-1}

3.2.3 Titanium (Ti)

Ti bought from the Iraqi market in sheet form (15x15x3) mm. The properties of Ti are shown in Table (3.3).

Table (3.3) Titanium properties.

Molecular Weight	47.86
Melting Point	1668 C°
Density	4.54 g/cm^3
Crystal Phase / Structure	Hexagonal
Poisson's Ratio	0.32
Tensile Strength	140 MPa
Thermal Conductivity	21.9 W/(m·K)
Young's Modulus	116 GPa

3.2.4 Poly(methyl methacrylate) PMMA

PMMA bought from the Iraqi market in form consist of resin and monomer. The properties of PMMA listed in Table (3.4).

Table (3.4) properties of PMMA [84].

Tm	160 C°
Tg	105 C°
Solubility	25 mg/mL
Density	1.200 g/cm^3

3.3 Coating Preparation

Chitosan dissolved into Acetic acid CH_3COOH and Formic acid CH_2O_2 (30 and 70 ml respectively) using magnetic stirrer to produce the coating solution.

PCL dissolved in (30 ml (CH_3COOH) and (70 ml CH_2O_2) using magnetic stirrer and add nHA with different percentage (0.1, 0.5, 1) wt% with dispersion using ultra-sonication for 30 min to produce the coating solution.

3.4 Titanium and PMMA Substrates Modification, and Surface Treatment for Coating

Titanium sheet was polished to remove any oils and debris on surface. The samples were first cleaned by cleaner sonication in a detergent solution, followed by acetone, ethanol, and de-ionized water, and then dried at 60 C°. The cleaned samples were immersed in a 5 M NaOH solution for 2 hours at 60 C°, followed by de-ionized water at 80 C° for 2 hours, then were cleaned with de-ionized water, and last dried at 60 C°.

PMMA prepared by mix the resin and monomer (3:1) respectively and pouring the mixture into the mold in the form of squares, then After thoroughly cleaning the surface with acetone, methanol, before drying it in N_2 to remove any oils and debris, then rinsing it with deionized water and drying it in N_2 to create a hydrophilic surface, 30 minutes were spent submerging the substrate in a solution of (2% APTES + 98% acetone). Thus, a surface of $-NH_2$ was obtained.

3.5 Coating Technologies

For LBL and Spin Coating, four samples of (Ti or PMMA) were immersed in chitosan solution for 30 min, after which deionized water cleaned and N_2 dried. This is the first layer of coating. Then immersed in pure PCL solution, then rinsed with deionized water and dried in N2. This is the second layer. Repeated this operation to get five layers of coating (CS +PCL + CS + PCL + CS). That for sample number 1. Then used different percentage of nHA (0.1, 0.5, 1) wt% with PCL solution for the three samples. For example the second sample coating consist of five layers coating [CS + (PCL+0.1% nHA) + CS+ (PCL+0.1% nHA) + Cs]. As show in Table (3.5).

Table (3.5) Code of Coating Layers (5 Layers).

No. of Samples	Substrate	Coating Technology	Coating Layers	Code
1	Ti	LBL	[CS+PCL+CS+PCL+CS]	LBL Ti Pure
2	Ti	LBL	[CS+(PCL+0.1 nHA)+CS+(PCL+0.1nHA)+CS]	LBL Ti 0.1 PCL
3	Ti	SP	[CS+(PCL+0.5 nHA)+CS+(PCL+0.5nHA)+CS]	SP Ti 0.5 PCL
4	Ti	SP	[CS+(PCL+1 nHA)+CS+(PCL+1nHA)+CS]	SP Ti 1 PCL
5	PMMA	LBL	[CS+PCL+CS+PCL+CS]	LBL PMMA Pure
6	PMMA	LBL	[CS+(PCL+0.1 nHA)+CS+(PCL+0.1nHA)+CS]	LBL PMMA0.1 PCL
7	PMMA	SP	[CS+(PCL+0.5 nHA)+CS+(PCL+0.5nHA)+CS]	SP PMMA0.5 PCL
8	PMMA	SP	[CS+(PCL+1 nHA)+CS+(PCL+1nHA)+CS]	SP PMMA 1 PCL

3.6 Surface Characterization

3.6.1 Fourier Transform Infrared (FTIR) Spectroscopy

The sample that prepared for this test by taken a part of film coating. Infrared spectrum gives a chart between transparency and the wave number that exhibit the chemical structure of the material. This method is carried out for thin film coating of pure Chitosan and is also for coatings (LBL Ti Pure) and nHA, so as to know effect of nanoscales and distinguish any reaction if is chemical or physical. This test was done

by FTIR device type (IR Affinity) made in (Kyoto Japan) and this device existing in College of Materials Engineering / Polymer and Petrochemicals Department show in Figure (3.2).

Figure (3.2) Fourier Transform Infrared Spectroscopic device.

3.6.2 Wettability

The water contact angle (WCA) determined using the contact angle test. The results from the contact angle measurements which done using saliva solution Table (3.6). The test is performed by placing the specimen's surface on the device's plate and using a syringe pump to transfer saliva solution drops to the surface. The contact angle is then recorded on the computer's software. This sort of gadget can calculate dynamic and static contact angles with a base angle of (0-90) to evaluate contact angle hysteresis and roll off angle. This device is made by Holmarc Opto- Mechatronics Pvt. Ltd. (India) and exists in the College of Materials Engineering / Ceramics and Building Materials Department as shown in Figure (3.3).

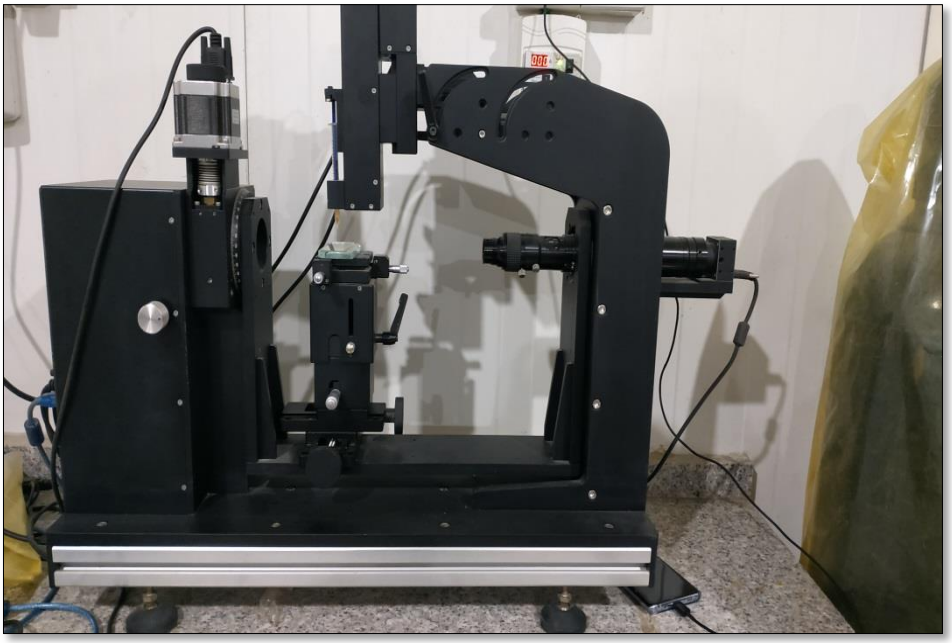


Figure (3.3) Contact Angle device (Optical Contact Angle & Intention Interface meter).

Table (3.6) Saliva Solution Properties.

Constituent	**(g/L)**
NaCl	0.4
KCl	0.4
$CaC_{12}.2H_2O$	0.906
$NaH_2PO_4.2H_2O$	0.69
$Na_2S.9H_2O$	0.005
Urea	1

3.6.3 Differential Scanning Calorimetric (DSC)

A thermocouple attached to a computer records the temperature change required for the sample to reach the same temperature as the reference sample. The chart then shows the melting point and glass transition temperature of the sample. The test is carried out on chitosan and PCL coating and with different percentage of nHA, and the

results are compared. The DSC device is manufactured by the Shimadzu Corporation The thermal properties of polymers, as well as changes in the polymer when heated and the degree of glass transition temperature, were studied using a differential scanning calorimetry system. The device consists of two crucibles, one for the tested sample and the other for the reference vessel, which is left empty. The crucibles are placed in a furnace that is heated at a specific pace, such as 10 degrees per minute, in order to perform DSC, and it is now in use at the College of Materials Engineering's Polymer and Petrochemicals Industries Department, as shown in Figure (3.4).

Figure (3.4) Differential Scanning Calorimetry (DSC) device.

3.6.4 Optical Microscopy (OM)

Optical microscopy is a technique employed to closely view a sample through the magnification of a lens with visible light. This is the traditional form of microscopy with high resolution efficiency also used to test the morphological of prepared coating samples**.**

Figure (3.5) Optical Microscopy.

3.6.5 Thickness Measurement

Thickness of film coatings were measured by a digital manual device. The thickness was measured in different area of coating and to all specimens and recorded different values and determine the range between these values. The type of device is (micro Printer, TT260, China) that located in the materials engineering college/polymers and petrochemicals industries department shown in Figure (3.6).

Figure (3.6) Thickness Measurement Device.

3.6.6 Corrosion Test

The corrosion resistance of materials was determined using an electrochemical approach and a corrosion test instrument. The results from the contact angle measurements which is done using saliva solution. The device comprises of a measurement cell and its electrode, with the cell being constructed of glass and having a one-liter spherical capacity, as well as different holes for the electrodes to be placed. The cell is made up of three poles: a platinum pole electrode helper (Auxiliary Electrode), a reference electrode, and the primary pole, which is in contact with the samples. Experiments were carried out in a salvia solution was placed in the measuring cell, the auxiliary electrodes and the reference electrode were filled with the cell solution, and the main electrode was prepared to be washed with alcohol before being immersed in the measuring cell. The circuit is then opened, and laparoscopic and posterior polarization curves are created using a computer coupled to a static device (Potentionstat) and a program (Bank). To draw these curves, Elechtionies) was used. This device belongs to the (Mlab 200) category. This device exists in the College of Materials Engineering / Metallic Materials Department Figure (3.6).

Figure (3.6) Corrosion test device (Tafel's device).

3.7 Biologics Tests

3.7.1 Biofilm Formation

The Test is held at the Faculty of Biological Sciences at the University of Babylon. The following biofilm development assays were carried out using the technique[85]. Before treatment, the samples had strong biofilm formation, while after treatment the samples had non-biofilm formation as in the table below.

Table (3.7) Interpretation of Biofilm Formation

Mean of OD value at630nm	**Adherence**	**Biofilm formation**
<0.120	Non	Non/Weak
0.120-0.240	Moderately	Moderate
>0.240	Strong	High

1. Fresh Tryptic Soy Broth TSB (is used in microbiology laboratories as a culture broth to grow bacteria) is diluted with fresh isolates from freshly prepared agar plates containing 1% glucose and incubated at 37 C° for 18 hours.
2. The only substance tested for non-specific media binding was broth, and 150 diluted plant aliquots were placed in each well. Each isolate was injected in triplicate.
3. At 37 C° for 24 hours, tissue cultivation plates received an inoculation. After incubation, the sections of each well were gently separated by tapping the ground. The wells are cleaned four times with Phosphate Buffer Saline (PBS pH 7.2) to get rid of free-floating planktonic bacteria.
4. Biofilms created by adhering sessile organisms were fixed in a 37 C° oven for 30 minutes.

5. The hue of every well is mauve glass (0.1 percent w/v). The dishes are kept for drying after being thoroughly washed with deionized water, which removed any remaining stains.
6. In order to dissolve the bonded crystal mauve, 150 ml of an 80:20 by volume mixture of ethanol and acetone were added. According to Mathur et al, (2006) [85], At 630 nm, optical density (O.D.) was measured, and the findings were deciphered.

3.7.2 Antimicrobial Activity

The examination took place at the University of Babylon/ College of Science/department of Biological. The antibacterial activity of the sample solutions was evaluated using the agar-well diffusion technique [87]. Gram-positive bacteria (P. aeruginosa, E. coli) and gram-negative bacteria (P. aeruginosa, E. coli)were among the bacterial isolates investigated (S. aureus; Staphylococcus epidermidis). Gram-negative and gram-positive bacteria were mixed in 0.1 ml of 0.5 Mcfarland tube {1.5 X 108 CFU / ml} agar nutritional medium. Pure chitosan solutions were made, as well as three PCL solutions with varying concentrations of nHA (0.1, 0.5, 1)% in 100 ml of (2%) acetic acid solution. From the bacterial suspension and spreader, one should obtain an inoculum, a sterile swab was placed on a agar tray of Muller-Hinton. Each culture tray had a six mm-diameter hole punched into it, using a sterile plastic pipette, and 20 µl of Chitosan and PCL solution were introduced to the agar plate of Muller-Hinton test pipe in the hole. After a one-hour pre-diffusion period, the plates incubated at 37 C° for 24 hours. After that, the inhibition regions measured in millimeters.

3.8 Mechanical Tests

3.8.1 Pull-off adhesion Test

Pull-off adhesion tests are used to measure adhesion strength for a certain diameter of coating by applying hydraulic pressure, displaying the pressure results on a screen, and then calculating the adhesion strength for the coating on the surfaces.

Before the test, all the ballast (dully) and coating surface must be prepared and preambled and then a neat adhesion material (strong glue) but must be adhesive (Epoxy) must be placed on the basis of dully (2-1) ml and linked with the surface that was prepared to test, pressed to dully lightly to remove the adhesive to the outside and let the adhesive dry.

Pull the dully up and show the values of pressure on the screen that arrive at a higher value after the separation of dully by pressing the handle of the pump down and running the pump (very slowly) by using the handle and pulling the dully up and showing the values of pressure on the screen that arrive at a higher value after the separation of dully. The national center for packing and packaging, which is affiliated with the ministry of industry and minerals, conducts the test on both surfaces coated with pure Chitosan and PCL (CS/PCL) and with different percentage of nHA as shown in Figure (3.7).

Figure (3.7) Pull-off Adhesion device.

Chapter Four

4.1 Introduction

This chapter includes and discusses the results of all prepared specimens involves FTIR , DSC, contact angle results, also it contains the corrosion resistance results of Ti specimens, and effect the adding of nHA nanoscales on the adhesion, also antibacterial activity of coating discussed.

4.2 Surface Test Result

4.2.1Characterizing of Surface Coated by FTIR

Fourier Transform Infrared (FTIR) Spectroscopy is to look at the chemical interactions between PCL and nHA, done. Figure (4.1) display FTIR spectra of (LBL Ti Pure) and (LBL Ti 0.1) (PCL LBL Ti 0.5 PCL) (LBL Ti 1 PCL) composite films. Weak peaks at 2942 cm^{-1} and 2865 cm^{-1} in the spectrum of pure PCL film were due to the asymmetric elongation of the methylene-oxygen (CH_2O) and symmetric methylene groups, respectively. The vibration of -C=O bonds is represented by the acute and powerful peak at 1721 cm^{-1}. Representative peaks for the C-O-C bond and the stretching of the bond were also found at 1166 cm^{-1} and 960 cm^{-1}, respectively. Peaks in the spectra of the PCL/nHA composite films and the pure PCL film were comparable. However, a broad peak at 3300 cm^{-1} that was evident in the spectra of the PCL/nHA composite films and gradually appeared as the nHA content from the spectrum of pure PCL film. In short, the FTIR peaks in the PCL/nHA composite films spectra were comparable to those in the spectrum of the pure PCL film, indicating that the addition of nHA to the PCL matrix not effect in any chemical bonds, such as the formation of new chemical bonds between the PCL chains and nHA. This in agreement with Campos et al [88].

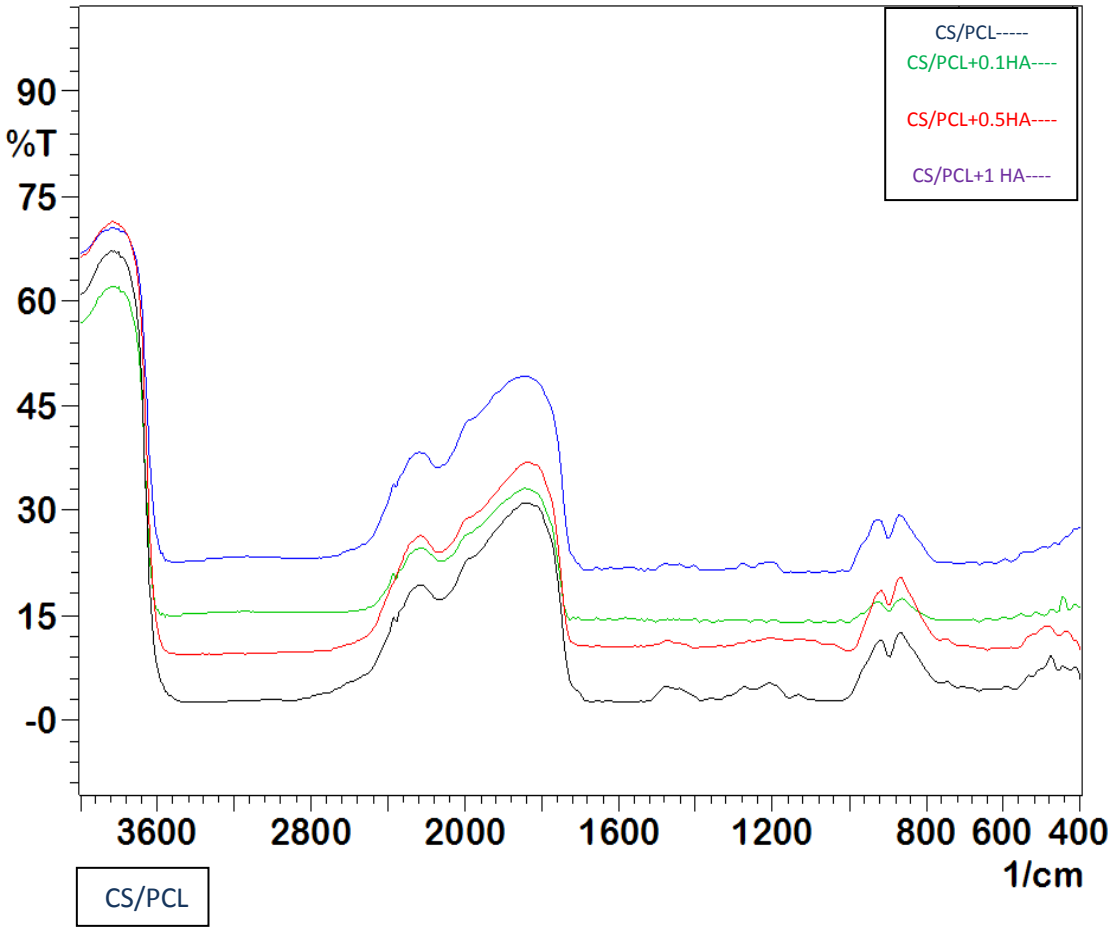


Figure (4.1) FTIR spectra of(LBL Ti Pure)(LBL Ti 0.1 PCL)(LBL Ti 0.5 PCL)(LBL Ti 1 PCL)..

4.2.2 Wettability Result

The results from the contact angle measurements which is done using saliva solution for two groups of the prepared samples using different preparation methods

The first method is layer by layer (LBL) coated samples, first group on Titanium substrate and second group on PMMA substrate where the first layer chitosan and PCL/nHA with different weight percentage (0.1,0.5,1)wt% nHA as shown in Appendix(1) using LBL method to prepare coating on Ti substrate, showed angles within the range of 82.45◦for Ti substrate to 35.871◦ for (LBL Ti 1 PCL) coating, which indicated that the surfaces of the coatings were hydrophilic. The results

also showed that the wettability of the LBL coatings of nHA/PCL/CS increased and the enhanced which is important factor for good adhesion for coating on dental implants. Due to the amino groups that were present on the coating surfaces, every coating was hydrophilic, this is agree with Bei et al. 2019 [89]

Chitosan is more hydrophilic than PCL, which is hydrophobic; nevertheless, when these two polymers are coated with LBL coating, the composite coating's wettability is altered. These outcomes demonstrated that nHA accelerated the pace at which water absorbed into the coating. While maintaining its distinctive qualities, such as a low degradation rate and strong mechanical strength, LBL technique has improved PCL's capacity to absorb water. Coatings with a high porosity, hydrophilicity, mechanical strength, and slower rates of degradation were created by combining the two polymers.

The second method is spin coating (SP) coated samples, first group on Titanium substrate and second group on PMMA substrate where the first layer chitosan and the second layer PCL/nHA with different weight percentage (0.1, 0.5, 1%) wt. As shown in Appendix(2) using SP method to prepare coating on Ti substrate, showed angles within the range of 77.861◦for Ti substrate to 58.646◦ for (SP Ti 1 PCL) coating, which indicated that the surfaces of the coatings were hydrophilic. The results also showed that the wettability of the SP coatings of nHA/PCL/CS increased and the enhanced which is important factor for good adhesion for coating on dental implants. Due to the amino groups that were present on the coating surfaces, every coating was hydrophilic, this is agree with Liling et al. 2003, [90].

Comparing the first substrate Ti with second substrate results as shown in Appendix (1 and 2) noticing that wettability in PMMA substrate is lower than Ti substrate where it decreased from 101.281◦on PMMA

substrate to 68.768°on (LBL PMMA 1 PCL) coating sample. Table (4.1) show contact angle results for all samples.

Table (4.1) Contact Angle Results for all Samples.

Code samples	**Contact angle**
Ti substrate	82.45°
LBL Ti Pure	45.94°
LBL Ti 0.1 PCL	37.45°
LBL Ti 0.5 PCL	39.59°
LBL Ti 1 PCL	35.87°
PMMA substrate	101.28°
LBL PMMA pure	59.13°
LBL PMMA0.1 PCL	60.06°
LBL PMMA0.5 PCL	67.49°
LBL PMMA1 PCL	68.77°
SP Ti Pure	100.23°
SP Ti 0.1 PCL	75.78°
SP Ti 0.5 PCL	67.93°
SP Ti 1 PCL	56.55°
SP PMMA Pure	85.33°
SP PMMA0.1 PCL	85.49°
SP PMMA0.5 PCL	67.55°
SP PMMA 1 PCL	55.77°

4.2.3 Differential Scanning Calorimetry Results

DSC describes the thermal properties for pure coat (LBL Ti Pure) and (LBL Ti 0.1 PCL) coating. The coating samples were heated to 200 C°.

The DSC heating curves for pure coat are shown in Figure (4.2). Noted the (LBL Ti Pure) starts melting at 89.36 C° and it continue to endset melting point about 118.36 C°, this is due to a biomorphic structure with crystalline region of (LBL Ti Pure). This agreement with Baur, et al. 2012 [91]. The estimated thermal parameters values are presented in Figure (4.3) present there are small changing range of melting points of (LBL Ti 0.1 PCL) resulted addition of nHA into (LBL Ti Pure) coating as notice, this nanoscales addition leads to decrease the starting melting point of (LBL Ti Pure)coating to 88.20 C°, on the other hand, the endset melting point is about 111.52 C°. This is due to the role of nHA nanoscales, this is suggested to the nanoscales allowing for simultaneous growth of crystallites, resulting in a smaller crystalline. In Figure (4.4) for coat (LBL Ti 0.5 PCL) noted melting started in 90.84 C°, and continue to endset melting point about 119.65 C° also for the addition of nHA. In Figure (4.5) for coat (LBL Ti 1 PCL) starts melting at 85.66 C°, and continue to endset melting point about 110.77 C°, due to large amount of nHA lead to decrease crystallinity. According to these findings results, the nHA content had an impact on the DSC heating curves [91]. Table (4.2) show Thermal Properties of samples.

Table (4.2) Thermal Properties of samples by DSC Thermal Analysis.

Sample	**Tm_1 C°**	**Tm_2 C°**	**Transition Energy MJ**	**Crystallinity J/g**
LBL Ti Pure	89.36	118.36	-111.23	-22.39
LBL Ti 0.1 PCL	88.20	111.52	-26.59	-5.26
LBL Ti 0.5 PCL	90.84	119.65	-11.57	-2.31
LBL Ti 1 PCL	85.66	110.77	-34.71	-6.94

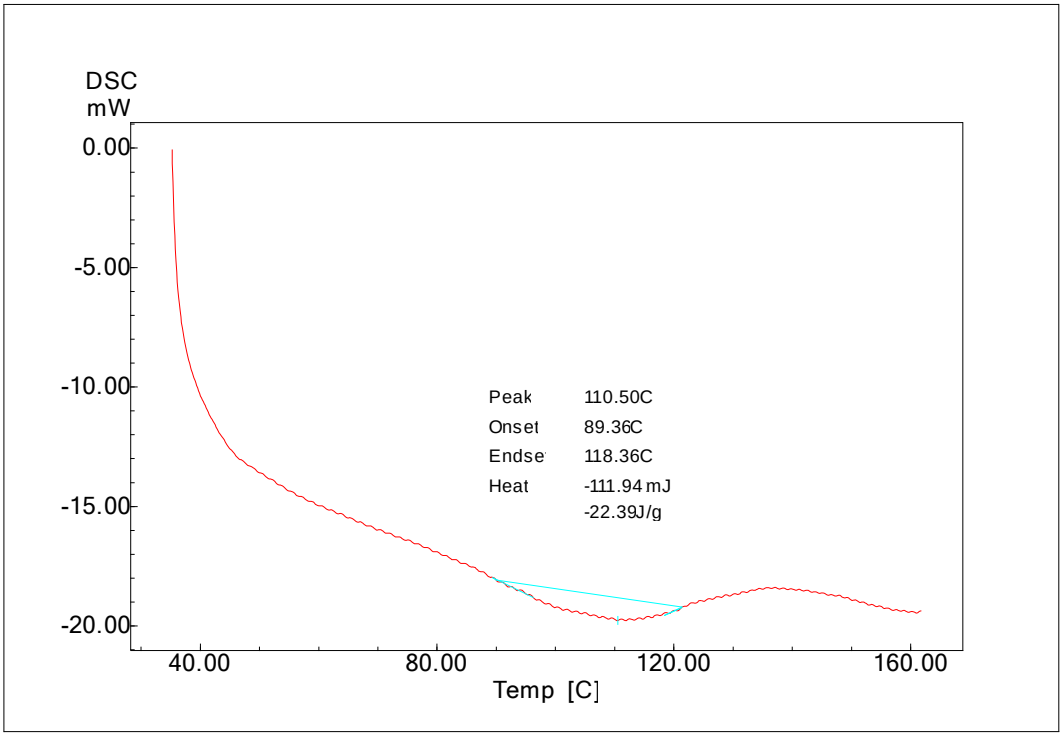


Figure (4.2) DSC heating curve for pure coat (LBL Ti Pure).

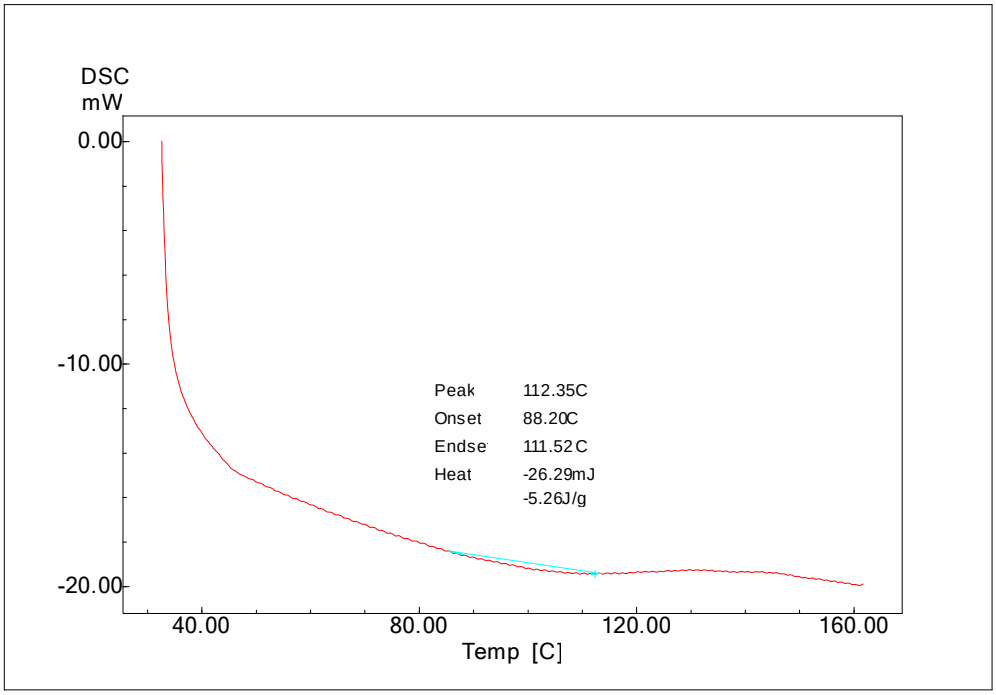


Figure (4.3) DSC heating curve for coat LBL Ti 0.1 PCL.

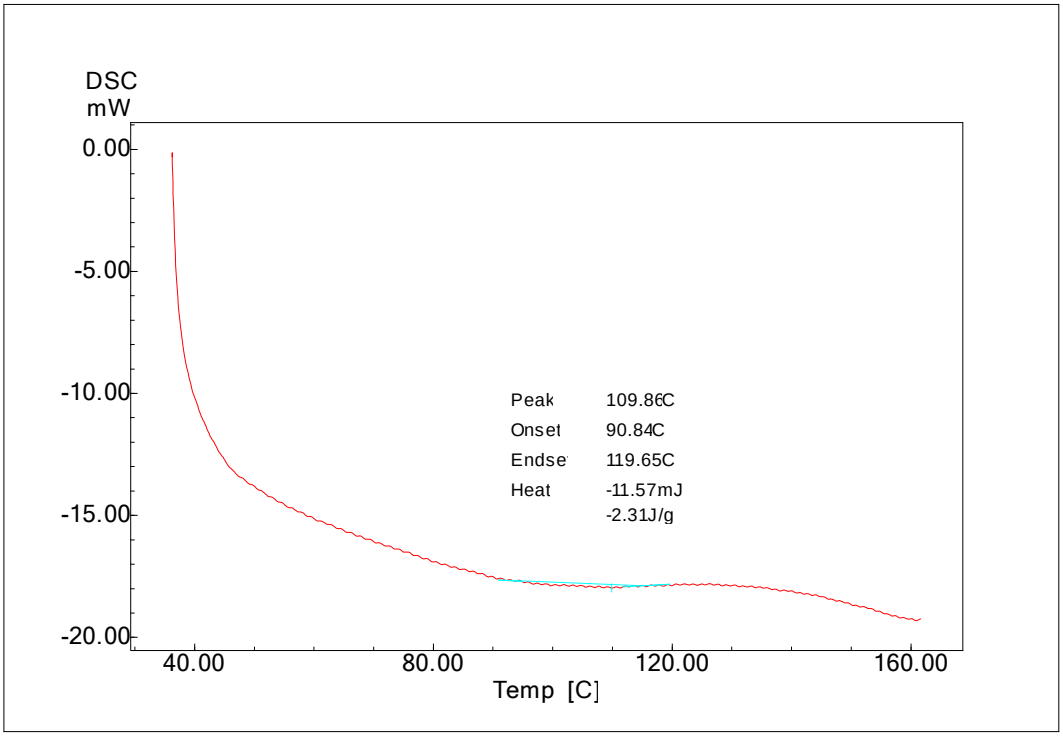


Figure (4.4) DSC heating curve for coat LBL Ti 0.5 PCL.

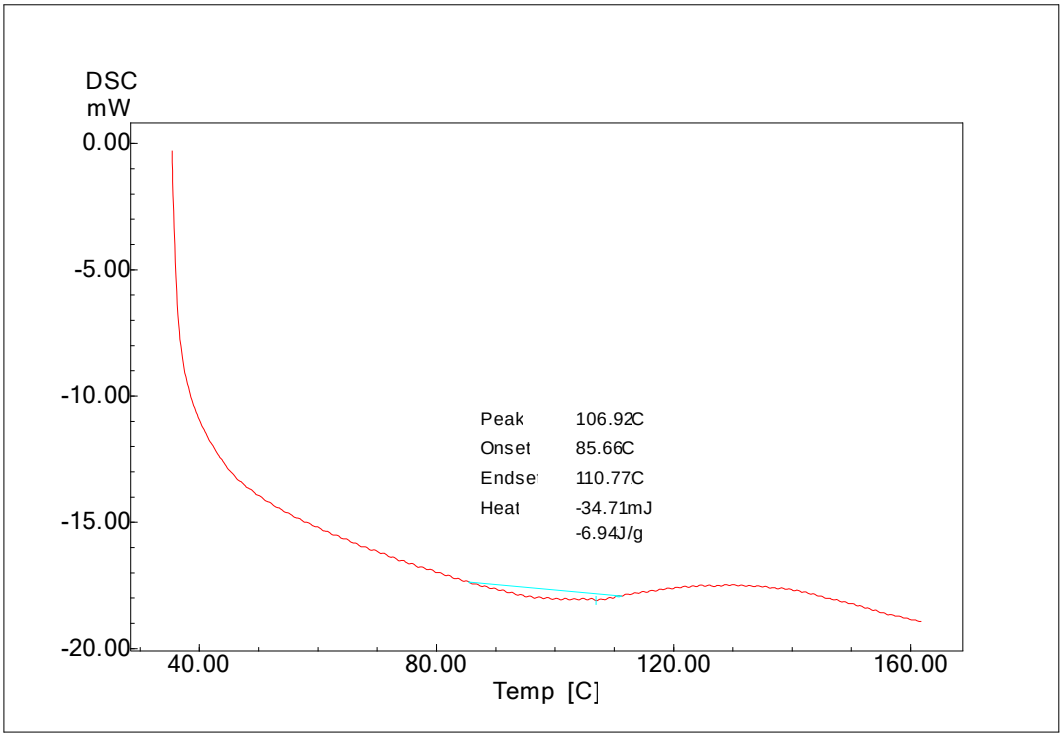


Figure (4.5) DSC heating curve for coat LBL Ti 1 PCL.

4.2.4 Optical Microscopy (OM)

Notice from Figure (4.6) **a** and **b** the samples without coating contains an rough surface and zigzag surfaces, this is according to condition of preparations .

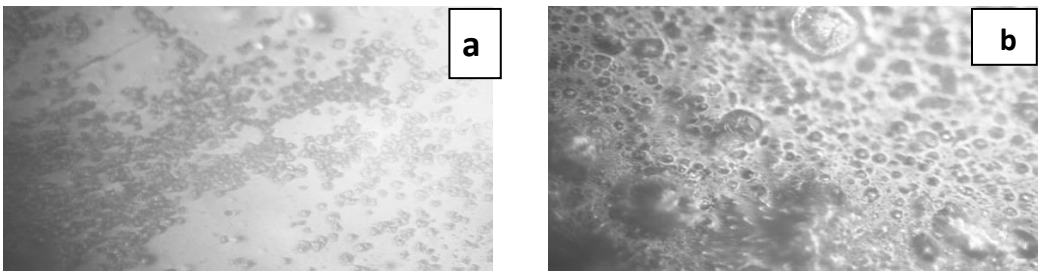


Figure (4.6) **a**- Ti substrate without coting.

b- PMMA substrate without coting.

Figure (4.7) **a** to **d** refers to Ti samples with coating of chitosan and PCL with different percentages (0.1,0.5,1)wt% of nHA using LBL technique, this coating works on covering the zigzag topography of surfaces gradually, and decrease the roughness of surface.

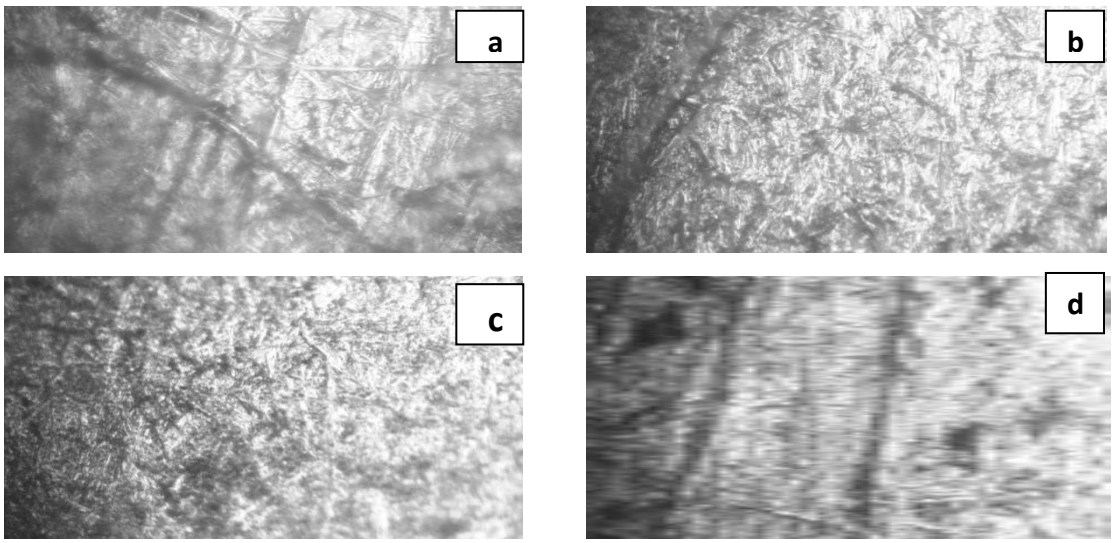


Figure (4.7) Ti substrate coating by LBL technique **a-** pure

b- PCL 0.1

c- PCL 0.5

d- PCL 1

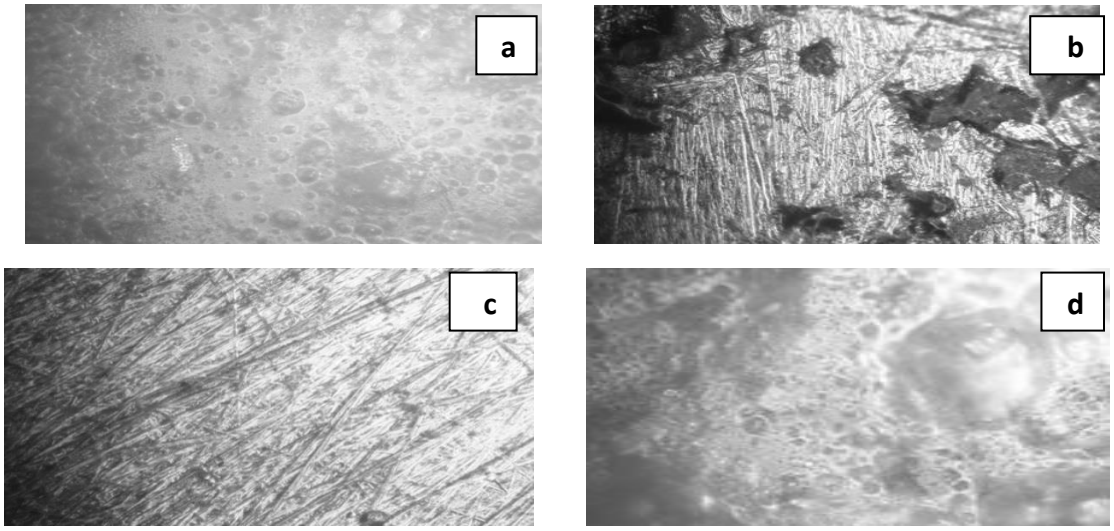


Figure (4.8) PMMA coating by LBL technique **a-** pure PCL

b- PCL 0.1

c- PCL 0.5

d- PCL 1

Also notice, the increasing of nHA leads to increasing of covering area of surface samples with the same coating conditions. Notice there are discontinues regions in coating surfaces while with increasing of nHA there are more homogeneity of coating.

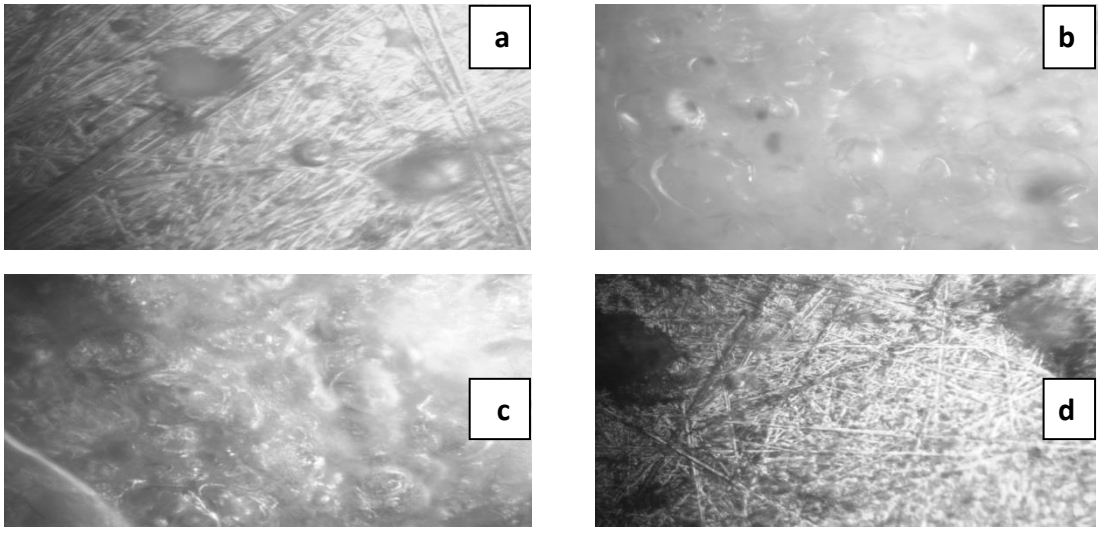


Figure (4.9) Ti coating by SP technique **a-** pure PCL

b- PCL0.1

c- PCL/0.5

d- PCL 1

4.2.5 Thickness Measurement Test

For this test, the average thickness of three samples was taken for both coating techniques for all samples. For LBL was (200-500) µm. For SP (100-200) µm.

4.3 Biologics Tests Results

4.3.1 Biofilm Formation

The results of this test are displayed in Table (4.3). It demonstrates the adherence of bacteria to the Titanium and PMMA substrate surfaces and the development of the Biofilm layer.

Moreover, it indicated the absence of biofilm formation and the absence of bacterial adhesion to the surface of chitosan. Despite the fact that they grow rapidly without chitosan in PCL/0.1nHA sample while the other samples shows non adherence and nonformation of biofilms by increasing the weight ratio of nHA.

Table (4.3) Results of bacterial formation's biofilm and adherence.

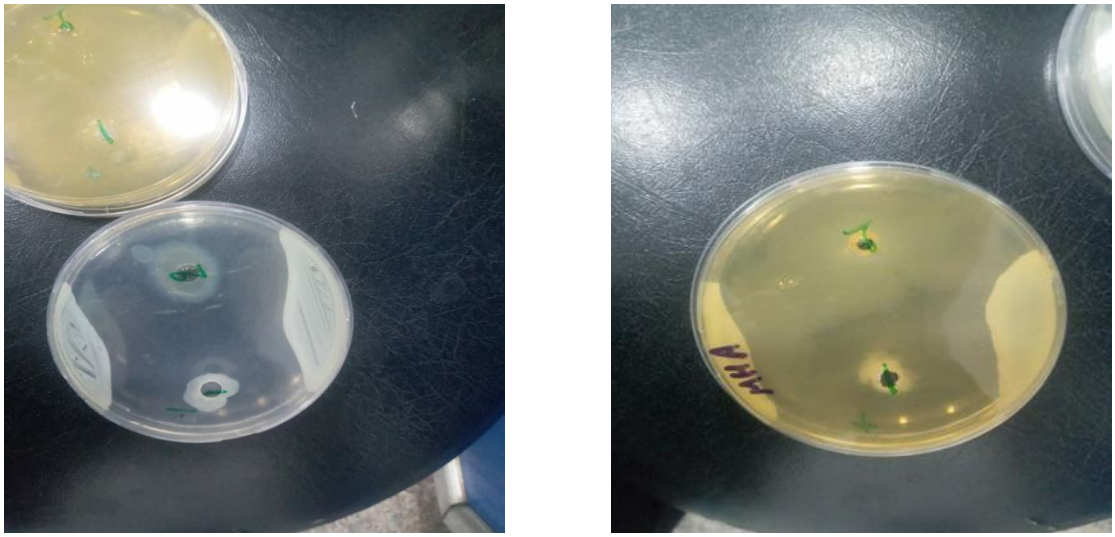
Type of sample	**Adherence**	**Formation's Biofilm**
Titinum substrate (G+ve bacteria) and (G-ve bacteria)	Strong	High
PMMA substrate (G+ve bacteria) and (G-ve bacteria)	Strong	High
Pure CS (G+ve bacteria), and (G-ve bacteria)	Non	Non
PCL +0.1 nHA (G-ve bacteria)	Strong	Strong
PCL+0.5 nHA **(**G-ve bacteria**)**	Non	Non
PCL+1.0 nHA	Non	Non

4.3.2 Antibacterial

Figure illustrates how various prepared coatings, as given in Table (4.4), affected the development of S. aurous, a positive type, and E. coil, a negative type Figure (4.10). The antibacterial activity of various prepared solutions in liquid media for various coating solutions that are pure CS and PCL with various weight ratios (0.1,0.5,1)g nHA for both bacterium kinds shows in Figure (4.11).

Table (4.4) Influencing of chitosan and PCL solution for and of E. coil. Inhabitation of S. aurous

Type of sample	Inhabitation of S. aurous (mm)	Inhabitation of E. coil (mm)
Pure chitosan/PCL	10	8
CS /PCL +0.1 Nha	15	10
CS/PCL+0.5 nHA	18	12
CS/ PCL+1.0 nHA	20	19



-a- **-b-**

Figure (4.10) **a**- The action of PCL/nHA solutions on S. aurous and Ecoil bacteria **b**- The action of chitosan solutions on S. aurous and Ecoil bacteria.

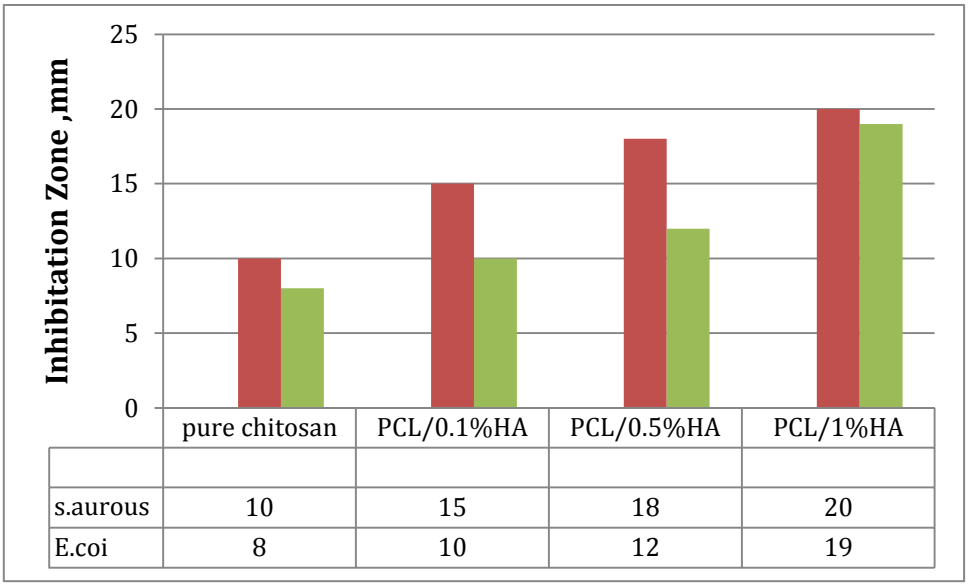


Figure (4.11) show inhibition zone in mm for both types of bacteria.

This analysis, along with the figures and the table above, show that the inhibition area for S. aurous as a positive type is better than inhabitation of E. coil for all type of prepared liquid solutions.

4.4 Mechanical Tests Result

4.4.1 Pull-off adhesion Results

The adhesive strength of first sample (Titanium substrate coated with (LBL Ti Pure) is (1.3858MPa) and then when increasing the concentration of nHA in PCL coating, the adhesion strength will be increased to (2.0546MPa) in (LBL Ti 0.5 PCL) as shown in Table (4.5) below then it decreased at 1%nHA to (0.8274MPa) because of ununiformed of preparation and low homogeneity of surface film.

Table (4.5) shows the results of adhesive strength which tested at Titanium substrate using LBL (5layers) method.

Samples No.	Coating	Adhesive Strength MPa
1	LBL Ti Pure	1.3858
2	LBL Ti 0.1 PCL	1.6341
3	LBL Ti 0.5 PCL	2.0546
4	LBL Ti 1 PCL	0.8274

The adhesion strength of (PMMA substrate coated with LBL PMMA Pure) is (0.8343 MPa), and then when increasing the concentration of nHA in PCL coating, the adhesion strength will be increased to (1.0687 MPa) in (LBL PMMA 0.5 PCL) as shown in Table (4.6) then it decreased at 1%nHA to (0.6757 MPa) because of ununiformed of preparation and low homogeneity of surface film. This is suggest to mechanism which believed that rough surface might increases interaction between coating and Ti, PMMA, and nanoparticles strengthen this effect consequently afforded more chances for mechanical interlocking between coating and the substrates , this is agreement with Zhai et al. 2006 and Mukesh et al. 2017 [92][93].

Table (4.6) shows the results of adhesive strength which tested at PMMA substrate using LBL (5layers) method.

Samples No.	**Coating**	**Adhesive Strength MPa**
1	CS/PCL	0.8343
2	LBL PMMA 0.1 PCL	1.0342
3	LBL PMMA 0.5 PCL	1.0687
4	LBL PMMA 1 PCL	0.6757

On the other hand, the effect of changing coating method was studied. Table (4.6) clarify the adhesion strength of the Ti and PMMA substrates using spin coating method in the preparation of coating where the results shows adhesive strength for Ti substrate using different coating at different composition for the same number of layers (n=5) decrease to (0.7033 MPa) at (1 nHA), also in PMMA substrate decrease to (0.7515 MPa) at (1 nHA).

Table (4.7) shows the results of adhesive strength which tested at Titanium and PMMA substrate using spin coating (SP) method.

Samples No.	Content	Adhesive Strength MPa
1	SP Ti PCL	0.8825
2	SP Ti 0.1 PCL	1.1652
3	SP Ti 0.5 PCL	1.1032
4	SP Ti 1 PCL	0.7033
5	SP PMMA Pure	1.9167
6	SP PMMA0.1 PCL	0.9982
7	SP PMMA0.5 PCL	0.9653
8	SP PMMA1 PCL	0.7515

4.5 Electrochemical Tests

4.5.1 Tafel Extrapolation Test

Potentiostatic polarization test is used in artificial saliva solution. The corrosion characteristics of Ti substrate and Ti with coating are depicted by the polarization curves shown in Figures (4.13).

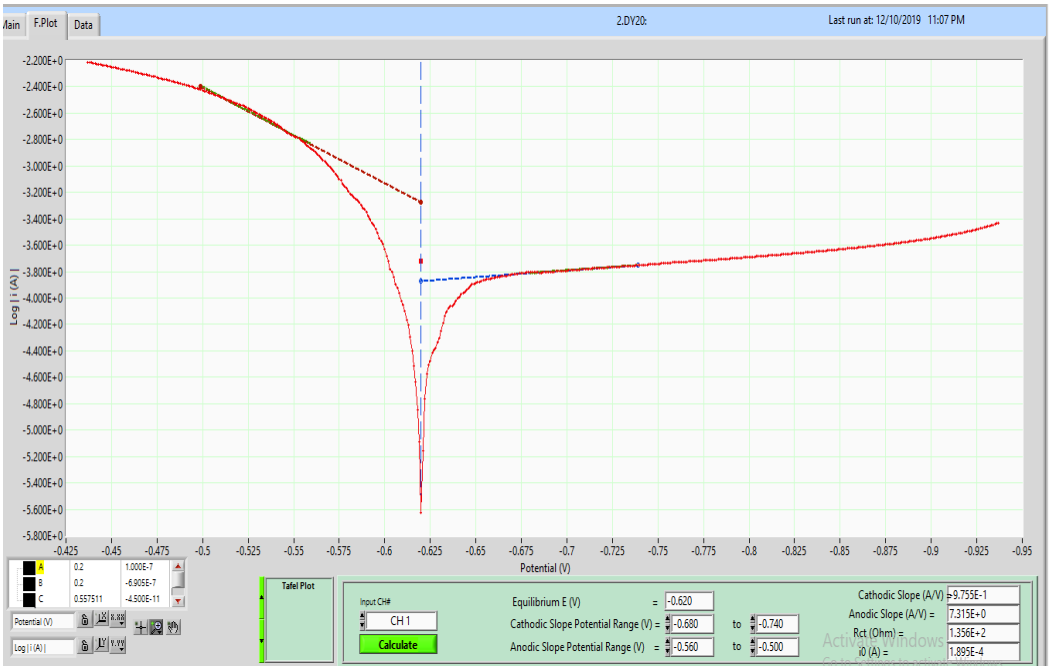
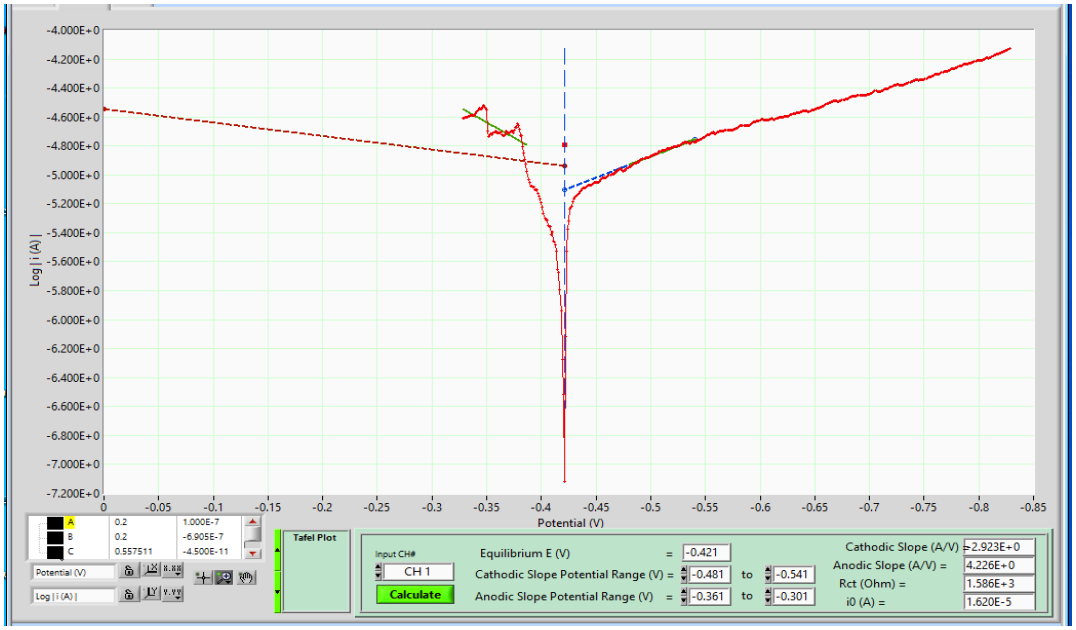
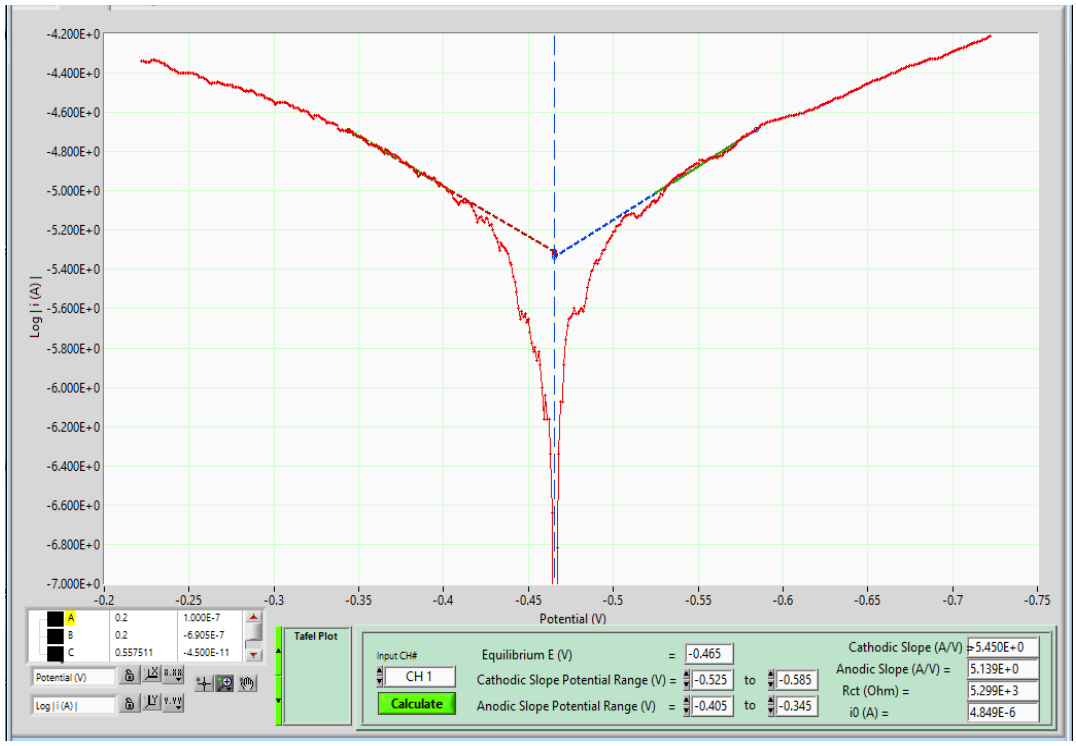


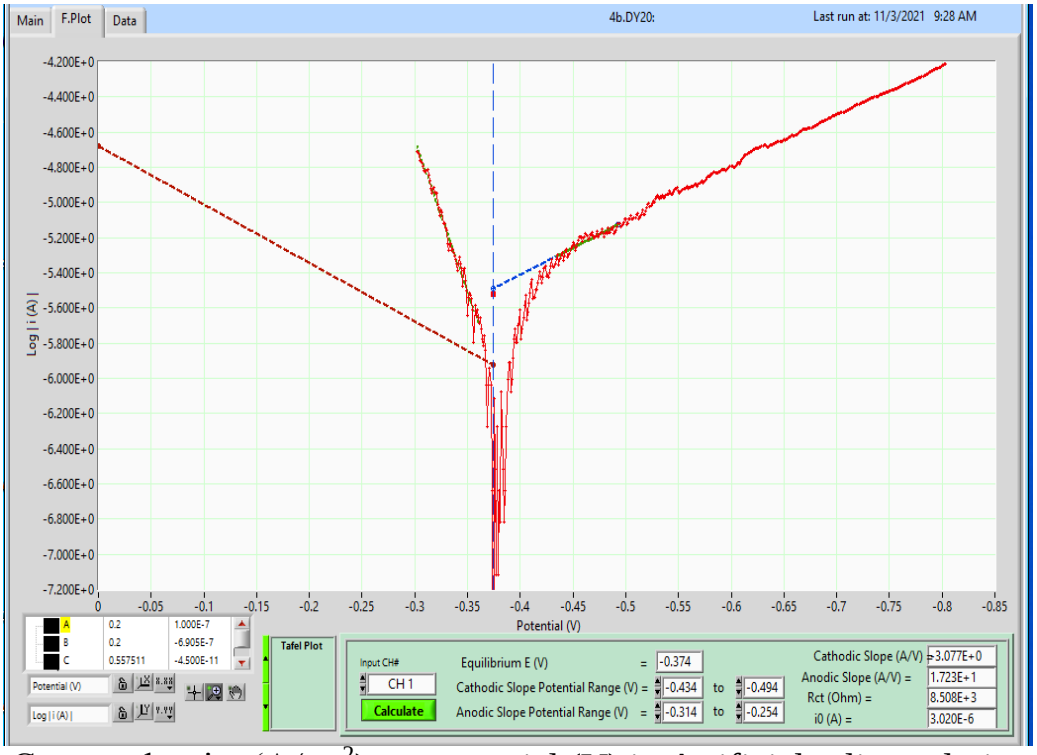
Figure (4.13) **a**-Current density (A/cm^2) vs. potential (V) in Artificial saliva solution at 25 C° for Ti substrate.



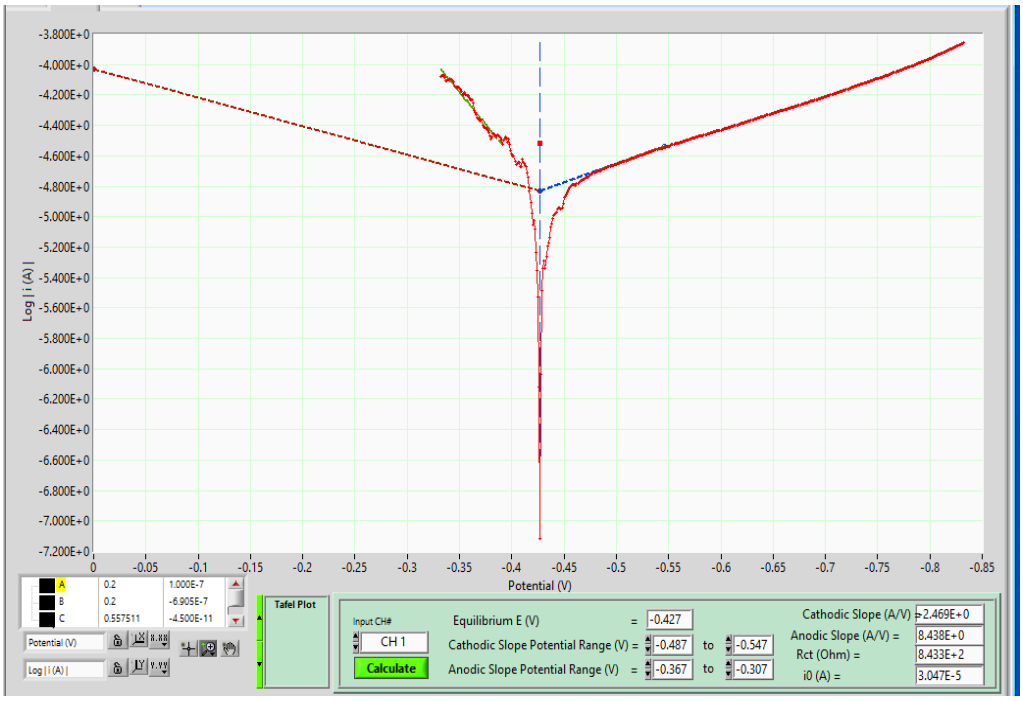
b- Current density (A⁄cm^2) vs. potential (V) in Artificial saliva solution at 25 C° for (LBL Ti Pure).



c- Current density (A⁄cm^2) vs. potential (V) in Artificial saliva solution at 25 C° for (LBL Ti 0.1 PCL).



d- Current density (A⁄cm^2) vs. potential (V) in Artificial saliva solution at 25 C° for (LBL Ti 0.5 PCL).



e- Current density (A⁄cm2) vs. potential (V) in Artificial saliva solution at 25 C° for (LBL Ti 1 PCL).

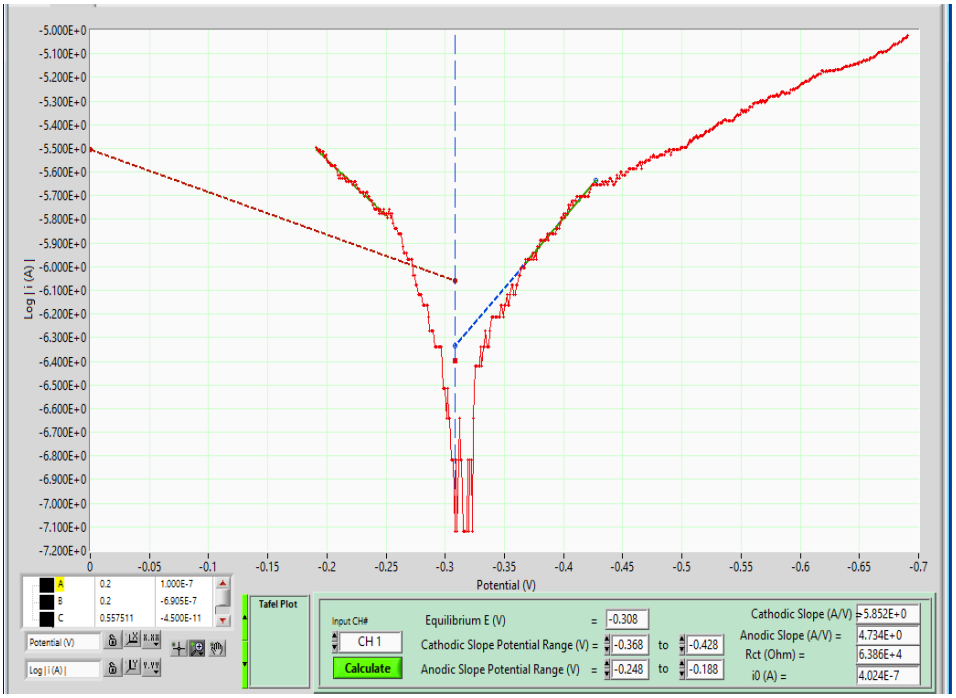
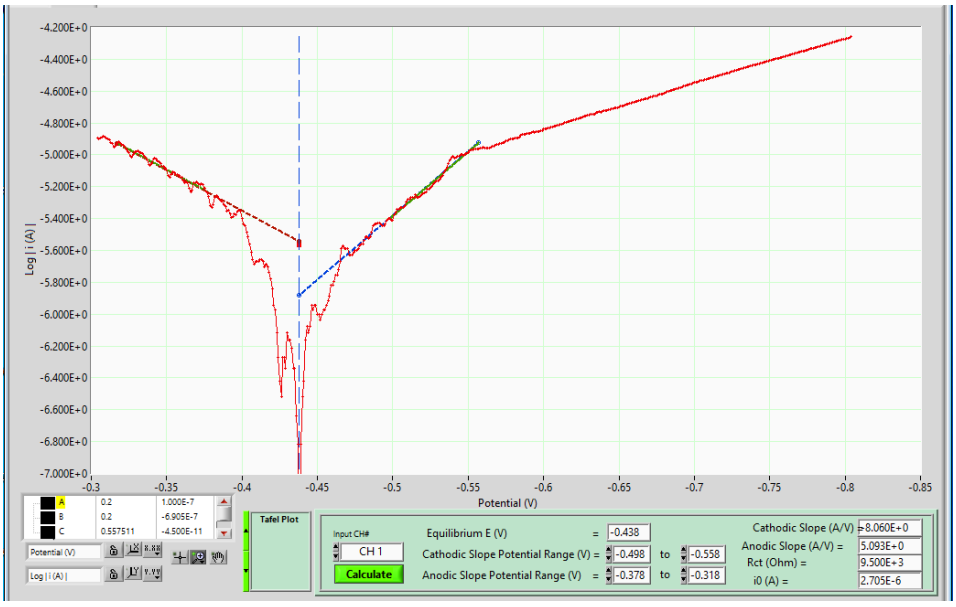
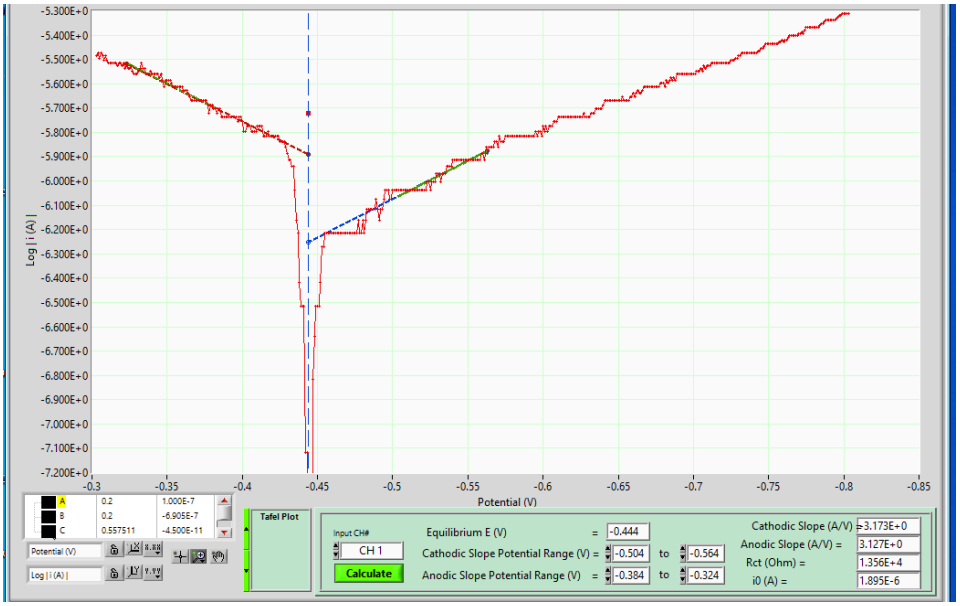


Figure (4.14) **a-**Current density (A/cm^2) vs. potential (V) in Artificial saliva solution at 25 C° for (SP Ti 0.1 PCL).



b- Current density (A/cm^2) vs. potential (V) in Artificial saliva solution at 25C° for (SP Ti 0.5 PCL).



c- Current density (A⁄cm2) vs. potential (V) in Artificial saliva solution at 25 C° for (SP Ti 1 PCL).

Notice from table (4.6), the corrosion current (1.895e-4) for Ti before coating higher than Ti with coating (3.020e-6). On the other hand the corrosion current decreases with increasing nHA, this is because the coating leads to hydrophobic surfaces, which has low surface energy and high corrosion resistance. The coating by CS/PCL leads to prevent the formation of the oxide layer by isolating the surface from the surrounding oxygen ,this is agree with Su et al. 2014 [94]. Notice from results that fixed in table (4.6) decreases corrosion rates clearly, with increasing nHA concentration, this is due to hydrophobicity and low surface energy of coating which is prevent the formation of oxidation layer and isolate of surfaces of Ti from corrosive media. This is agree with Su et al. 2014 [94]. Figure (4.13) (4.14) present the corrosion curves to this test for LBL and SP respectively.

According to electrochemical measurements, Ti and Ti with coating which represent the substrate after polymer coating are more resistant to corrosion than the Ti without coating. This improvement was mostly

owing to the bare metal's surface developing a more uniform passive layer.

These finding are in agreement with other studies. Corrosion parameters (corrosion potential, corrosion current), extracted from these curves, are shown in Table (4.8).

Table (4.8) Corrosion potential and Corrosion current parameters.

coating	**I-corr (μA)**	**E-corr (μV)**
Base Ti	1.895e-4	-0.620
LBL Ti Pure	3.020e-6	-0.374
LBL Ti 0.1 PCL	4.8e-6 0. 0048	-0.465
LBL Ti 0.5 PCL	1.620e-5	-0.421
LBL Ti 1 PCL	2.70e-6	0.438
SP Ti Pure	4.02e-7	-0.308
SP Ti 0.1 PCL	4.02e-7	-0.302
SP Ti 0.5 PCL	3.047e-5	-0.427
SP Ti 1 PCL	1.89e-6	-0.444

Chapter five

5.1 Conclusions

Coating Titanium and PMMA substrates using two coating methods (LBL and spin coating) in order to make comparison and show the more efficient method. The first and second method are with CS/PCL+[(0.1,0.5,1)wt nHA] coating to prevent implant-associated infections. The following inclusions were found.

1. The LBL method is utilized extensively with promising results to modify Titanium and PMMA, laying the groundwork for additional clinical applications.
2. The coated materials were Antibacterial and prevent biofilm formation. In this analysis, it is noted that the inhibition area for S. aurous as a positive type is better than inhabitation of E. coil for all prepared liquid solutions .
3. The adhesive strength is improved for coated materials and it was more enhanced with the addition of nHA concentration reach to 14%
4. The wettability of coating with chosen substrate was enhanced on Ti substrate 20%, PMMA,33% which led to improve the adherence of coating
5. According to electrochemical measurements, the substrate Ti after polymer coating in salvia solution is more resistant to corrosion than the base Ti. The corrosion resistance enhanced 60%.

5.2 Recommendations

1. Using natural polymer as a coating for dental implants.
2. Studying the impact of natural pigments on antibacterial, biofilm formation on dental implants.

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Appendix 1 Contact Angle Results

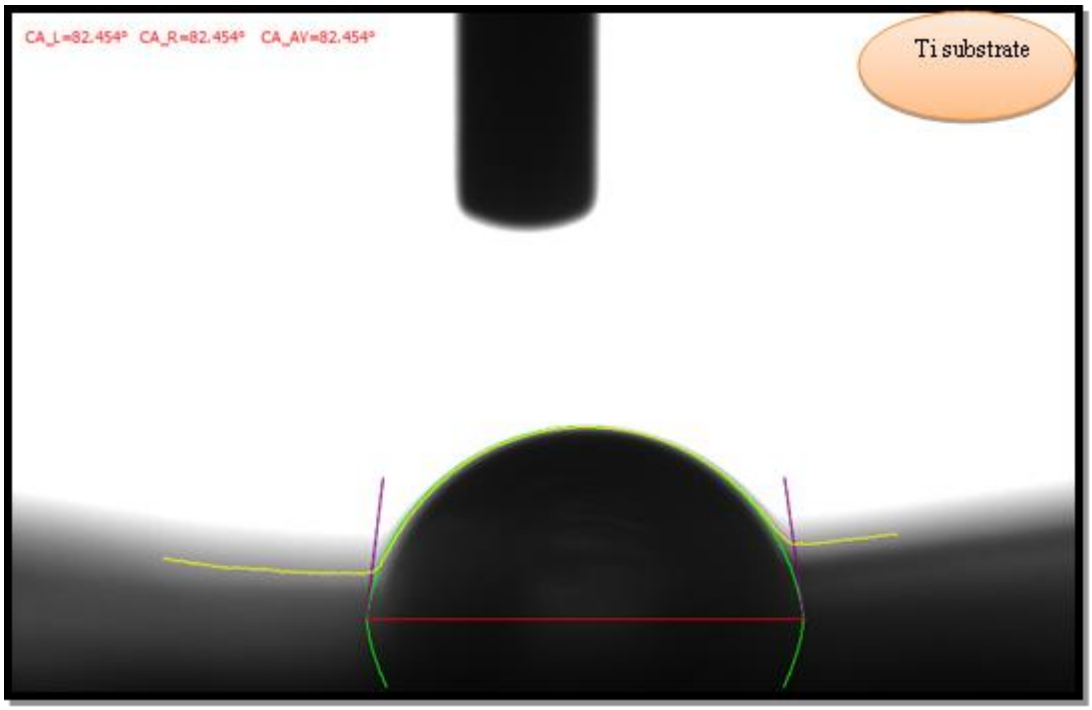
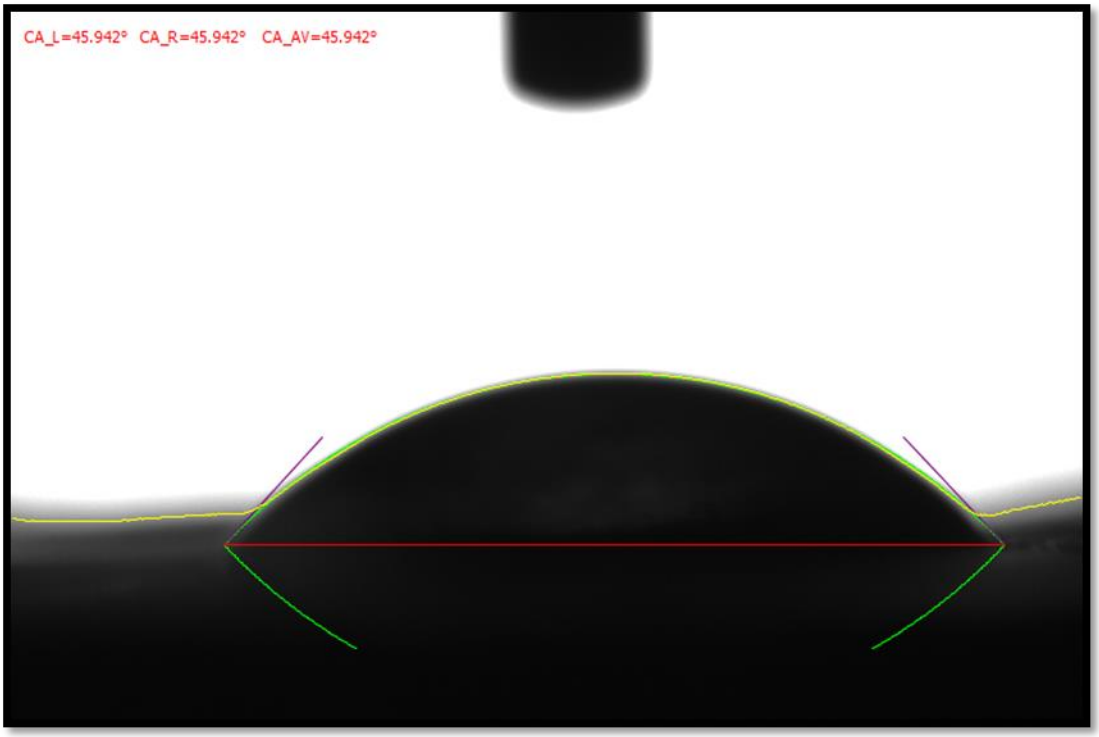
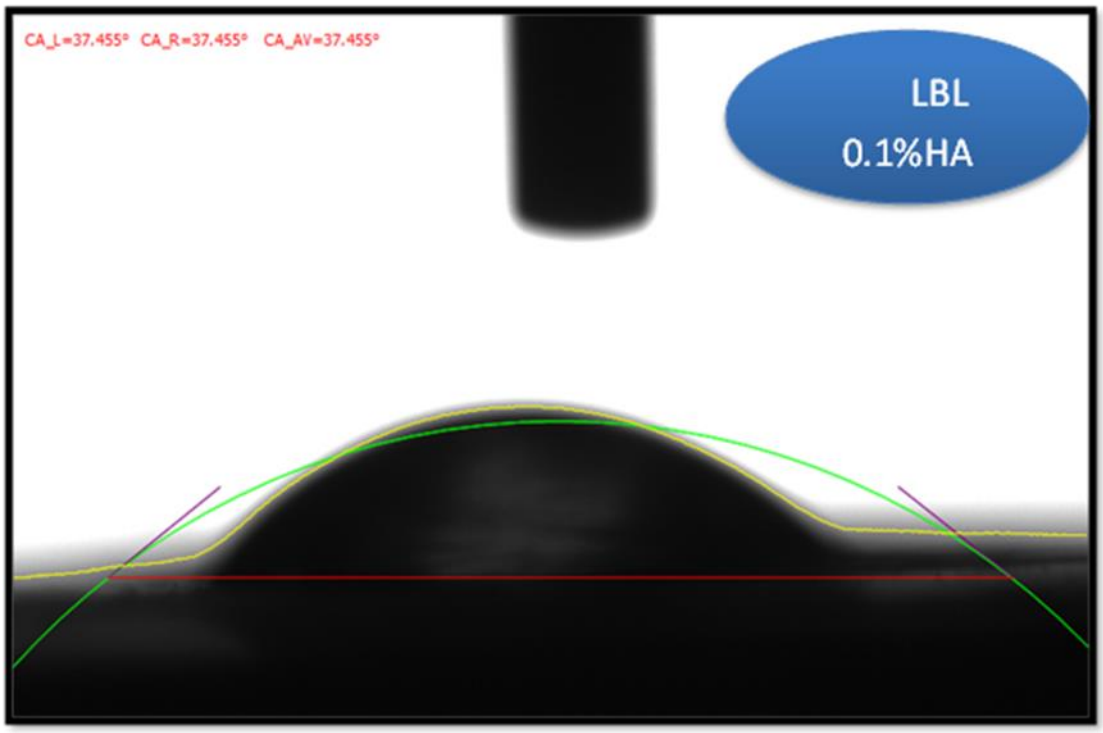


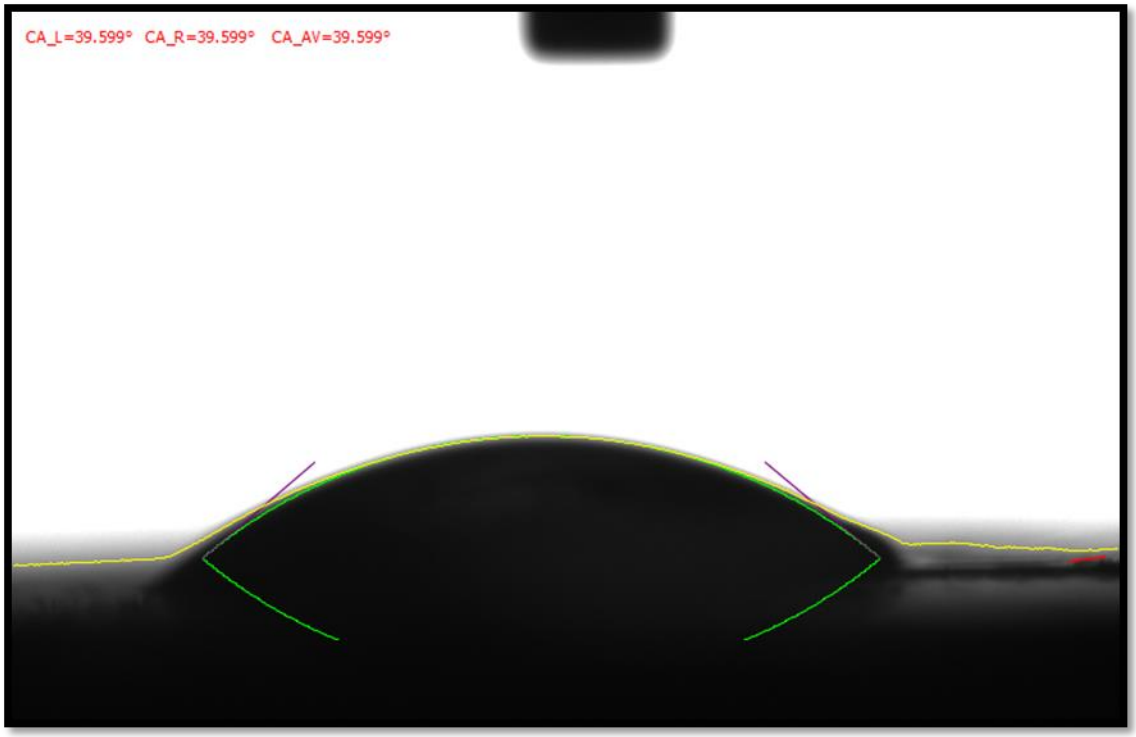
Figure (1) **a-** Contact angle results for Titanium substrate.



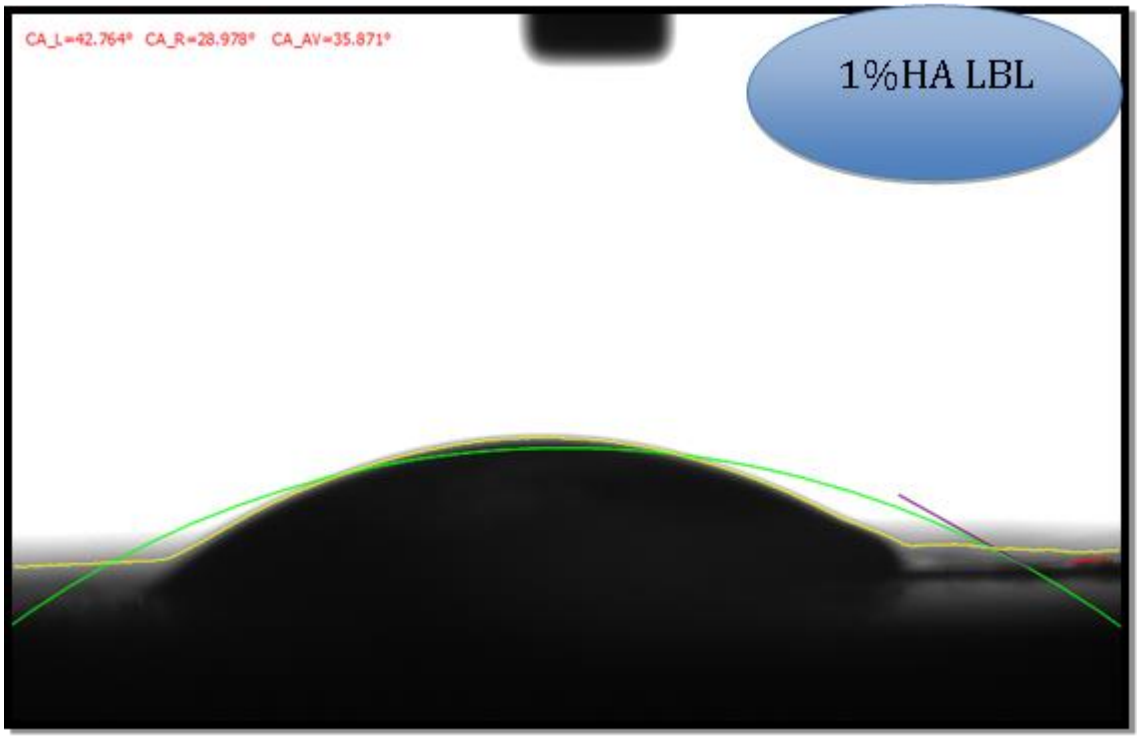
b- Contact angle results for pure Ti substrate (LBL).



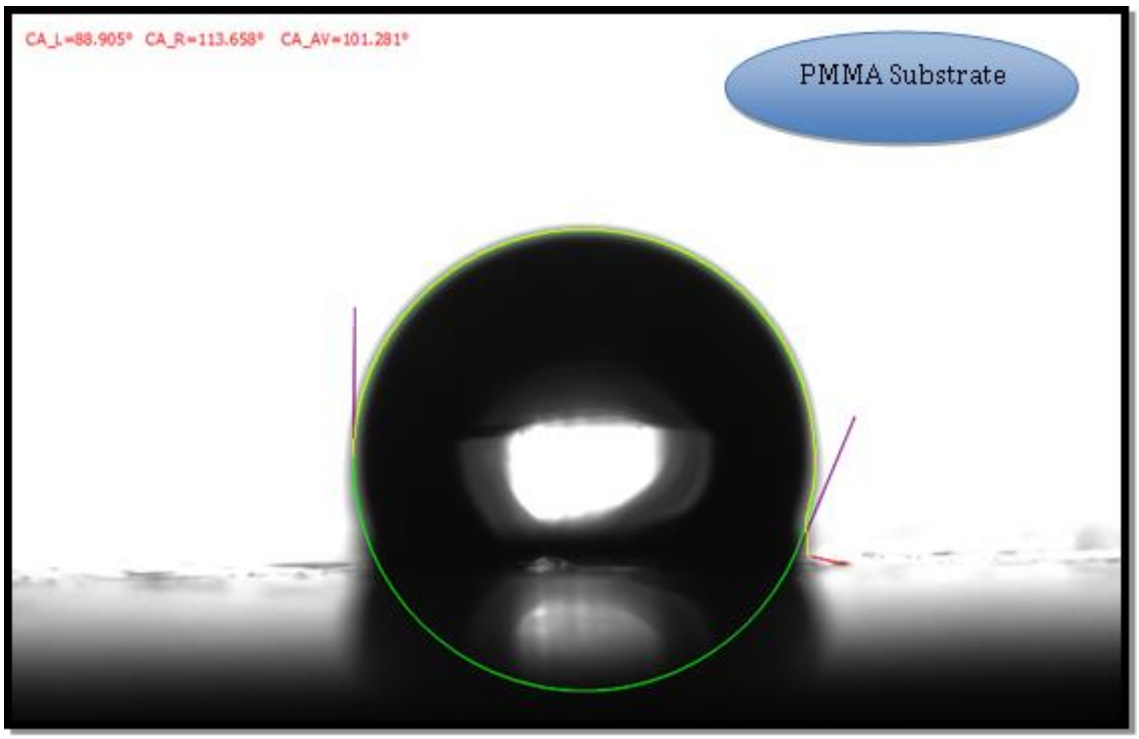
c- Contact angle results for coat PCL/0.1 Ti substrate (LBL).



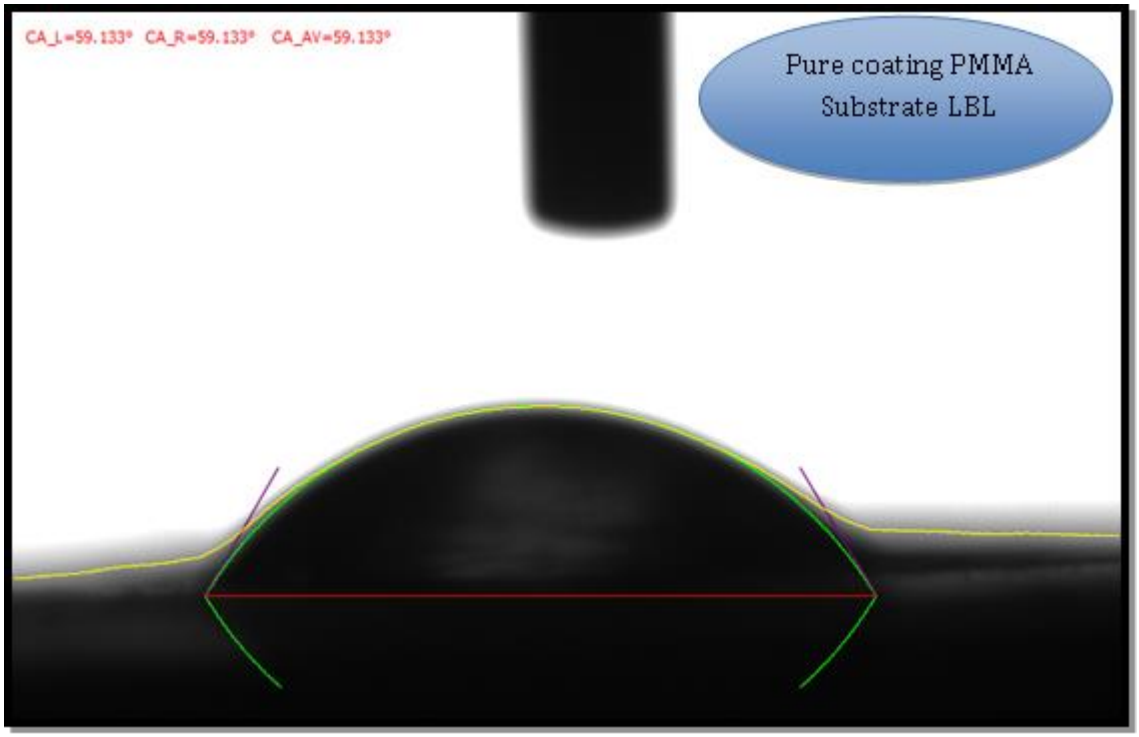
d- Contact angle results for coat PCL 0.5 Ti substrate (LBL).



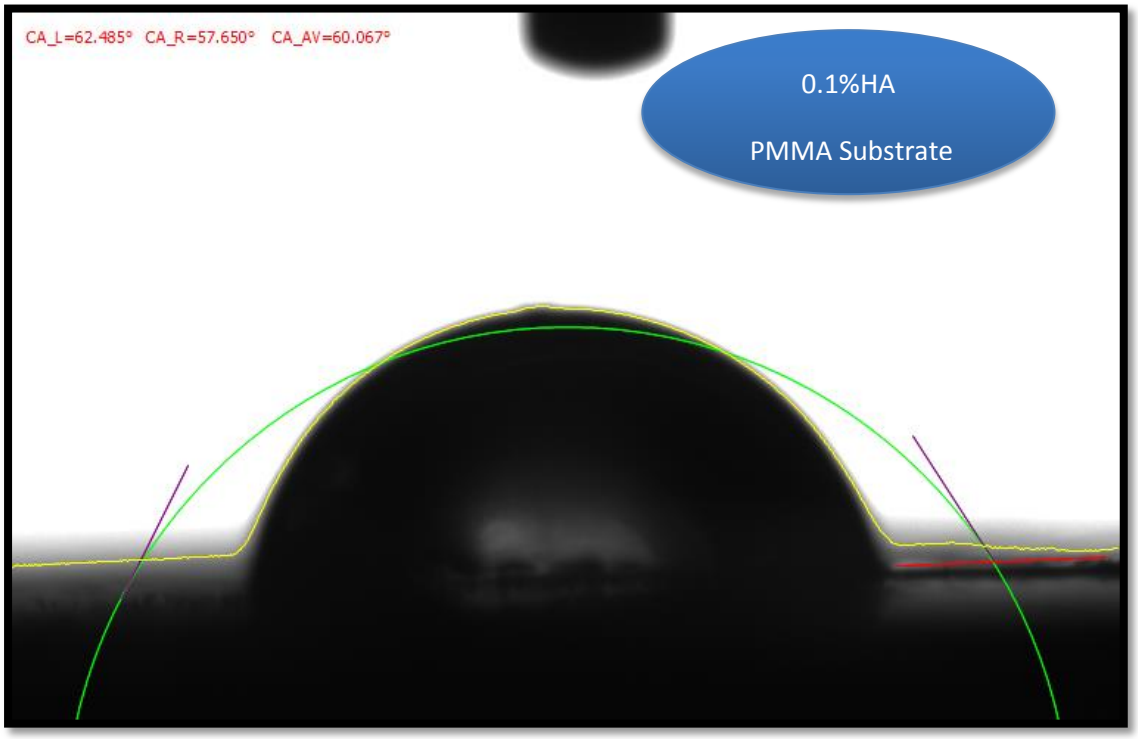
e- Contact angle results for coat PCL1 Ti substrate (LBL).



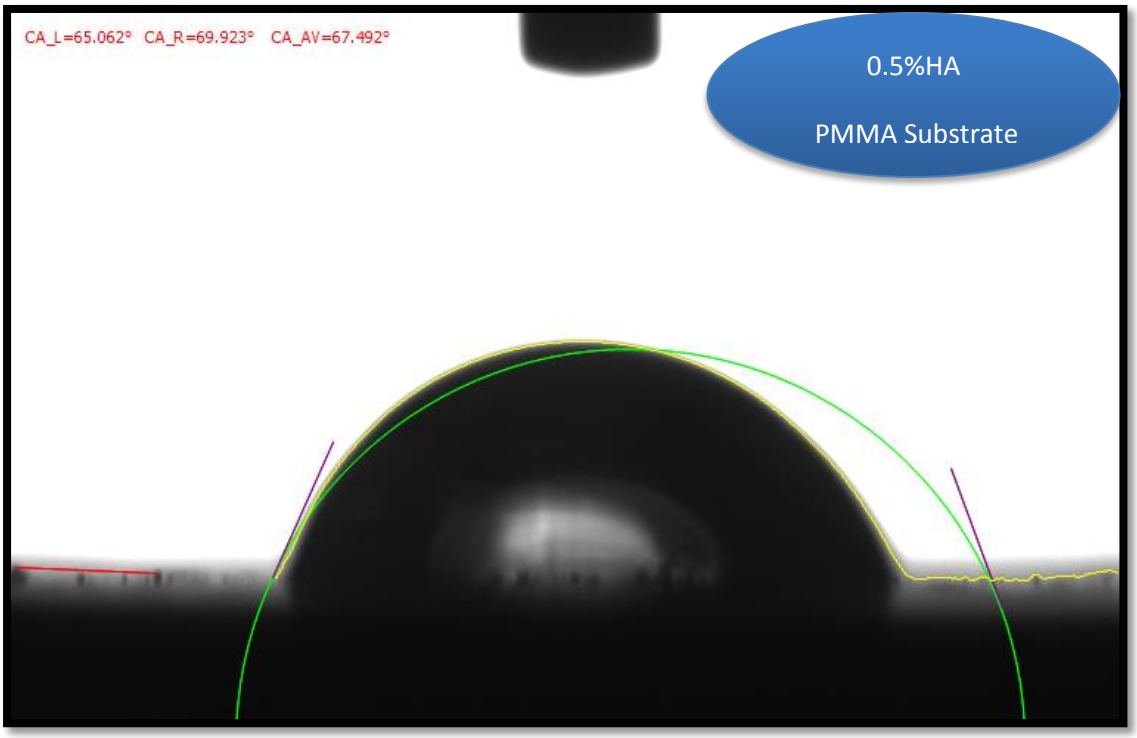
f- Contact angle results for PMMA substrate.



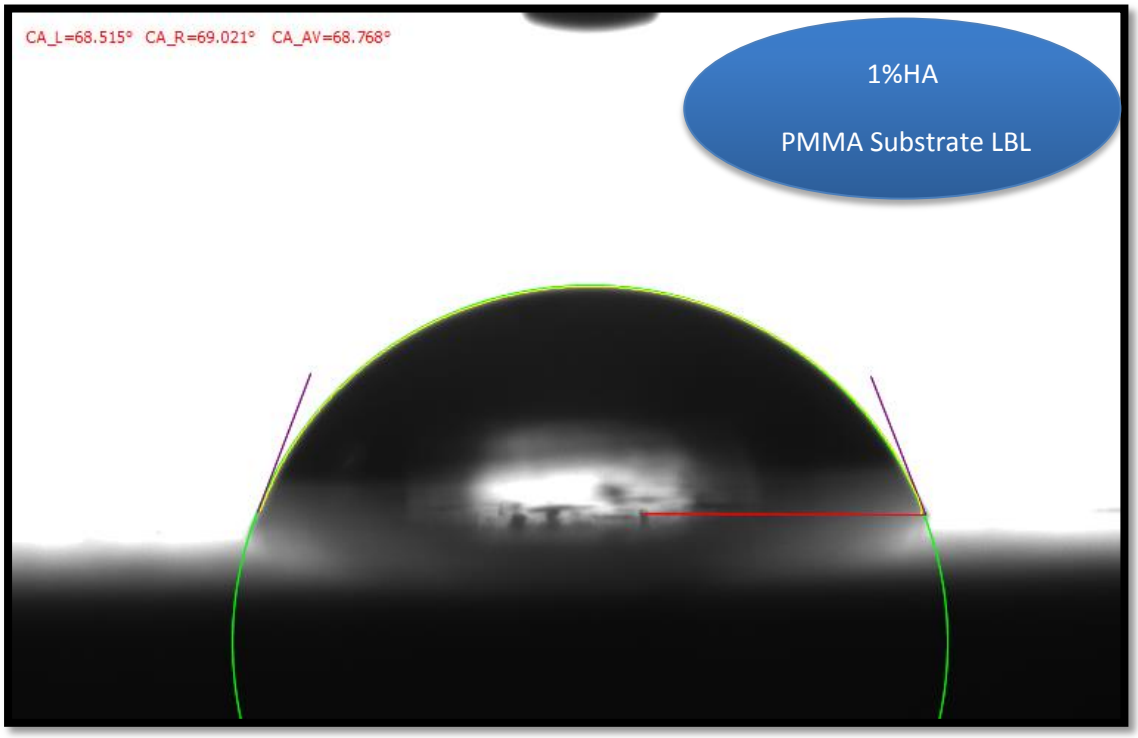
g- Contact angle results for pure PCL PMMA substrate (LBL).



h- Contact angle results for coat PCL 0.1PMMA substrate (LBL).



i- Contact angle results for coat PCL 0.5 PMMA substrate (LBL).



j- Contact angle results for coat PCL1 PMMA substrate (LBL)

Appendix 2 Contact Angle Results

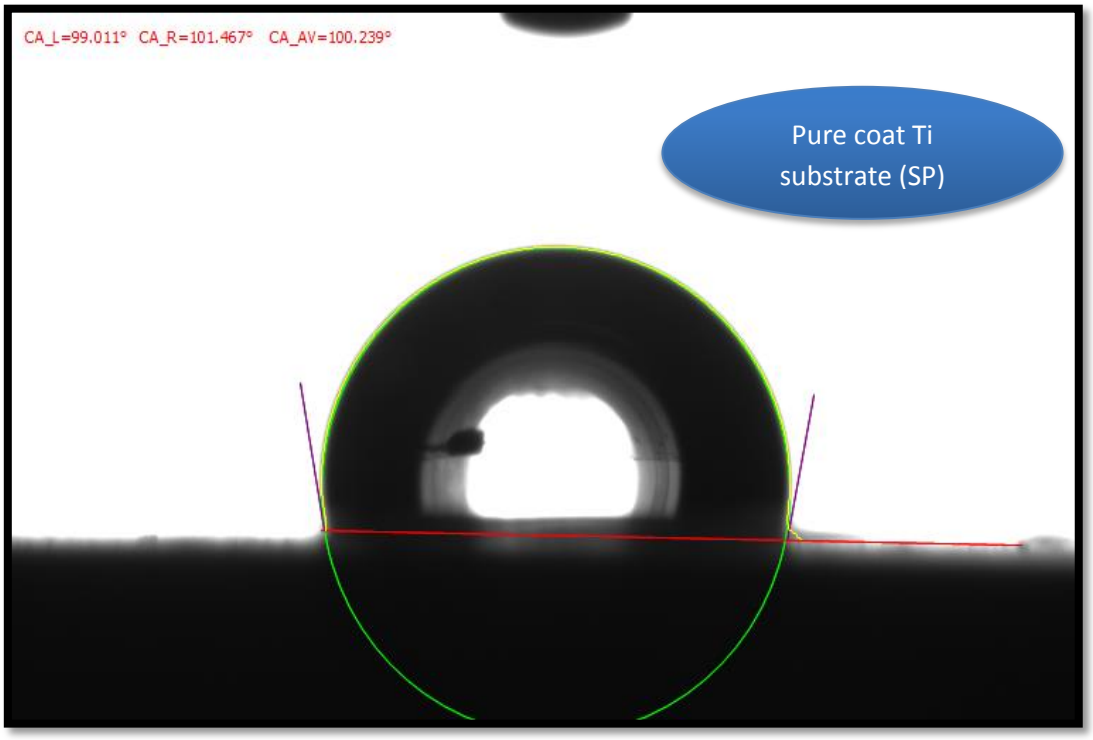
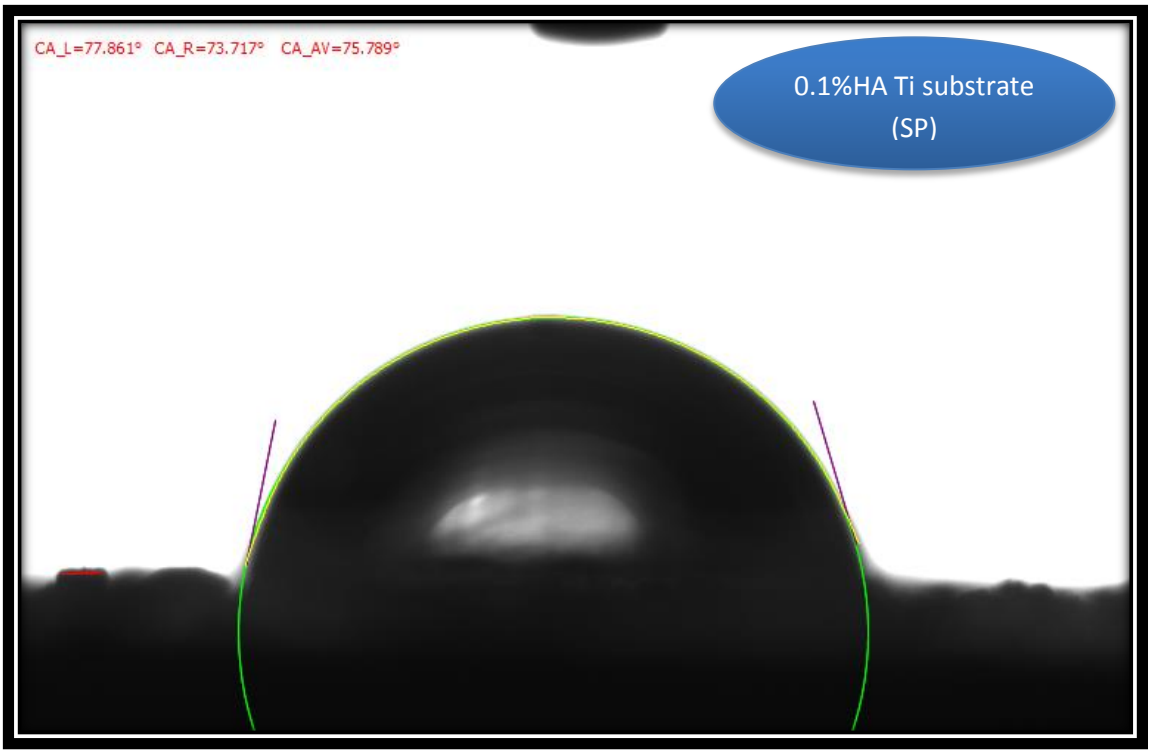
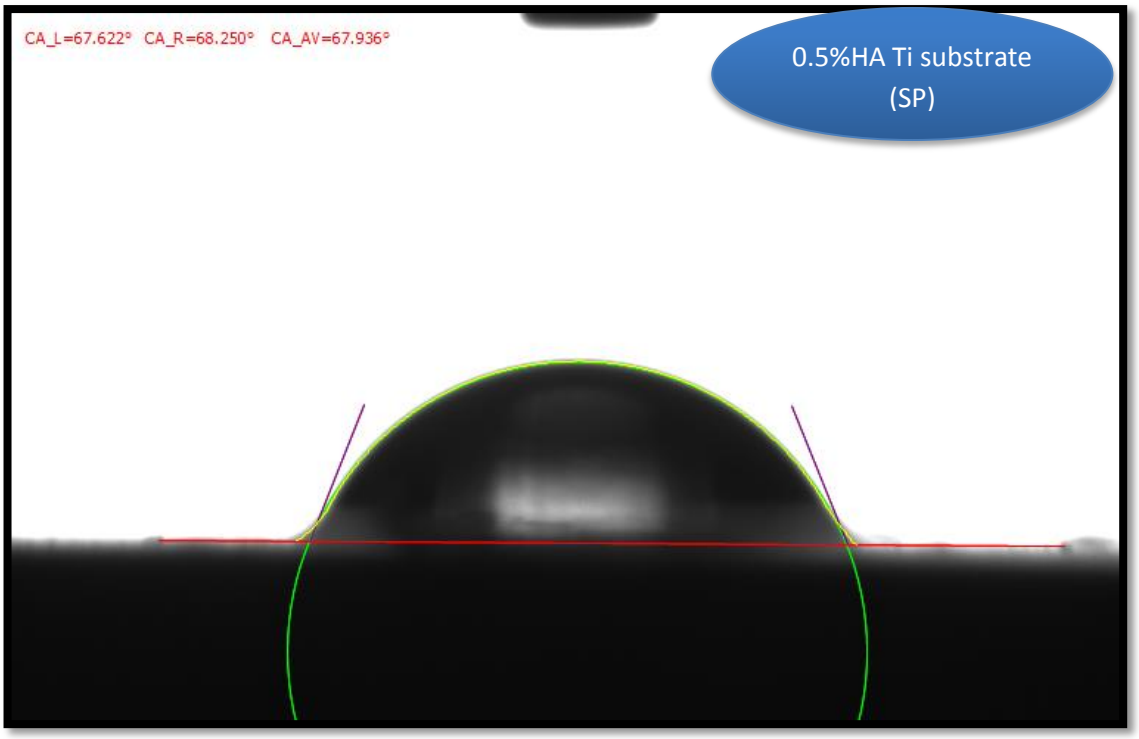


Figure (2) **a-** Contact angle results for pure PCL Ti substrate SP.

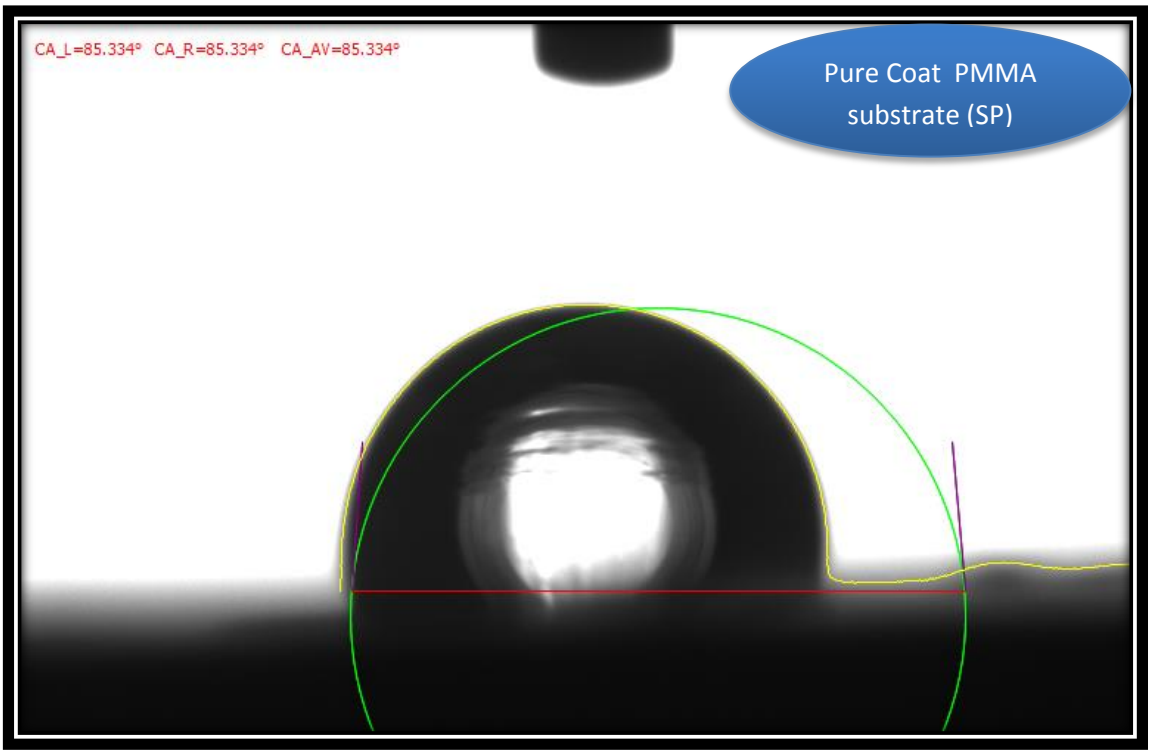


b- Contact angle results for coat PCL 0.1 Ti substrate (SP).

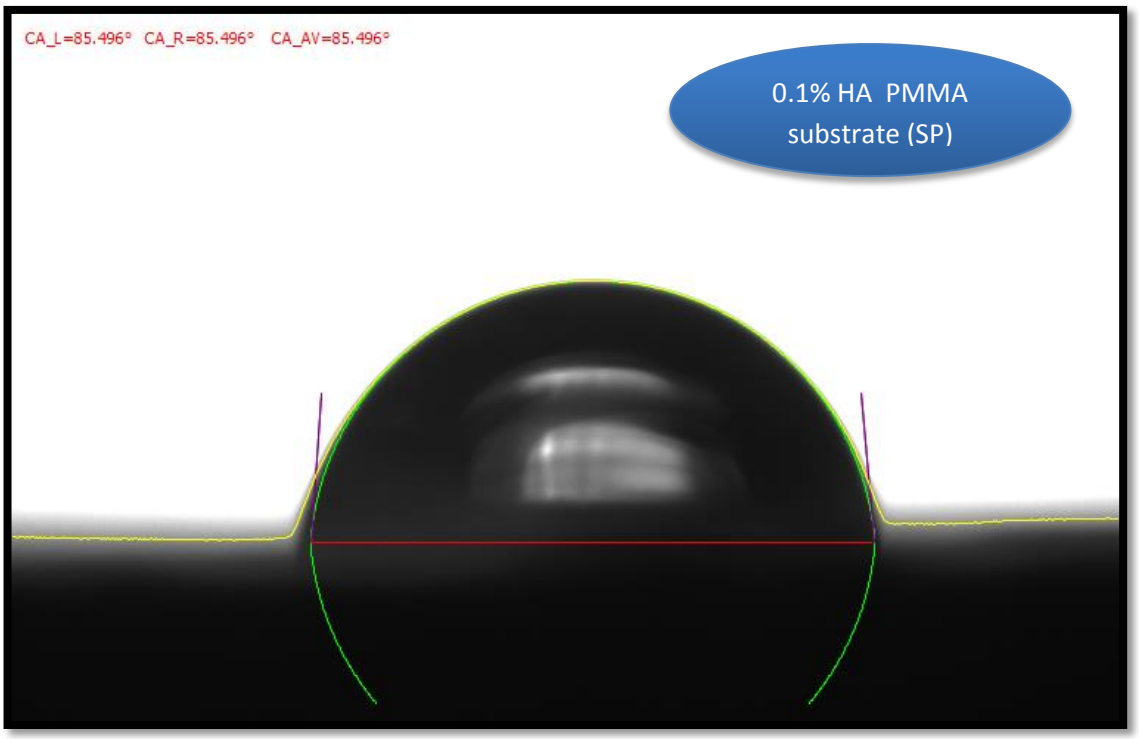


c- Contact angle results for coat PCL 0.5 Ti substrate (SP).

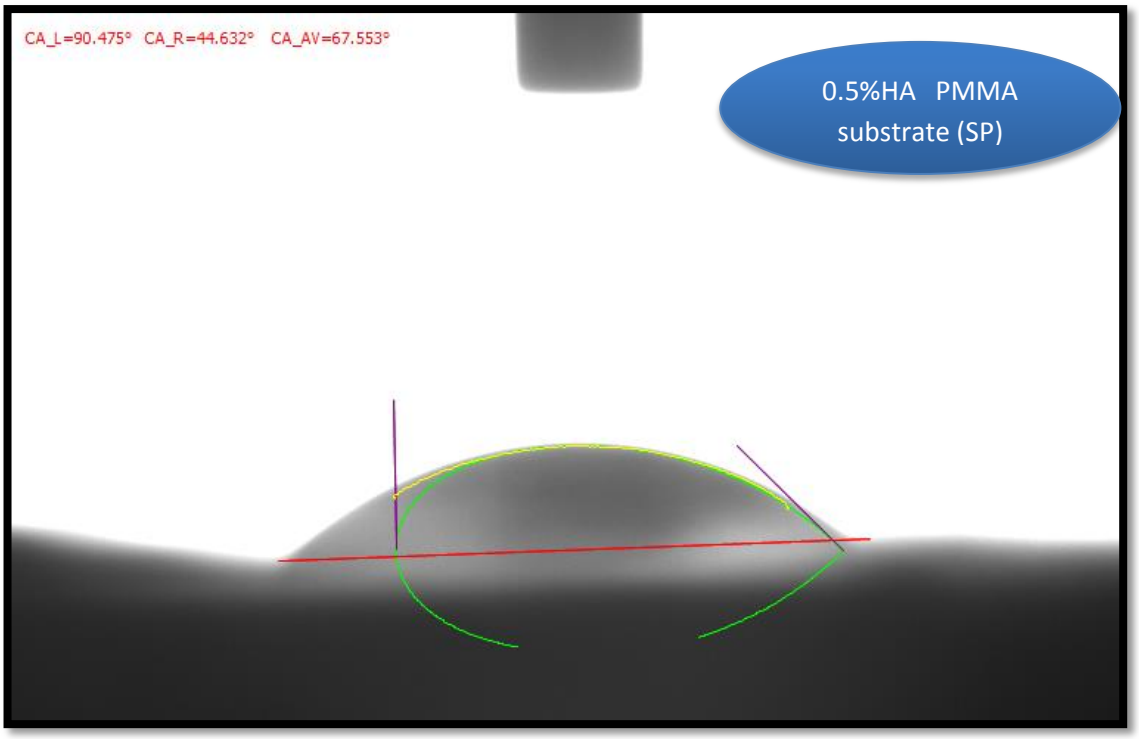
d- Contact angle results for PCL 1 Ti substrate (SP).



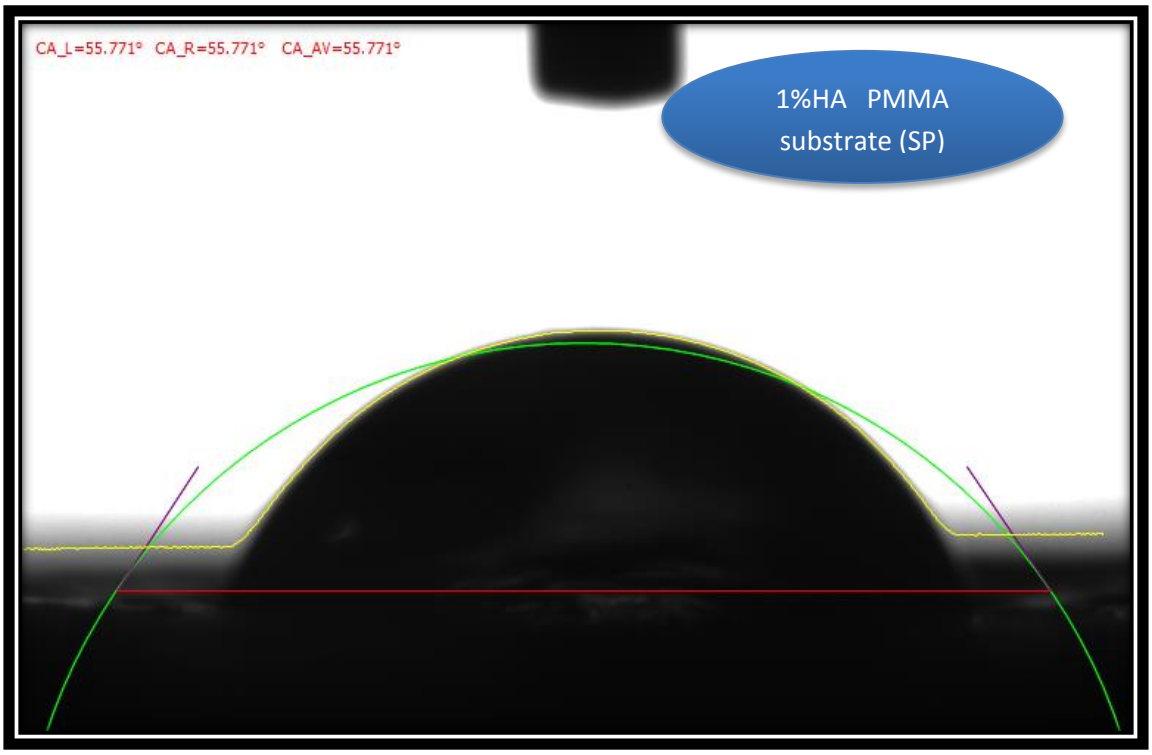
e- Contact angle results for pure PCL PMMA substrate (SP).



f- Contact angle results for coat PCL 0.1 PMMA substrate (SP).



g- Contact angle results for coat PCL 0.5 PMMA substrate (SP).



h- Contact angle results for coat PCL 1 PMMA substrate (SP).

الخلاصة

المشاكل الأكثر شيوعًا في زراعة الأسنان هي تشقق الأسنان ، كسر الأسنان ، أمراض اللثة ، عدوى الجذور ، تسوس الأسنان وتشكيل الأغشية الحيوية. للتغلب على ذلك ، فإن الإجراء المقترح لحل هذه المشكلة هو اختيار مادة أساس ذات خواص ميكانيكية جيدة واستقرار حراري عالي ومقاومة للتآكل كذلك يجب أن يؤخذ بنظر الاعتبار ان يكون سطح هذه المادة متعادل بكتيرياً. التيتانيوم والبولي (ميثيل ميثاكريلات) يستعمل لهذا الغرض بسبب خصائصها الفريدة وكذلك يجب ان تطلى بطلاء بوليمري حيوي للحصول على سطح مضاد للبكتريا

في هذه الدراسة ، تم استخدام نوعين من المادة الاساس ، التيتانيوم النقي التجاري (Ti) والبولي (ميثيل ميثاكريلات) (PMMA) كغرسات أسنان ومطلية بواسطة الشيتوزان النقي وبولي كابرولاكتين (PCL) ممزوجًا بنسب وزنية مختلفة من النانو هيدروكسي اباتايت (٠.١ ، ٠.٥ ، ١)غم بواسطة خلاط الموجات فوق الصوتية لتعزيز قوة اللصق بطريقتين من تقنيات الطلاء:

١- الطلاء بالطبقات المتعددة (LBL) ٢- الطلاء بالدوران (SP).

تمت دراسة العديد من الخصائص في هذا البحث ، مثل الخصائص الحرارية والميكانيكية والبيولوجية.

تم اجراء فحص مطياف الاشعة تحت الحمراء للطلاء للتعرف على الاواصر الموجودة في المادة والتفاعلات الكيميائية الحاصلة بعد اضافة المواد النانوية.

تمت دراسة قابلية البلل على سطح المادة الاساس باستخدام اختبار زاوية التلامس حيث كانت زاوية التلامس قبل تطبيق الطلاء للتيتانيوم 82.45° والبولي (ميثيل ميثاكريلات) 101.281° أقل مما تم الحصول عليه من الطلاء,35.871°، 55.7° .

تمت دراسة النشاط البكتيري لكل المواد الداخلة بالطلاء باستخدام طريقة انتشار البكتريا حيث يتم اخذ طبقين من المواد ويتم زراعة نمطين من البكتريا هما البكتريا سالبة الغرام والبكتريا موجبة الغرام وأظهرت النتائج أن (PCL، Chitosan) له نشاط بكتيري ممتاز كمنطقة تثبيط لكل من البكتريا موجبة الجرام والبكتيريا سالبة الجرام حيث وصل قطر التثبيط ٢٠ ملم.

تم أيضًا دراسة نتائج اختبار قوة اللصق ، حيث اظهرت النتئج ان قوة اللصق تزداد مع زيادة النسبة الوزنية المضافة من nHA لتصل إلى 14%.

تمت دراسة اختبار التآكل للطلاء وأظهرت النتائج أن مقاومة التآكل تزداد عندما تكون المادة الاساس من التيتانيوم. حيث قل تيار التآكل من 1.895e-4 الى 4.02e-7.

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كلية هندسة المواد
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تحضير وتقييم الطلاءات البوليمرية لتطبيقات طب الاسنان

رسالة مقدمة إلى

عمادة كلية هندسة المواد / جامعة بابل
وهي جزء من متطلبات نيل درجة الماجستير في
هندسة المواد / البوليمر

من قبل
حسام محمدعلي حسين

(بكالوريوس هندسة مواد ٢٠١٣)
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١٤٤٤ هـ ٢٠٢٢ م