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Theoretical and Experimental Study of the Physical Properties of Nanocomposites Used in the Synthesis of Dental Fillings

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الخلاصة

من الناحية النظرية ، تتناول الأطروحة الحالية الهياكل الإلكترونية للمركبات النانوية الجديدة المقترحة (PMMA) و (PMMA–ZnO–TiO$_2$) و (PMMA–ZnO–MgO) من خلال تطبيق نظرية دالة الكثافة. أجري التحسين الهندسي للمركبات النانوية واجراء حسابات الخصائص الإلكترونية والطيفية بتطبيق نظرية دالة الكثافة في برنامج (Gaussian 09). تم أيضًا حساب حالات الانتقال وأطياف الأشعة فوق البنفسجية المرئية للهياكل المدروسة. يتوافق التحسين الهندسي الذي تم الحصول عليه لـ (polymethyl methacrylate) النقي مع القيم العملية وفقًا للمعاملات الهندسية الناتجة عن الاسترخاء. بالنسبة للحشوات ، لم يتم الحصول على بيانات سابقة ، وبالتالي فإن الدراسة الحالية زودتنا ببيانات جديدة في هذا المجال. حيث ان الطاقة الإجمالية لاتعتمد على موقع الجسيمات النانوية في المركبات النانوية ، ولكن فقط على عدد الإلكترونات في كل مركب نانوي. أظهرت النتائج التي تم التوصل اليها أن الحشوة المحتوية على الاكاسيد النانوية (PMMA–ZnO–TiO$_2$) تحوي فجوة طاقة منخفضة. يرجع التغيير في فجوة الطاقة في الهياكل إلى التغيرات في كل من طاقات HOMO و LUMO ، حيث تشكلت المدارات الجزيئية وفقًا للتركيبة الخطية للمدارات الذرية لـ LCAOs. كما أوضحت النتائج ، إن الالفة الالكترونية والجهد الايوني والكهروسالبية لجميع المركبات النانوية أكبر من تلك الموجودة في البولي ميثيل ميثاكريلات النقي ، بينما تقل الصلابة وتزداد المرونه الالكترونية مع إضافة الجسيمات النانوية إلى البوليمر ، علاوة على تكوين مستويات الطاقة لكل منها يعتمد الهيكل على الجسيمات النانوية المضافة إلى البوليمر. بشكل عام ، تشير النتائج التي تم الحصول عليها في هذه الدراسة إلى إنشاء هياكل جديدة لها خصائص إلكترونية جديدة مختلفة.

حيث تمتاز الحشوة المتكونه من ($PMMA-ZnO-TiO_2$) بامتصاص عالي في منطقة الأشعة فوق البنفسجية.

عمليًا ، تم تحضير حشوات نانوية ($PMMA-ZnO-TiO_2$) و ($PMMA-ZnO-MgO$) بطريقة الصب بالمحلول، حيث تمت إضافة المواد النانوية بتركيزات($0, 2.5, 5, 7.5$) ٪ إلى البوليمر النانوي. تمت دراسة تأثير تراكيز الجسيمات النانوية على الخواص التركيبية والميكانيكية للحشوات النانوية. أظهرت النتائج زيادة في خشونة السطح المحتوي على المواد النانوية ، حيث أن الحشوة ($PMMA-ZnO-TiO_2$) لها خشونة أعلى وأكثر مقاومة للانضغاط والصلابة. كما تم دراسة تأثير الحشوات على البكتيريا وعملها كمضادات للبكتيريا موجبة الجرام ($Streptococcus$).تم تصنيع بنية جديدة من المركبات النانوية لوصفها بأنها مضادة لنمو المكورات العقدية الطافرة المعزولة من فم الإنسان ومقاومة المضادات الحيوية. شملت هذه الدراسة المقطعية (60) مريضاً تتراوح أعمارهم بين ثلاثة عشر إلى خمسة وستين عاماً. تم الحصول على هذه العينات من مرضى الأسنان المصابين بالعدوى وتم زراعتها في أطباق تحتوي على مضادات حيوية أموكسيسيلين، وكليندامايسين، وموكسيفلوكساسين (بتركيزات 16، 32 أو 64 ميكروغرام/مل). تم إجراء اختبار الحساسية المضادة للميكروبات لمركبي ($PMMA-ZnO-TiO_2$) و($PMMA-ZnO-MgO$) حيث تم تحديد العينة المختبرة من المركبات النانوية باستخدام طريقة الانتشار بالقرص . تم إجراء أنشطة مضادة للجراثيم مع الكائنات الحية إيجابية الجرام (المكورات العقدية الطافرة) المستزرعة في وسط مولر هينتون.أظهرت النتائج أن منطقة التثبيط تزداد مع زيادة تركيز الجسيمات النانوية.

Summary

Theoretically, the present thesis deals with the electronic structures of the proposed nanocomposites (PMMA-ZnO-TiO$_2$) and (PMMA-ZnO-MgO) nanocomposites by applying density function theory. Geometric optimization of the nanocomposites and calculations of the electronic and spectroscopic properties were carried out by applying density function theory in the (Gaussian 09) program. The transition states and UV-visible spectra of the studied structures were also calculated. The geometric improvement obtained for pure polymethyl methacrylate agrees with practical values according to the geometric coefficients resulting from relaxation. For fillers, no previous data were obtained, so the current study has provided us with new data in this field.

The total energy does not depend on the location of the nanoparticles in the nanocomposites, but only on the number of electrons in each nanocomposite. The results obtained we shewen that the nanofiller containing oxides (PMMA-ZnO-TiO$_2$) has a low energy gap. The change in the energy gap of the structures is due to the changes in both HOMO and LUMO energies, where the molecular orbitals were formed according to the linear combination of the atomic orbitals of LCAOs.

As the results showed, the electronegativity, Ionic potential and Electronegativity of all nanocomposites are greater than those of polymethylmethacrylate, while the Hardness decreases and Electronic Flexibility increases with addition of nanoparticles to the polymer, in addition to the formation of the energy levels of each structure depends on the nanoparticles added to the polymer. Overall, the results obtained in this study indicate the creation of new structures with different new

electronic properties.The filling consisting of (PMMA-ZnO-TiO$_2$) is characterized by high absorption in the ultraviolet region.

Practically, nanofillers (PMMA-ZnO-TiO$_2$) and (PMMA-ZnO-MgO) were prepared by solution casting method, where nanomaterials were added at concentrations of (0, 2.5, 5, 7.5)% to the nanopolymer. The effect of nanoparticle concentrations on the structural and mechanical properties of nanofillers was studied. The results showed an increase in the surface roughness containing the nanomaterials, as the filler (PMMA-ZnO-TiO2) has a higher roughness and is more resistant to compression and hardness. The effect of the fillings on bacteria and their action as antibiotics against Gram-positive bacteria (Streptococcus) was also studied.

A new structure of nanocomposites was manufactured to describe it as an anti-growth of Streptococcus mutans isolated from the human mouth and resistance to antibiotics. This cross-sectional study included (60) patients aged between thirteen and sixty-five years. These samples were obtained from dental patients with infections and cultured in plates containing the antibiotics amoxicillin, clindamycin, and moxifloxacin (at concentrations of 16, 32, or 64 μg/ml). An antimicrobial susceptibility test was conducted for the two compounds (PMMA-ZnO-TiO$_2$) and (PMMA-ZnO-MgO), where the tested sample of nanocomposites was determined using the disk diffusion method. Antibacterial activities were performed with Gram-positive organisms (Streptococcus mutans) cultured in Mueller-Hinton medium. The results showed that the zone of inhibition increases with increasing nanoparticle concentration.

Contents

List of Symbols

Symbol	Meaning
PMMA	Poly(methyl methacrylate)
ZnO	Zinc Oxide
TiO$_2$	Titanium Dioxide
MgO	Magnesium Oxide
DFT	Density Functional Theory
ρ(r)	Electron Density
G09	Gaussian 09
STO'S	Slater Type Orbitals
GTO	Gaussian Type Orbitals
CGF	Contracted Gaussian Function
Ψ	Wave Function
E	Total Energy of The system
C$_{\mu i}$	The Molecular Orbital Expansion Coefficients
N	Principal Quantum Number
X^{STO}	Slater Wave Function
N	Normalization Factor
Y_{im}	Angular Function
ξ	Orbital Exponent
X^{GTO}	Gaussian Wave Function
VDZ	Valence Double-Zeta
VTZ	Valence Triple –Zeta
E$_{HOMO}$	Energy of The Highest Occupied Molecular Orbital
E$_{LUMO}$	Energy of The Lowest Unoccupied Molecular Orbital
E$_g$	Energy Gap
S	Chemical Softness
χ	Electronegativity
I$_E$	Ionization Energy
E$_A$	Electron Affinity
IP	Ionization Potential

HF	Hartree Fock
E_T	Total Energy
μ	Chemical Hardness
S	Chemical Softness
ω	Electrophilicity Index
χ	Electronegativity
UV-Vis	Ultraviolet-Visible
MOs	Molecular Orbitals
SCF	Self-Consistent Field
Mpa	Mega Pascal
LCAOs-MO	Linear Combination of Atomic Orbitals- Molecular Orbital
AFM	Atomic Force Microscope
FESEM	Field Emission Scanning Electron Microscopy
RMS	Root Mean Square
Σ	Compressive Strength
BHN	Brinell Hardness Number
KHN	Knob Hardness Number

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Chapter One

Introduction

and

Literature Review

1.1 Introduction

The preservation of oral tissues is the main goal in dentistry and health care, the progress in the field of science and nanotechnology paved the way to bring this goal closer, as the applications of nanotechnology in dentistry led to the development of nano-dentalism, an innovative branch of science. Many studies have led to wide applications of medical nano-systems in many nano-dental fields such as prevention, diagnosis, treatment, restoration and tissue regeneration to cover all dental specialties such as dental restoration, prosthodontics, orthodontics implants and regenerative dentistry [1]. These dental nanosystems are nano-structured materials that form new innovative products and are among the important materials used in the manufacture and restoration of teeth. There is a lot of research concerned with the preparation of restorative materials dental. These materials have important physical and mechanical properties that make them resistant materials that withstand different ambient conditions inside the oral environment such as drinking hot, cold, solid and liquid drinks as well as other influences such as (pH) and the effect of bacteria [2].

Many researches had been conducted for the purpose of developing the work of restoration materials (dental restoration composites) and improving their work from a medical point of view [3,4]. The first restoration compounds used were called (Macro filled) or (Traditional), which consisted of high percentages of quartz fillers, and these fillers are widely available and have an appearance that matches the type of polymer used [5] . Most of the common and available types of fillers are glass fillers, but there was a need to improve the overlays and search for ways to develop them in order to increase their efficiency to withstand the surrounding conditions within the oral environment [6].

Developing nano composites could be a solution to adjust the properties of individual nanomaterial's appropriately like, optical, electrical, thermal, mechanical properties[6].In particular, nanoparticles represent as advanced technological materials because of their attractive electrical/electronic properties and high refractive index[7]. Nano composites of organic and inorganic materials can possess advantages of both organic polymers (dielectric, ductility ,flexibility) and inorganic materials (high thermal stability, rigidity, strength, high refractive index, hardness), thus have many applications[8].

1.2 Oral Environment

It is important to consider the complex oral environment in order to understand the interactions between fillings and oral tissues necessary for successful intraoral alignments. The oral environment plays a vital role in many functions within the mouth, such as keeping it moist with saliva, which helps in swallowing, tasting, and touching food. The oral environment differs from other parts of the body in structural and functional aspects and may produce different types of biological response to life materials. For example, it can cause corrosion of substances within the oral cavity or permeate the teeth, or alternatively the oral environment may react with the substances to release cytotoxic or harmful components

In addition, there are factors that affect the fillings inside the mouth:

1 -Changes in temperature in the mouth (hot and cold food) leading to contraction

2 -A large number of microorganisms (bacteria) that can produce acids and other chemicals that affect fillings.

3 -Changes in tooth enamel as a result of some pathological conditions such as bruxism, bulimia nervosa (loss of tooth enamel from inside the upper front teeth) .

4 -The materials are subjected to high and harsh chewing forces

5 -Decomposition of materials and eaten by products and food residues in the mouth .

6 -Interaction with various food chemicals such as nicotine, caffeine, alcohol and medications that can also affect the longevity of substances and the effectiveness of enzymes in saliva.

Anatomically, there are two basic groups of tissues in the oral cavity: soft tissues, and hard tissues where soft tissues represent muscles and tendons, and connective tissues include teeth and bones [7].

1.3 The Internal Structure of Tooth

Tooth, plural teeth, any of the hard, resistant structures occurring on the jaws and in . Teeth are used for catching and masticating food, for defense, and for other specialized purposes. The tooth consists of the following parts[9]:

- Enamel: The hardest, white outer part of the tooth. Enamel is mostly made of calcium phosphate, a rock-hard mineral.
- Dentin: A layer underlying the enamel. It is a hard tissue that contains microscopic tubes. When the enamel is damaged, heat or cold can enter the tooth through these paths and cause sensitivity or pain.
- Pulp: The softer, living inner structure of teeth. Blood vessels and nerves run through the pulp of the teeth.
- Cementum: A layer of connective tissue that binds the roots of the teeth firmly to the gums and jawbone.

• Periodontal ligament: Tissue that helps hold the teeth tightly against the jaw[8].
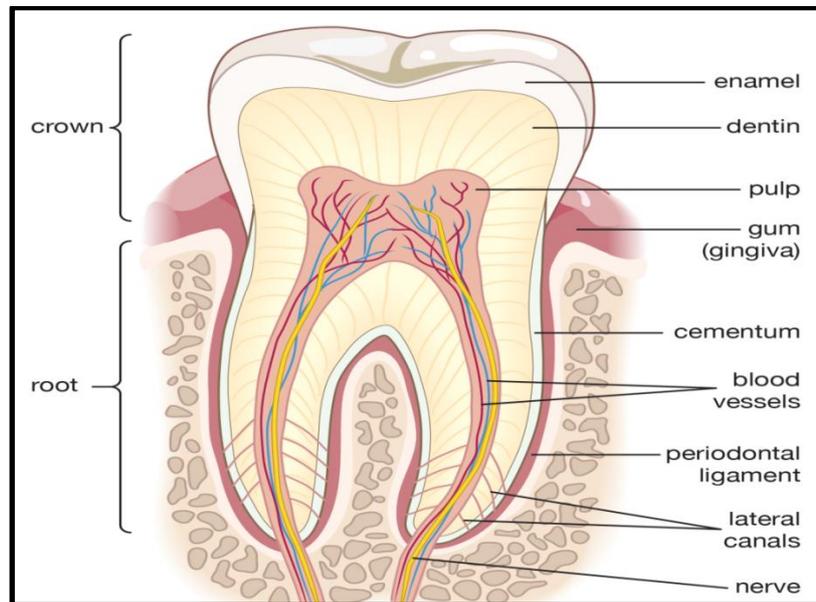
Figure (1.1): Internal structure of the tooth[8].

1.4 Tooth Decay

Caries, or tooth decay, is the most common disease of the teeth among humans. Tooth decay originates in the buildup of a yellowish film called plaque on teeth, which tends to harbour bacteria. The bacteria that live on plaque ferment the sugar and starchy-food debris found there into acids that destroy the tooth's enamel and dentine by removing the calcium and other minerals from them. Caries usually commences on surface enamel, especially in pits and fissures and between adjacent teeth. From the enamel the process of decay spreads to the underlying dentine, and may finally involve the tooth pulp. Caries is treated by removing decayed dental tissue and replacing it with filling substances[9].
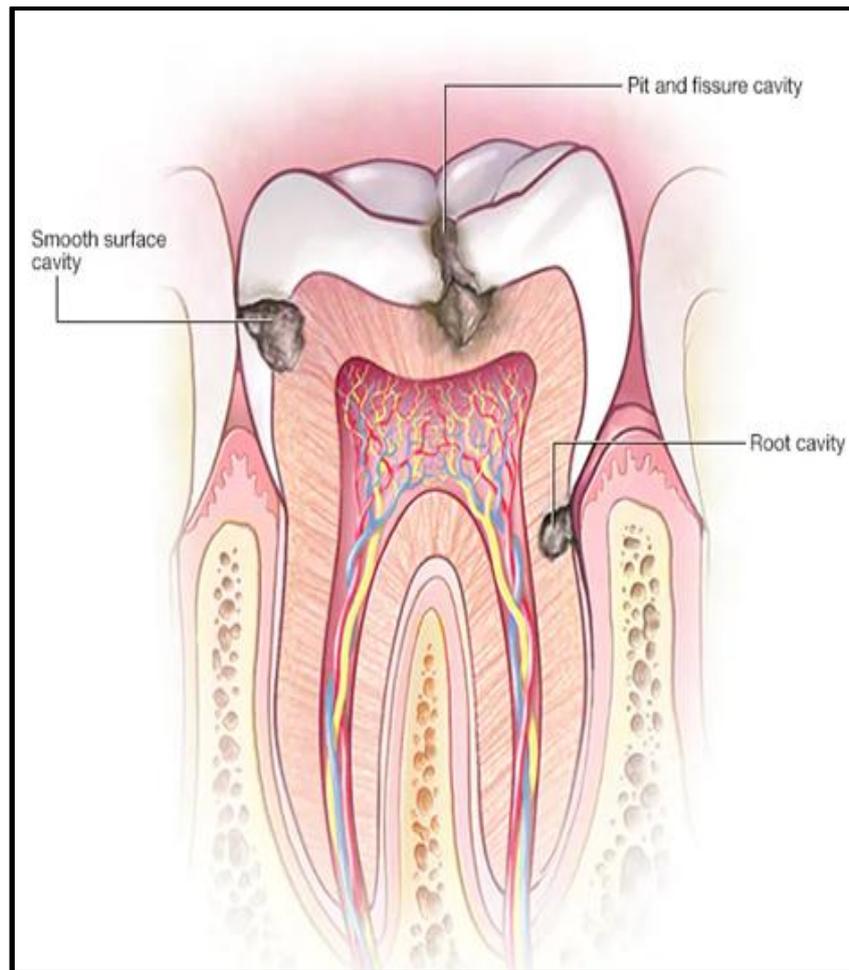
Figure (1.2): Tooth decay[9].

1.5 Classification of Dental Composites

The dental composites are classified according to its constituents. Lutz classified dental composites depending on the volume of inorganic fillers[10,11]. Dental composites are classified into:

1. Macro filler: in this type, the filler used are quartz and barium glass with particles volume of (10-40) μm.

2. Micro filler: this type of fillers was produced in 1970. It contains on silica with volume of (0.04) μm; this kind of filler make the composite surface smooth but doesn't give good physical properties, in comparing with the first type[12].

3. Hybrid: The hybrid type is being used until this moment; it contains the two kinds, macro and micro, where it contains fillers with volume of (15-20) µm, and the others are small size, from silica, in volume of (0.01- 0.05) µm[13].

4.Nanoparticles fillers: nanoparticles fillers were used recently to solve drawbacks that faced light-cured filling; the size of these nanoparticles ranges from (5 ~ 100) nm. The most common nanoparticles fillers that were used are SiO_2, Al_2O_3, TiO_2, ZnO, CaO, CaP, ZnP, and others[14].

1.6 Nanocomposites

Nanocomposites is a multiphase solid material where one of the phases has one, two or three dimensions about (100) nanometers (nm), or structures having nanoscale repeat distances between the different phases that make up the material[15]. The idea behind nanocomposites is to use building blocks with dimensions in nanometer range to design and create new materials with unprecedented flexibility and improvement in their physical properties [16].

Polymeric nanocomposites consisting of inorganic nanoparticles and organic polymers represent a class of materials that have motivated considerable interest in recent years[17]. The nanocomposites applications are quite promising in the fields of microelectronic packaging, medicine, automobiles, optical integrated circuits, drug delivery, injection molded products, sensors, membranes, aerospace, packaging materials, coatings, fire-retardants, adhesives and consumer goods…etc. These advanced nanocomposites have many advantages such as low cost production and the possibility of device fabrication on large scale and flexible substrates[18].

Developing nanocomposites could be a solution to adjust the properties of individual nanomaterial appropriately like, optical, electrical, thermal and mechanical properties. In particular, nanoparticles represent as advanced technological materials because of their attractive electrical / electronic properties [19].

1.7 Nanomedicine

Nanomedicine is the medical application of nanotechnology, and it is a relatively new field of science and technology for treatment, monitoring, control of diseases and diagnosis[20]. Nanomedicine ranges from the medical applications of nanomaterials and biological devices, to nanoelectronic biosensors[21].

Nanomaterials can be useful for both in vivo and in vitro biomedical research and applications, the integration of nanomaterials with biology has led to the development of diagnostic devices, analytical tools, physical therapy applications, and drug delivery. It is worth noting that the most important properties found in medical materials, especially in the mouth, are: 1. Nontoxicity, 2. Biocompatible, 3. Absence of foreign body reaction 4 . Mechanical properties and performance[22].

1.8 Base material

1.8.1 Poly(methyl methacrylate)(PMMA)

Poly(methyl methacrylate) (PMMA)($C_5H_8O_2$) is an important type of polymer among thermoplastics. The trade names of poly methyl methacrylate are PMMA, Plexiglas, Lucite; the family class is vinylidene polymers (acrylics)[24]. The chemical formula of PMMA structure is: [CH2-C(CH_3)(COOCH_3)].It is a synthetic polymer made from methyl methacrylate monomer. PMMA was discovered in the early 1930s by British chemists .This type of polymers has a special optically properties, where its transparent about 92% [23].

PMMA is a colorless polymer having glass transition temperature in the range of (100-130)°C. It may possess density of(1.20) g/cm^3 at room temperature. Also, PMMA has optical properties with a refractive index of 1.490 and a good degree of compatibility with human tissue[24]. In the field of mechanical strength, PMMA has a high Young's Modulus and a low elongation at breakage. Therefore, it does not shatter upon rupture, and happens to be one of the hardest thermoplastics with high scratch resistance[24]. This polymer has a reasonable resistance to chemicals ,being unaffected by the aqueous solution of most laboratory chemicals .However, it has a low resistance to chlorinated and aromatic hydrocarbons, esters, or ketones[25].

PMMA used in several applications, it can used instead of glass as well as can be used in component deep UV and as a resistance free electron beam or ion-beam resists in microelectronics chips manufacturing . PMMA has been prepared using different polymerization techniques chemical equation illustration produced Poly methyl methacrylate by free radical polymerization of methyl methacrylate in mass or suspension polymerization [25]:

PMMA is an amorphous polymer with good chemical, weather, scratch, and corrosion resistance. It is lightweight, shatter-resistant, and possess favorable processing conditions. PMMA has been employed in a range of applications such as coatings, sealers and optical fibers. Still, neat PMMA is deficient in sufficiently high thermal and mechanical stability for several technical applications. PMMA is used in the manufacture of rigid intraocular lenses which are implanted in the eye when the original lens has been removed in the treatment of cataracts[25].
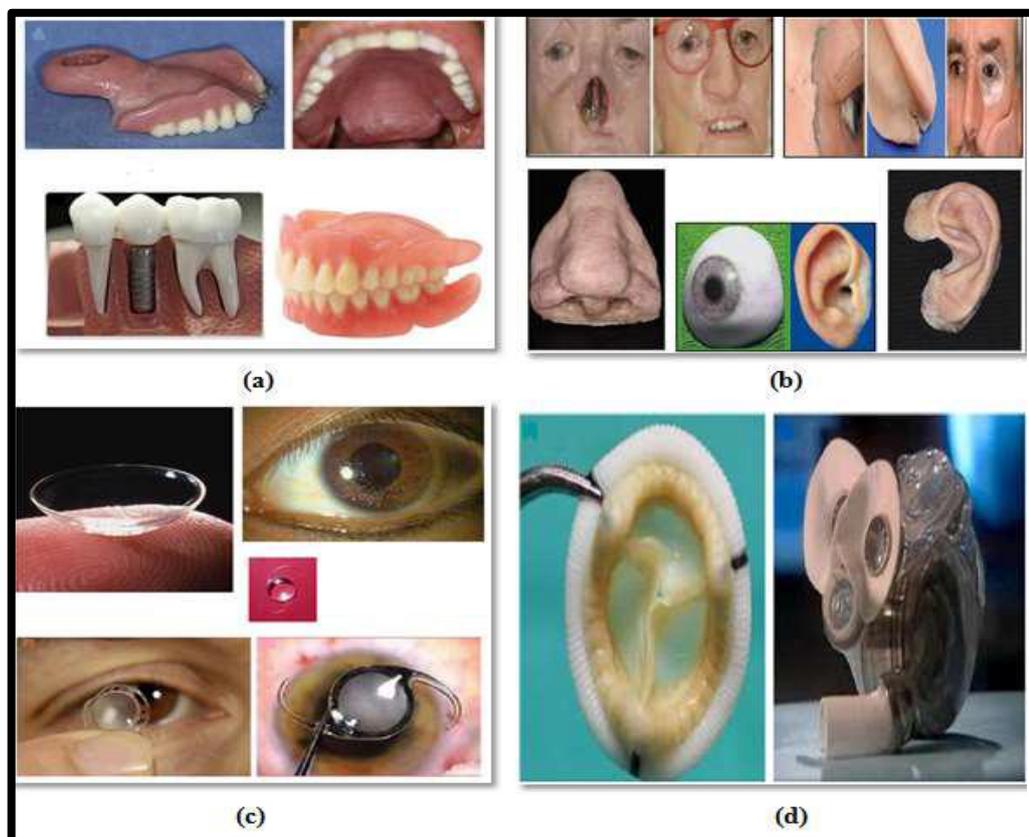
Figure (1.3): Polymer matrix composites: (a) For dental applications .(b) For maxillofacial prostheses . (c) For artificial cornea hip and intraocular lenses applications; (d) For cardiovascular (heart valve and artificial heart) applications [25].

1.9 The Fillings

They are relatively inert materials that are added to some polymers to improve hardness, friction resistance, shock resistance, solvent resistance and to change electrical properties, and some are added to polymers to reduce cost [26].

1.9.1 Zinc Oxide (ZnO)

Its white color is an oxide that does not dissolve in water, has a density (5.606)g/cm^3. Zinc oxide (ZnO) is one of the most important semiconductor materials is characterized by a wide band-gap (3.3 eV) . It is also suitable for human tissue .Zinc oxide (ZnO) thin films had been investigated in recent years as transparent conducting oxide because of their good electrical and optical properties in combination with a high electron mobility, good transparency, wide and direct band gap at room temperature, easiness of growing it in the nanostructure form by many different methods making ZnO suitable for a wide range of applications [26], including light-emitting devices, varistors , solar cells and gas sensors [27]. Moreover, ZnO is a promising material for short wavelength optoelectronic devices, especially for ultraviolet (UV) [28].

Apart from the technological significance of ZnO nanostructures, their nano-dimensional structure with diameters in the range of ten to hundreds of nanometers makes them quite interesting from a scientific point of view, ZnO have broad range of applications, is already widely used in our society, and indeed it is a key element in many industrial manufacturing processes including paints, pharmaceuticals, plastics, batteries, electrical good isulator, transparent, biocompatible with bio tissues, good photo catalytic agent, new properties in structure, electricity, electronics, photo electronics [29].

At the ratio 10%, they are assumed to be as antimicrobial agent . Cosmetics, toothpaste, sunscreens, textiles, building materials, and fillings in teeth and bones, civil materials and Catalytic in chemical reactions[30] .
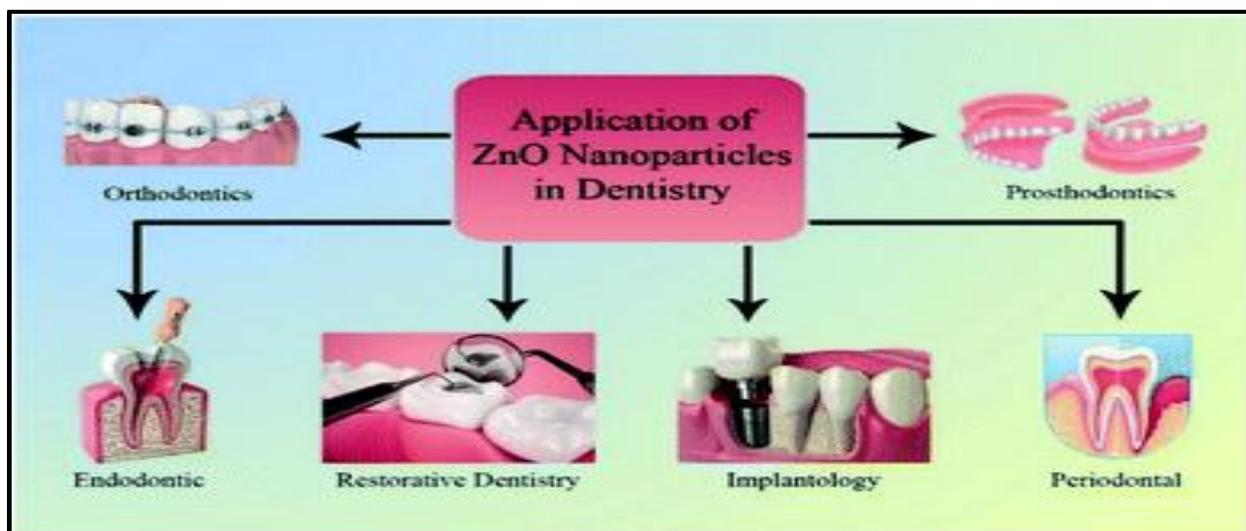
Figure (1.4): Applications of Zinc Oxide ZnO in dentistry [30].

1.9.2 Titanium Dioxide (TiO$_2$)

Its white color is an oxide that does not dissolve in water and dielectric material , has a density (4.23)g/cm^3 with an energy gap (3.05)eV, it is one of the oxides that is resistant to corrosion ,the high strength, low weight, and corrosion resistance of Titanium and its alloys have resulted in a wide variety of successful applications that require high levels of reliable performance in surgical and medical procedures, as well as in the aerospace, automotive, plant chemicals, oil and gas extraction. it also has the ability to stick to the bone, The hardness of titanium and its resistance to corrosion led to its widespread use in the world and in the medical field in particular, where it was used for the manufacture of prosthetic limbs, jaw surgery, dental implants and surgical tools due to its light weight and durability. Biocompatibility with the human organs, and very special properties in cost [31].

Titanium dioxide is used to give properties such as whiteness, brightness and opacity to the product. Titanium dioxide is a mineral used in cosmetics as a thickener, bleach and sunscreen. They have good optical and chemical properties. antibacterial and anti-microorganisms. delivery drugs, fillers, catalytic and photocatalytic materials [32], industrial and medical applications. as photocatalytic in antiseptic and anti-microbial materials, and in producing inks, coatings and cosmetic creams [33].

Figure (1.5): Applications of Titanium Dioxide (TiO₂) in dentistry [33].

1.9.3 Magnesium Oxide (MgO)

It is a white oxide that does not dissolve in water. It has a density (3.58) g/cm^3 and an energy gap (7.8) eV that is characterized by its resistance to cracking and corrosion and is widely used in the medical field and the pharmaceutical industry. It is considered one of the oxides of antibacterial and anti-inflammatory, Magnesium Oxide (MgO) is a white hygroscopic solid mineral that occurs naturally .Magnesium oxide was historically known as magnesia alba (literally, the white mineral from Magnesia), to differentiate it from magnesia negra, a black mineral

containing what is now known as manganese[34] .While MgO is prized as a refractory material, i.e. a solid that is physically and chemically stable at high temperatures . Fireproofing It is a principal fireproofing ingredient in construction materials. As a construction material, Magnesium is a necessary and essential mineral for the proper functioning of cells in the body. It is the fourth most abundant mineral in the body, and the second most abundant in the cells of the body. This mineral is important for the proper functioning of the various systems in the body such as the cardiovascular system, immune system, nervous system, bones and muscles.

About 50% of the magnesium in the body is found in the bone. Excess is present in the cells of body tissues and organs[34].

Magnesium helps maintain the proper functioning of muscles and nerves, maintain a steady heart rate, support the proper functioning of the immune system and build bones. It also helps in controlling blood sugar levels and maintaining healthy blood pressure. Magnesium is a good measure for preventing headaches and migraines, and improving breathing, as a result of relaxing the airways, meaning that the body's need for magnesium is very high, as the body needs three grams of it. Daily. Magnesium hydroxide $Mg(OH)_2$ which is an alkaline substance with low solubility in water and is used in the treatment of drinking water and waste water[34].

Magnesium deficiency in the body is associated with heart rate disturbances, which predict death, as a result of myocardial obstruction. , It is also used in the medical field for its biological compatibility with the tissues of the human body[34].

Figure (1.6): Applications of Magnesium Oxide (MgO)in dentistry [34].

1.10 Literature Survey

In (2008) Yang Xia *et al*., [35] used Titanium dioxide (TiO$_2$)that was treated with organochloromethyl to improve the mechanical properties of dental resin-based compounds (PMMA). FTIR, TEM were used to analyze the nanoparticles. Five groups of composite resin samples were prepared either the nanoparticles that were treated with organochloromethyl, and they include the addition of 0.5%, 1% by weight. The mechanical properties (hardness and bending strength) were measured. The results showed that the treated samples of resin (PMMA) including Nano-TiO$_2$ had significantly better mechanical properties than samples that were not treated with organochloromethyl. The improvement of adding modified Nano-TiO$_2$ particles by (1%) was better than the weight ratio of 0.5% .

In (2012) L. N. Ismail *et al.*,[36] studied the influence of doping concentration (TiO$_2$) on dielectric, optical and morphological properties of PMMA thin films. (PMMA)thin films were deposited by sol-gel spin coating method . Toluene was used as the solvent to dissolve the PMMA powder. PMMA concentration was varied from (30 ~ 120) mg. The morphologies of the samples show that all samples are uniform and the surface roughness increased as the concentration increased. Where it showed a clear improvement in the surface and increased roughness by increasing the percentage of added oxide**.**

In(2015) Sama A. Alwan *et al*., [37] studied the effect of addition of 3% wt of treated Titanium oxide Nano filler on some physical and mechanical properties of heat cured acrylic denture base material. 100 specimens were constructed, 50 specimens were prepared from heat cure (PMMA) without additives and 50 specimens were prepared from heat cure (PMMA) with the addition of (TiO$_2$) Nano fillers. Each group was

divided into(5) sub-groups according to the test performed which was mixed by probe ultrasonication machine .A highly significant increase in impact strength and transverse strength was observed with the addition of (TiO_2) Nano particles to (PMMA). A significant increase in surface hardness and in surface roughness. The water sorption and solubility were significantly decreased . The addition of (TiO_2) Nano particles to heat cure acrylic resin improve the impact strength, transverse strength and surface hardness of heat cure acrylic resin at the same time this addition decrease water sorption and solubility. On the other hand there was an increase in surface roughness with the addition of 3% wt .(TiO_2) Nano particles.

In(2016)**R. Balena et *al*., [38**] studied synthesized films and fibers of zinc oxid/poly mythel methacrylate nano composite to study the structural and optical properties for these composites.Where the absorbance value increased when adding (ZnO) near 370 nm the absorption was intense and broad that mean optical properties of PMMA improved due to inclusion of ZnO nano particles inside the composite.studied the structural properties before and after adding the oxide, as he found an improvement in the structural properties and an increase in the surface roughness.

In(2016) **Wan.F. Hammad** *et al.* , **[39]** studied prepare PMMA incorporated with zinc oxide as an antibacterial agent at different compositions and investigate the flexural properties of the produced PMMA/ZnOcomposites. Pure PMMA as control and zinc oxide manually according to the percentages specified until it has reached the homogeneous state. Flexural specimens were prepared by casting the paste in silicone mould which has been fabricated using 3D printed flexural template. The addition of   (ZnO) decreased the flexural

properties and it showed significant differences as compared to pure PMMA 5%wt (ZnO) filled PMMA showed higher flexural properties as compared to 2.5%wt (ZnO) filled PMMA. Where we notice an increase in the mechanical properties, including bending, when adding (ZnO).

In(2017) Nehal S. El.Kemary *et al.* , [40] studied Polymethyl methacrylate-zinc oxide (PMMA/ZnO) nanocomposites with different ZnO morphology . The composition, structure, and morphology of the nanocomposites were characterized by Fourier-Transform infrared spectra (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM). The effect of ZnO morphology and contents on the mechanical properties including impact, flexural, and hardness was studied. The results demonstrated that the mechanical and thermal properties of denture base materials were improved by incorporation of nano-sized (ZnO) into the polymethyl methacrylate matrix.

In (2017) A. Goyal *et al.*,[41] investigated the optical and electrical properties of (Ag-TiO$_2$-PMMA) nanocomposites films it prepared via ex situ chemical route by employing sodium borohydride (NaBH$_4$) as a reducing agent. The alteration in optical and structural performances of PMMA was established by UV-visible spectroscopy, SEM and Raman spectroscopy. It is observed that the concentration of Ag nanoparticles has strongly influenced the optical, structural and electrical properties of PMMA matrix. The increase in the electrical conductivity with increase in the concentration of (TiO$_2$) nanoparticles in PMMA matrix can be correlated to the formation of the localized energy states within HOMO-LUMO gap of PMMA matrix Where we notice an improvement in the electrical and optical properties and the composition when adding (TiO$_2$) and adding (Ag).

In(2019) Fadhi K. Farhan *et al*. **, [42]** investigated the light filling with Titanium Oxide(1-0.5)wt% was that formed as an anti-corrosion and antibacterial. The white acrylic powder was used with its solvent after mixing it with different percentages of biologically active Titanium Oxide using the liquid mixing method and the ultrasound technique to obtain a homogeneous mixture free of aggregates and then molded into special molds for the required examination. The hardness device was examined along with the test of dry sliding wear , as well as the examination of the samples to resist the bacteria of tooth decay. Structural tests were performed on X-ray diffraction techniques, scanning electron microscopy techniques, and infrared technique.Where the presence of Titanium Oxide showed a significant improvement in the antibacterial, corrosion resistance, and its resistance to bacteria that cause tooth decay, and an improvement in the structural properties.

In(2019) Md. Alamgir *et al*., **[43]** studied the application of the in-situ synthesized nanocomposites of poly (methyl methacrylate) (PMMA) and TiO_2 for use as dental materials. (TiO_2) nanoparticles with different percentages (1wt% and 2 wt%) were blended with PMMA through a melt compounding process. The prepared nanocomposites were characterized by a micro-indentation test, scratch test, and field emission scanning electron microscopy analysis. The effects of different vol. % of (TiO_2) on the mechanical properties of the composites were studied. The evaluation of the mechanical properties of the composites revealed that the utilization of (TiO_2)as a reinforcing agent strengthened the polymer. The morphological observation demonstrated the presence of significant adhesion between (TiO_2) and the polymer matrixes with a homogeneous distribution of (TiO_2) in the polymer matrix. The proper compatibilization

between (TiO_2) and the polymer matrix enhanced the mechanical properties.

In(2019) Angham Hazim *et al*., [44] studied the geometrical parameters, electronic and optical properties of the (PMMA-ZrO2-Ag)nanostructures. The electronic properties include electrochemical hardness and electronic softness while the optical properties include absorbance, transmittance, absorption coefficient, extinction coefficient, refractive index, real and imaginary parts of dielectric constants and optical conductivity. The properties calculated by using Gaussian 0.9 program using density function theory (DFT). The results showed that the addition of Ag nanoparticles lead to decrease the chemical hardness and increase in the softness. The optical properties for (PMMA-ZrO$_2$-Ag) nanocomposites showed that the absorbance, absorption coefficient, extinction coefficient, refractive index, real and imaginary parts of dielectric constants and optical conductivity of (PMMA-Al$_2$O$_3$)nanocomposites increase while the transmittance and energy band gap decrease with increase in Ag nanoparticles concentrations.

In(2020) Rafaella D.Leão *et al*. , [45] studied systematic review to evaluate the effect of the incorporation of zirconia (ZrO2) particles on the mechanical properties of PMMA (polymethyl methacrylate), and to establish which characteristics of this material yield the best results aiming their biomedical applicability. The concentrations of zirconia ranged from (0.5% to 20%) and the particle sizes were between 15 nm and 10 μm. Thus, the addition of zirconia particles showed a positive effect on PMMA enhancing their use in the medical and dental field, especially when certain anatomical areas requires higher strength of the materials, providing longevity for the rehabilitation.Where the

mechanical properties of hardness and corrosion were studied, notice a high improvement of the properties when adding (ZrO_2).

In(2021) Ban A. Sabri *et al*. , [46] studied The incorporation of nano fibers or nanotubes and Titanium significantly improved the PMMA properties than the nanoparticle fillers. hybrid mixing materials provide superior balance and stability between the properties of the mixed fillers and produce an optimal combination in the obtained composite. Increasing the bonding strength between the added fillers and polymers is an important factor for improving the denture properties, where this could be achieved with the treatment of the filler surface by a coupling agent. Titanium-based coupling agents exhibit satisfactory interfacial bonding, enhanced homogeneous filler dispersion, and improved mechanical properties of the composites., filler incorporation, type of materials, hydrolytic stability, surface modification, processing, and curing methods influence the enhancements in mechanical, physical, thermal and biomedical properties.

In(2021) Maria F. Cascione *et al*. , [47] added two different kind of nanomaterials ,namely titanium dioxide nanoparticles (TiO_2NPs) and halloysite clay nanotubes (HNTs) at two concentrations (1% and 3%)wt in PMMA. Then, we assessed the effect of nanomaterials inclusion by the evaluation of specific physical parameters: Young's modulus, roughness, and wettability. Our experimental results showed an improvement of PMMA performance, following the addition of TiO_2NPs and HNTs, in a dose dependent manner. In particular, the presence of TiO_2NPs in the methacrylate matrix induced a greater increase in (PMMA) stiffness respect to HNTs addition. On the other hand, HNTs reduced the rate of C. albicans colonization more significantly than

(TiO$_2$NPs). The results obtained are of great interest for the improvement of PMMA physico-chemical properties, in view of its possible application in clinical dentistry.

In(2022) Kentaro Hata *et al*. , [48] studied Poly(methyl methacrylate) (PMMA) used in dental prostheses . PMMA had relatively poor mechanical properties, a novel nanoporous Silica filler was developed and introduced into PMMA to improve their mechanical properties. The filler was prepared by sintering a green body composed of silica and an organic binder, followed by grinding to a fine powder . The filler was added to PMMA. The filler was characterized by scanning electron microscopy (SEM), X-ray diffraction analysis, nitrogen sorption porosimetry, and Fourier transform infrared (FT-IR) spectroscopy. The PMMA-based resins were characterized by SEM and FT-IR, and the mechanical properties (Vickers hardness and flexural strength) and physicochemical properties (water sorption and solubility) were evaluated. The results suggested that the filler consisted of microparticles with nanopores. The filler at 23 wt % was well dispersed in PMMA matrix. The mechanical and physicochemical properties of (PMMA) improved significantly with the addition of the developed filler. Therefore, such filler-loaded PMMA are potential candidates for improving the strength and durability of polymer-based crown and denture base.

In(2023) Shivani Sat *et al*., [49] studied ,PolyMethyl-Methacrylate (PMMA) bases are the preferred option for replacing missing teeth . Though PMMA is the most preferable material for denture preparation,   , incorporation of certain nanoparticles may increase the antimicrobial potential, thermal conductivity and radiopacity of the PMMA . The available studies supported that the antimicrobial property

of PMMA can be improved by incorporation of nanoparticles such as graphene silver nanoparticles, (TiO2, ZnO, SiO2/Ag) These nanoparticles have been found to be effective against Staphylococcus aureus, Streptococcus mutans, Candida albicans, Escherichia coli.Where (TiO_2) showed a higher effective ability to penetrate the wall of bacteria and a high power to kill them**.**

In(2023) A. Nabhan *et al*. , [50] studied using hybrid filler of (Al_2O_3) and (TiO_2) NPs with various loading content to evaluate and minimize the wear rate. The tribological characteristics of the nanocomposites were evaluated by a reciprocating tribometer. And the wear resistance was assessed with 3D microscopic images and SEM. The PMMA nanocomposite samples containing (0.4%, 0.8%, 1.2%, 1.6%, and 2.0)wt% filling content of hybrid Al_2O_3 and TiO_2 NPs to compared to an unfilled sample, were fabricated. The XRD, density, modulus of elasticity, compressive yield strength, and fracture toughness were performed experimentally. Results showed that the incorporation of hybrid of (Al_2O_3) and (TiO_2) NPs showed a good enhancement in the mechanical and tribological properties of PMMA composites. Experimental results illustrated that, the nanocomposites with 0.8 wt% of filler content recorded a distinct performance among other filler amounts.

1.11 Aim of the study

The aim of this stady can be summarized in the following point:

1. Proposing a new structure of nanocomposites (PMMA-ZnO-TiO$_2$) and (PMMA-ZnO-MgO) that   they were used in dental fillings.

2. Theoretical construction of nanocomposites using Density Function Theory (DFT) and studying the electronic properties of the two proposed fillings.

3. Study of the structural and mechanical properties of the two proposed fillings

4. synthesize a new structure of nanocomposites to characterize them as anti-growth Streptococcus mutans isolated from human mouth and antibiotic resistance.
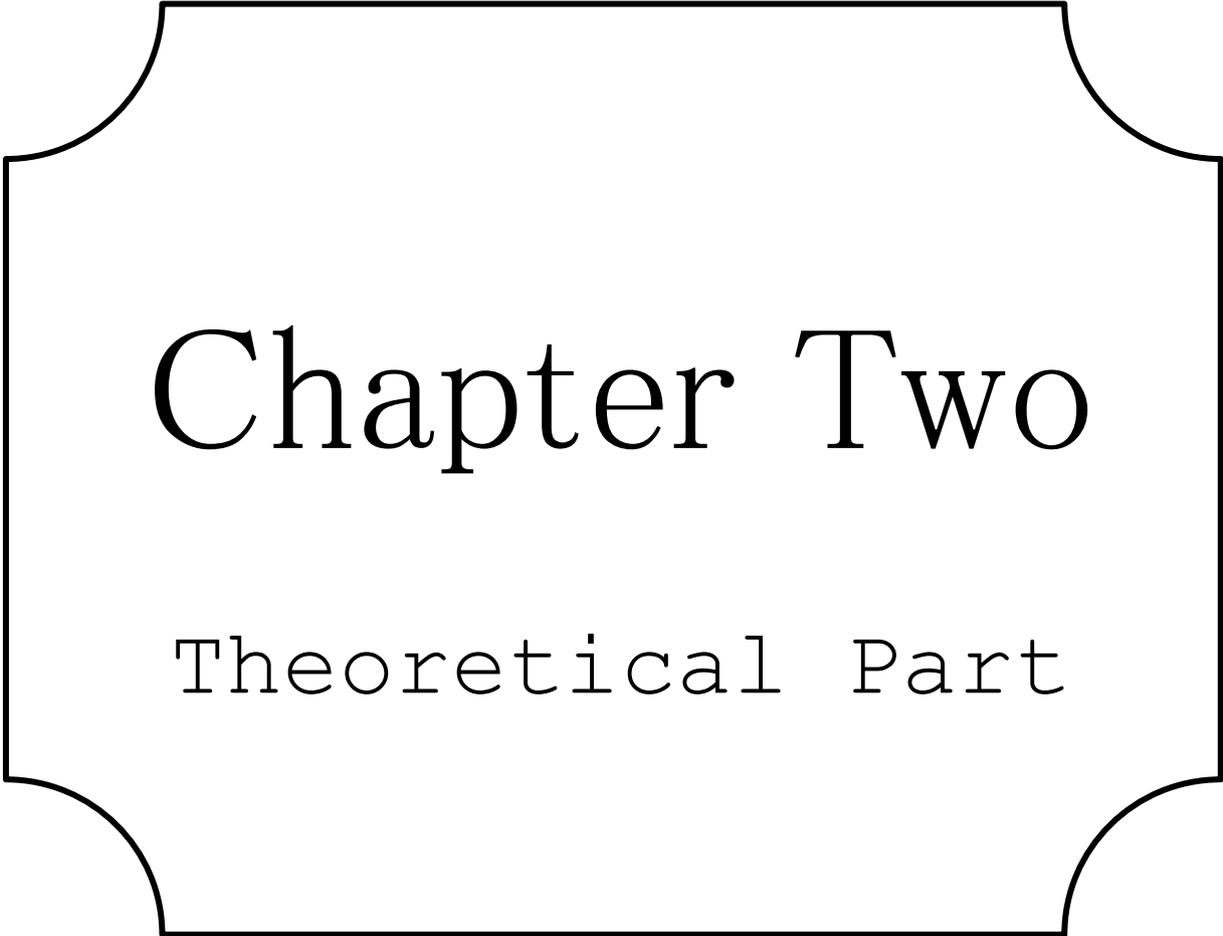
Chapter Two

Theoretical Part

2.1. Introduction

This chapter describes the theoretical part, the mathematical relations used the physical concepts, and the laws used to interpret the obtained results.

2.2. Density Functional Theory (DFT)

Density functional theory has gained considerable ground in recent years to become one of the most widely used techniques for the calculation of molecular structure. Its advantages include less demanding computational effort, less computer time, and in some cases better agreement with experimental values than is obtained from other procedures[51].

The starting point of density theory was the Thomas-Fermi model. In 1927, Thomas and Fermi were calculated the energy of an atom by representing its kinetic energy as a function of the electron density, combining this with the classical expressions for the nuclear-electron and electron-electron interactions, which can both also be represented in terms of the electron density[52,53]. The premise behind DFT is that the energy of a molecule can be determined from the electron density instead of a wave function. This theory originated with a theorem by Hoenburg and Kohn that stated this was possible. The original theorem applied only to finding the ground-state electronic energy of a molecule. A practical application of this theory was developed by Kohn and Sham who formulated a method similar in structure to the Hartree-Fock method[54].

DFT focuses on the much simpler electron density $\rho(r)$. In general, the electron density is the number of electrons N per unit volume for a given state. It is dependent only on three coordinates independently of the number of electrons of the system, thus[55]:

$$N = \int \rho(\vec{r})d\vec{r} \qquad (2.1)$$

The central concepts of DFT are dependent on the ground state energy and all other ground state electronic properties are uniquely determined by the electron density. Furthermore, the exact ground state of the system corresponds to the electronic density for minimal total energy.

2.3 Basis Sets

A basis set is a set of functions used to describe the shape of the orbitals in an atom [56,57]. Molecular orbitals and entire wave functions are created by taking linear combinations of basis functions and angular functions. Most semiempirical methods use a predefined basis set. When ab initio or density functional theory calculations are done, a basis set must be specified although it is possible to create a basis set from scratch, most calculations are done using existing basis sets. The type of calculation performed and basis set chosen are the two biggest factors in determining the accuracy of results.

2.3.1. Slater Type Orbitals (STO'S)

It seems to be the natural choice for basis functions. They are exponential that mimic the exact eigen functions of the hydrogen atom. A typical (STO) is expressed as [58,59].

$$X^{STO} = Nr^{n-1}e^{\xi r}Y_{LM}(\theta, \phi) \qquad (2.2)$$

Here n, is a principal quantum number and ξ is a constant related to Effective charge of the nucleus, i.e. the nuclear charge being partly shielded by electrons. Y_{LM} is a spherical harmonic which describes the angular part of the wave function. One of the disadvantages of (STO) is that many – center integrals such as coulomb and HF- exchange terms are difficult to compute with (STO). Therefore it does not play a role in modern wave function based quantum chemistry codes.

2.3.2. Gaussian Type Orbitals (GTO)

Gaussian type orbitals (GTO) can be written in terms of Cartesian coordinates as [60,61]:

$$X^{GTO} = N X^{LX} y^{Ly} Z^{LZ} e^{-\xi r^2} \qquad (2.3)$$

N is a normalization factor which ensures that $\langle X_\mu | X \rangle = 1$. The sum of LX, Ly and Lz determines the type of orbitals. ξ represents the orbital exponent that shows how compact. The r^2 dependence in the exponential is a deficiency of the (GTO) with respect to the slater- type orbitals (STO).

(GTO) have two main problems. First an improper behavior nears the nuclei at $r \to o$, while slater type functions show a correct behavior at $r \to o$ with a discontinuous behavior .GTO which is a bell shaped function has a slope of zero at $r \to o$. Another problem is that GTO falls of too rapidly far from the nuclei compared with the STO.

Therefore, the tail of the wave function in the (GTO) is represented poorly. A rough estimate says that three times as many (GTO) as (STO) are required in order to reach the same level of accuracy one of the advantages of the Gaussian basis set is that the product of two Gaussian functions is another Gaussian function. As a result, for the calculations of coulomb and HF- exchange terms the analytical solution is available for the Gaussian functions.

Therefore the (GTO) basis function in HF and related methods is popular because very efficient algorithms exist for analytically calculating the many- center integrals .In order to improve the GTO basis sets, one usually employs a contracted GTO basis set in which several primitive Gaussian functions are mixed to give a Contracted Gaussian Function (CGF) as [62,63]:

$$X^{CGF} = \sum_{i}^{M} C_{ij} X_a^{GTO} \qquad\qquad (2.4)$$

Here, M is the number of Gaussian primitives used in a linear combination. As discussed before at least M=3 is required to reach the accuracy of (STO). The basis sets used in Gaussian are classified in to minimal basis sets, split valency sets polarization and diffuse functions and others. [64,65].

2.3.3 Minimal Basis Sets

The minimal basis set is the minimum number of basis functions X needed to describe the ground states of the component atoms (represent all the electrons of each atom)in a molecule. A common name of minimal basis sets is STO- n G, the n (n=2-6) represents the number of Gaussian primitive functions that comprise a single basis function. In these basis sets, the same number of Gaussian primitives comprises core and valence orbitals. Minimal basis sets typically give rough results that are insufficient for research –quality publication, but are much cheaper than their larger counterparts. The following are examples of commonly used minimal basis sets: STO- 2G ,STO-3G,STO- 6 G[66].

2.3.4 Split–Valence Basis Sets

In a split-valence basis set the inner- shell atomic orbitals are represented by one basis function and the valence orbitals are represented by two or more basis functions (Pople basis sets) [67,68]. One easy method to extend a basis set is to increase the number of basis functions used per orbital. Split–valence basis sets employ more than one basis function of variable orbital exponents for each valence orbital and only one basis function for each core orbital for instance, Valence Double-Zeta (VDZ) basis set uses two basis functions per valence orbital while the

Valence Triple –Zeta (VTZ) uses three, and so on. Another example of these is the K- LMNG basis sets developed by pople and co- workers. Here, K represents the number of primitive Gaussians used for each core orbital while L, M and N represent the primitives used for the valence orbitals. For instance the 6-31G basis set uses a set of 6 primitives contracted to one basis function for each core orbital and a split- valence of 3 and 1 primitive for the valence orbitals. While the split valence basis sets provide a better description of the molecular orbitals because they allow for variable atom size, they still are not able to provide a balanced basis set on their own [69].

2.4 Calculated Properties

The mathematical equations used in the work included:

2.4.1 HOMO, LUMO and Band Gap

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the two most important molecular orbitals. These orbitals are called the frontier orbitals as they lie at the outmost boundaries of the electrons of the molecules. The HOMO, which is the highest energy (outermost) orbital containing electrons, is the orbital acting as an electron donor. On the other hand, the LUMO, is the lowest energy (innermost) orbital having space to accept electrons[70]. The band gap refers to energy difference between the highest occupied molecular orbital and lowest unoccupied molecular orbital according to the Koopmans theorem[71]:

$$E_g = E_{LUMO} - E_{HOMO} \qquad\qquad (2.5)$$

Where:

ELUMO : is the energy of the lowest unoccupied molecular orbital.

EHOMO: is the energy of the highest occupied molecular orbital.

HOMO and LUMO and their resulting energy gap not only determine the way the molecule interacts with other species, but their energy gap (frontier orbital gap) helps characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule[71].

2.4.2 Ionization Potential (IP)

The ionization potential (IP) for a molecule is the amount of energy required to remove an electron from an isolated atom or molecule and expressed as the energy difference between the positive charged energy E (+) and the neutral E(n) according to the following relation [72,73]:

$$IP=E(_+)–E(_n) \qquad\qquad (2.6)$$

$$IP = - E_{HOMO} \qquad\qquad (2.7)$$

2.4.3 Electron Affinity (EA)

The electron affinity (EA) of a molecule or atom is the energy change when an electron added to the neutral atom to form a negative ion and expressed as the energy difference between the neutral energy E(n) and the negative charged energy E(-) according to the following relation [74,75,76]:

$$EA=E(_n)–E(_-) \qquad\qquad (2.8)$$

In molecular orbital (MO) theory with the limitation of Koopman theorem [77,78], the orbital energies of the frontier orbitals are given by:

$$EA=-E_{LUMO} \qquad\qquad (2.9)$$

A molecule with high chemical potential will accept electrons from a molecule with lower chemical potential [76].

2.4.4 Chemical Softness (S)
The softness can be defined as the inverse of the hardness[79]:

$$S = 1/(2\mu)………\quad……….\quad……….\quad…….(2.10)$$

S can be represented by [105]:

$$S = 1/(IP - EA)………\quad……….\quad……….\quad………. (2.11)$$

2.4.5 Electronegativity (χ)
The electronegativity is a measure of the tendency to attract electrons by an atom in a chemical bond and defined as the negative of the chemical potential [80,]. Mulliken defined electronegativity as the average of the ionization energy and electron affinity as follows [81]:

$$x=(IP+EA)/2 \qquad\qquad (2.12)$$

To estimate the Electronegativity in the framework of Koopmans' theorem, it can be defined as the negative value for average of the energy levels of the HOMO and LUMO [82].

$$x= -(EHOMO+ELUMO) \qquad\qquad (2.13)$$

2.4.6 Chemical Hardness (μ)
Chemical hardness is the resistance of a species to lose electrons [85], for insulator and semiconductor, hardness is half of the energy gap [86]. we can calculate the chemical hardness (μ) [82]:

$$\mu = (IP - EA)/2……….\quad……….\quad……….\quad……….\quad….(2.14)$$

μ :Chemical hardness.

IP: Ionization potential.

EA: Electron affinity

The theoretical definition of chemical hardness has been provided by the density functional theory as a second derivative of electronic energy with respect to the number of electrons (n) [83]

2.5. Total energy (ET)

One of the most important properties of a molecule is the energy and the shape of its highest occupied molecular orbital (HOMO), because the HOMO is one of the major factors which controls the nucleophilic reactivity of the molecule according to Koopmans' theorem [83]. The total energy for a system is the sum of total kinetic and potential energy, at the optimized structure that the total energy of the molecule must be at the lowest value because the molecule is at the equilibrium point. This means that the resultant of the effective forces is zero [84].

2.6 The Software

All calculations in this study have been performed by using the Gaussian 09 package of programs, Gauss View 5.0.8, Gauss Sum 3.0 and other assistant programs. These programs are described as below:

2.6.1 Gaussian 09(G09) Program

Gaussian is a very high-end quantum mechanical software package, available commercially through Gaussian, Inc. The Software run on virtually all computer platforms, including Microsoft Windows. In addition, it can be, accessed through Web based, interface tools such as Web MO. In Gaussian09 (G09) the "09" refers to the year 2009 in which the software was published. G09 is most recent version. G09 contains about 500,000 lines (very approximate) of FORTRAN and C++ code[85].

2.6.2 Gaussian View 5.0.8 Program

Gauss view program was designed to import the input files for the Gaussian programs and also used to demonstrate the output files for Gaussian program in the dimensional photo, Gaussian view which not used as calculation program, but it facilitates the work on Gaussian program and supply the users with three major advantages[86].

First: enable the user to draw the molecules including the big one, also enables the rotation, transferring and changing it size easily and the mouse .

Second: Gaussian view permits to achieve many of the Gaussian calculation, making the complex input preparation for the routine work and the advanced method.

Third: Gaussian view permit the inspection of Gaussian calculations results using variety of geometrical techniques[86].

2.7 Practically

The goal of nanoparticle production is to manufacture materials with new properties, as these materials are characterized by the following properties:

1- There are few or no distances between particles. This feature made the nanomaterials extremely small and with durability, hardness and many other features.

2- The atoms on the borders of the particle are unsaturated, for example, if the atom on the borders of the particle has four bonds, this atom is linked by two bonds inside the particle, while the other two bonds remain outside the body without bonding. As a result, the atoms on the borders of the body are unsaturated, so nanoparticles are effective and need To interact with each other or with other materials[87,88].

The beginning of nanoscience was in the year 1950 by Richard Faynman, the owner of the nano phenomenon [89]. In 1974, the scientist Norio from the University of Tokyo defined the term (Nanotechnology) as a process of separation or merging of matter, an atom by another atom or a molecule by another [90].

In (2006), nanotechnology entered many life applications and occupied a wide area of many applied sciences such as medicine, biology, pharmacy, electronic materials and chemistry. Nanotechnology is also used in many industrial sciences such as drug delivery, semiconductors and dental materials as fillings [91]. Nanoparticles deal with atomic assemblies ranging from five atoms to a thousand atoms, which are dimensions much smaller than the dimensions of bacteria and living cells.[91]

The introduction of nanotechnology in dentistry has a great perspective hoped for by the dentist and the patient as nano dentistry has promoted increased dental and oral health protection by drug delivery and diagnostics [92,93]. In the last decades of the twentieth century, new technologies and materials called nanomaterials or nanotechnology were used, as these new materials carry new features, and thus we obtained new materials with new features that differ from the properties of the original materials. Making materials into nanostructures led to fundamental changes in the crystal structure of the material. These changes that are processed in the range of the conduction band, the valence band, and the value of the energy gap, where this transformation from a solid material to a nanomaterial changes the valence band and conductivity from continuous to discontinuous, as the conversion from a bulk material to a nano material does not only change the crystal structure, but also Also to modify the electron arrangement and optical properties as shown in Figure (2.1) [94, 95].
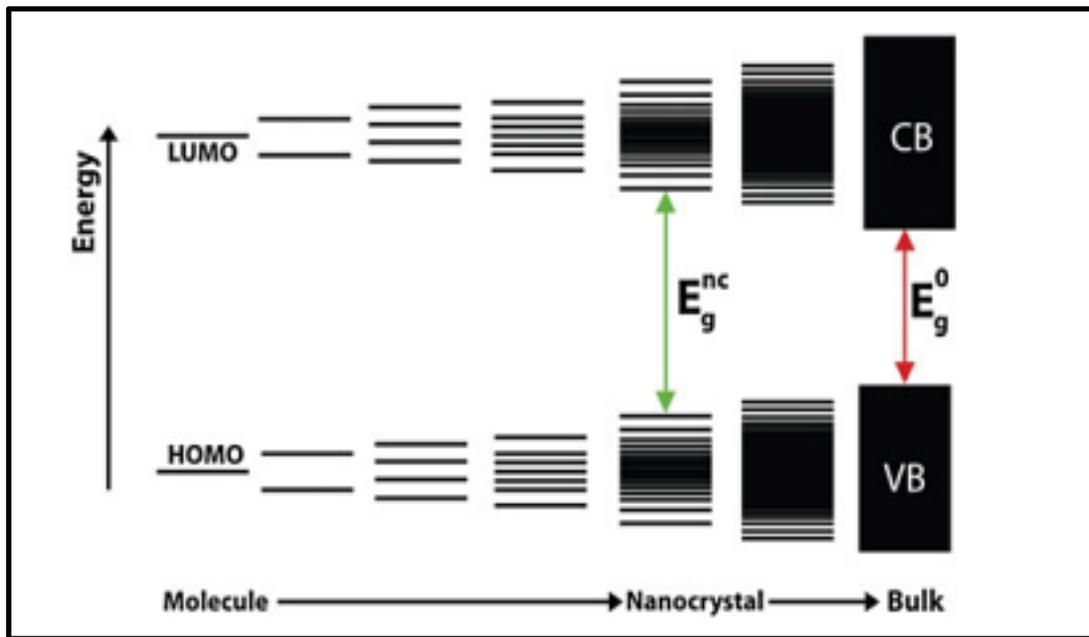
Figure: (2.1) Bundle conduction and valence for solids and nanomaterials [94].

When light containing many wavelengths falls on the nanomaterial where almost all wavelengths are absorbed, inside the nanomaterial there is at least a pair of planes (one in the VB band and the other in the conduction band CB) such that the energy gap of the two is equal to the energy of the incident wavelength Therefore, any falling wavelength is absorbed by the two levels, which leads to the absorption of all wavelengths at a close distance, so the absorbance of the nanomaterial is high [95]. An ordinary particle with a microscopic size contains a certain number of atoms or molecules on the surface of the particle, and therefore it has a limited ability to interact, but when the particles become smaller and smaller until they reach the size of the nanometer, the area-to-volume ratio increases, which leads to an increase in the number of particles on the surface. The interaction with the molecules of other materials or with each other will increase [96] .

The ability to react with chemicals increases as the particle becomes smaller because the atoms on the surface of the nanoparticle are

unsaturated so the unsaturated outer atoms will try to interact with other atoms to saturate their bonds. Changing particle size changes the size of
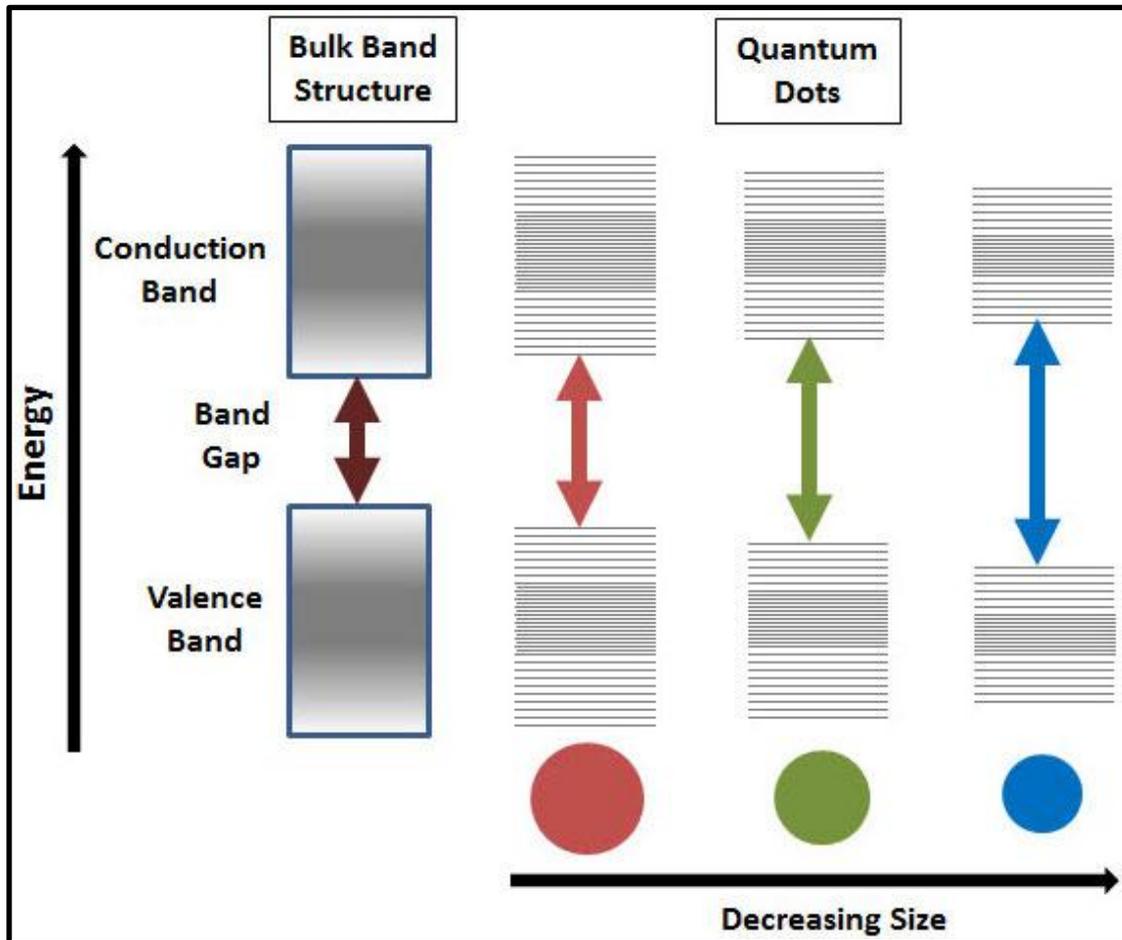
Figure: (2.2) Energy gap change with particle size reduction [97].

the energy gap, conduction band, and valence band. When the particle size becomes smaller, the energy gap becomes larger and larger because the conduction bands and Valance bands will get narrower [97].

The reason for our choice of dental nanomaterials is that it has low cost and distinctive properties for teeth (Dentin). Nanotechnology is a leap in the field of materials science as the properties will be improved, so nanocomposites have been widely used in dental restoration. One of the most important factors that cause tooth damage and thus lead to a decrease in antibacterial activity, shrinkage of polymerization, plaque accumulation, partial leakage and the formation of cavities. Recently,

scientists have come to the conclusion that oral biofilms play an important role in the development of caries .

2.8 Structural Properties

2.8.1 Atomic Force Microscope (AFM)

Atomic force microscope (AFM) is a high-precision technique type of scanning probe microscopy, through which to look at the surface of a very high accuracy from (100 μm to less than 1μm)[98]. AFM is used for surface imaging technology to obtain information about the surface morphology of the film, such as, distribution and standardization, of grain or defect forming a film on any surface, such as insulation or procedure without damaging the surface. Many materials are identified by this technique, including polymers, semiconductors, metals and composites[99]. Figure (2.3) shows a diagram for Atomic Force Microscope.
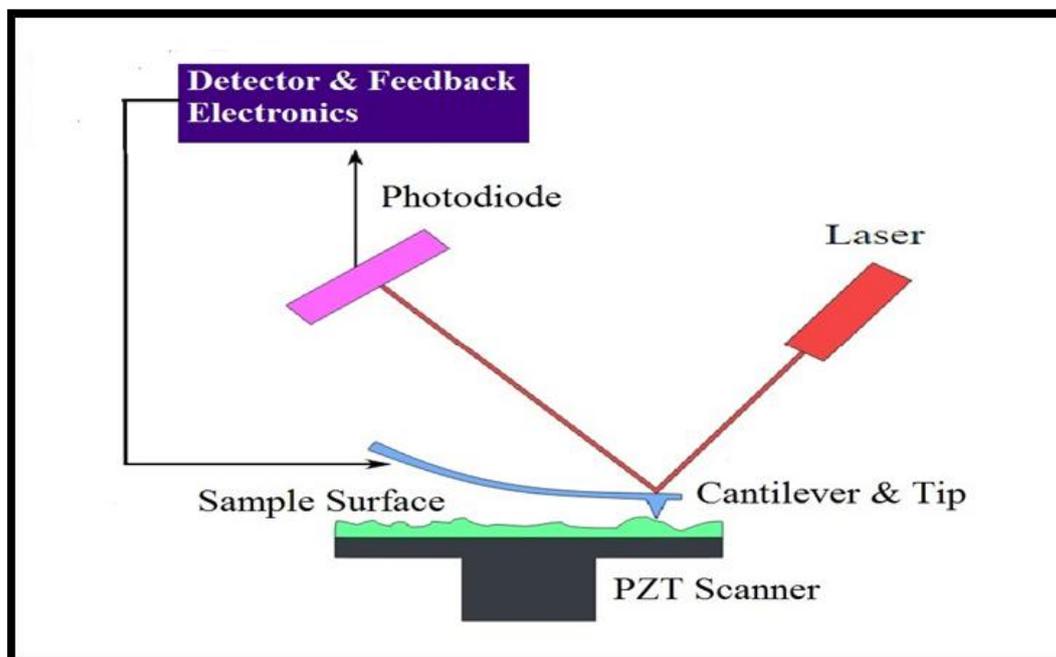

Figure (2.3): Diagram for atomic forces microscope[100]

2.8.2 Field Emission Scanning Electron Microscopy (FESEM)

Scanning electron microscope (FESEM) is the best known and most widely-used of the surface analytical techniques. High resolution images of surface topography, with excellent depth of field, are produced using a highly-focused, scanning (primary) electron beam. The primary electrons enter a surface with an energy of $0.5 - 30$ kV and generate many low energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sample[101].   The scheme of FESEM operation is illustrated in Figure (2.2), which consists of electron gun as electron source, two condenser lenses, scanning coils, which facilitates the deflection of electron beam in x and y directions, objective lens, and detectors for backscattered and secondary electrons. FSEM operates inside vacuum chamber with high-energy electron source (2-25kV). Condenser lenses focus the electron beam into a nanometer size. The reflected electron from the sample, backscattered or secondary electrons, are collected by the detector to provide an image of the sample. In many cases, the backscattered electrons reflected from the sample are used in analytical FESEM due to the relation of intensity and atomic number of materials[89].
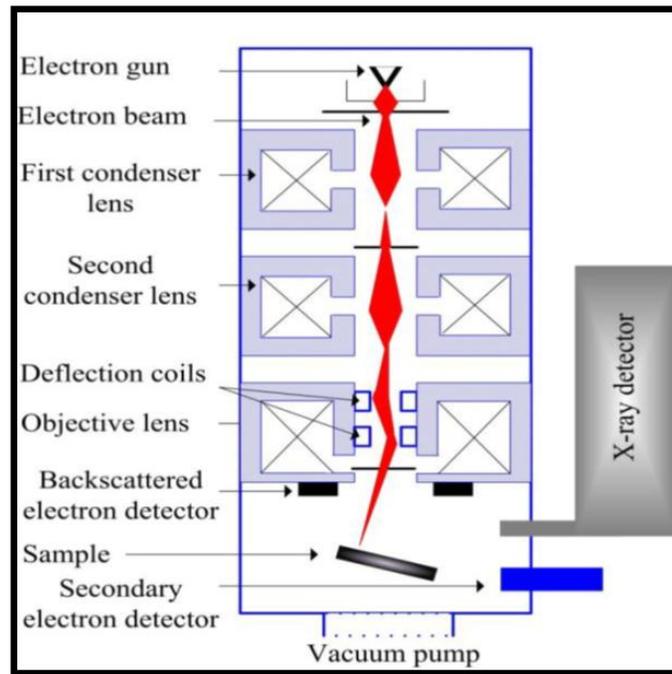
Figure (2.4): Schematic illustration of the operation of FESEM[101].

Two imaging modes are available in (FESEM); Secondary Electron Imaging (SEI) or Backscattered Electron Imaging (BEI). In the former, low energy secondary electrons (typically < 50 eV) emitted from the interaction between the incident beam of high energy electrons with the atoms of the sample via inelastic collisions are detected and used to build an image of the surface topography of the sample. Due to the relatively low energies of these secondary electrons, only those from the surface (a very thin layer of tens of nanometers) are able to emerge from the sample. In the case of BEI, the image is derived from scattered or reflected electrons from elastic collisions of the high energy electron beam with the nuclei of the atoms at high angles approaching 180°c Figure (2.5) [101].
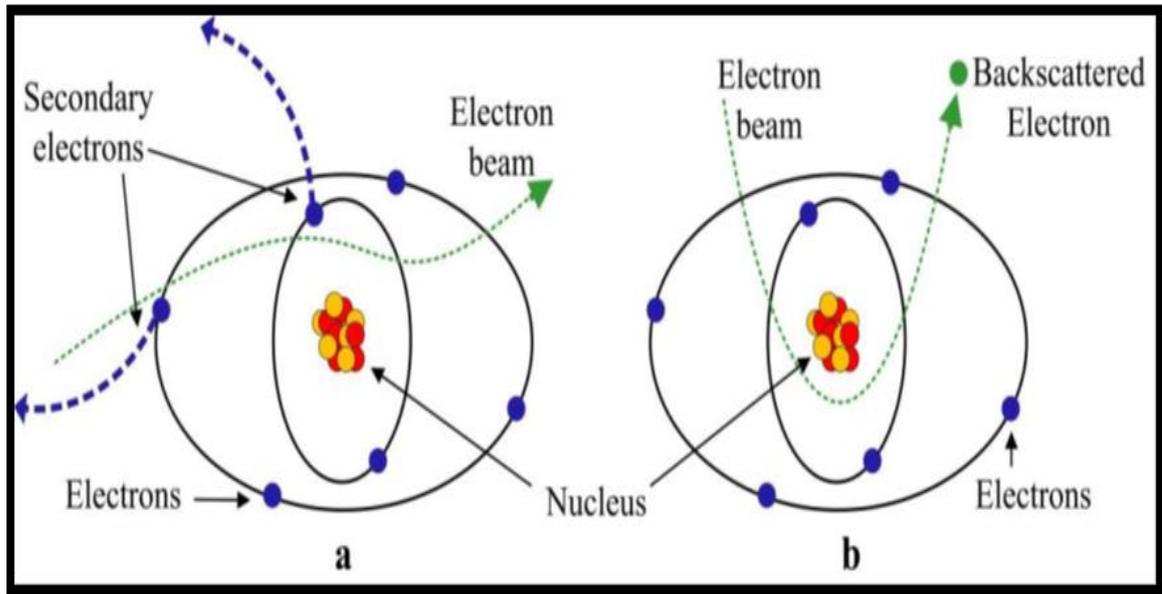
Figure (2.5): Interaction between electrons beam and sample producing (a)secondary electrons and (b) backscattered electrons[102].

The yield of backscattered electrons is a function of atomic number. Heavier elements, i.e. those with higher atomic number, reflect a greater proportion of electrons and so appear brighter, and lighter elements with a low atomic number reflect a lower proportion of electrons and appear darker. The contrast indicates the average atomic number of the elements present within the microstructure and is indicative of the varying elemental compositions[102].

2.9 Mechanical Properties

The materials used in dental treatment must have mechanical properties similar to those of the tooth or better than it. Knowing the mechanical properties of these materials is important to assess their performance. As long as these materials are used in the vicinity of the mouth, they are subjected to forces and stresses due to the chewing process. These forces lead to different reactions that lead to distortion and reduce the durability of the material over time.

There are several mechanical properties that must be known and know what is the behavior of the material when exposed to such forces by studying the properties of Specific such as Compressive-strength, Hardness [103].

2.9.1. Compressive Strength

Compressive strength is generally defined as the material's maximum resistance to the applied stress before it is crushed and is affected by several factors, including the components of the composite resin, especially the filler particles, as it is greatly affected by the size of the fillers, their diameter and type [104].

The composite, amalgam, cement and other dental materials are brittle materials (they resist compressive forces more than tensile forces), so the compressive strength test is very important for dental materials as these materials must have mechanical properties similar to the teeth in order to resist chewing forces .Which is compressive in a strength range ranging from (450-500)N.

As long as the chewing forces are compressive in nature, it is very important to know the behavior of the materials used as dental fillings under these conditions, so the compressive strength test is the most appropriate option for comparison between dental composites.

To perform the compressive strength test for dental overlays, according to (ISO 9917) [104], the models must be cylindrical in shape and have a ratio of length to diameter (2:1) as increasing this ratio will cause undesirable bending of the model, and the compressive strength is calculated from the equation [2].

$\sigma = P/A$ ……………(2.15).

where:

σ: the compressive strength measured in (N/mm^2).

P: the applied force measured in (N).

A: Surface Area in unit (mm^2).

2.9.2. Hardness

The property of hardness is one of the main and important properties to compare between materials used for teeth and the hardness in its general definition is the surface resistance to indentation or denting, and it is measured in units (N/mm^2). Depending on the definition of hardness, it became clear the importance of this property in dentistry, as it indicates on the nature of the fading of the system, the glossiness, which is important for aesthetic purposes, and that scratching leads to cases of stress and failure, and the hardness is affected by several factors, including the size of the fillers particles and the type of resin [105] explained that there is a correlation between the size of the fillers particles and the surface hardness, as it was found that the compound that has a higher particle size than the fillers has a higher surface hardness.

Hardness is measured in different ways and there are four main methods: (Knoop, Vickers, Rockwell, Brinel) Each of these tests differs from the other because it has advantages and disadvantages at the same time, but all tests are based on making a dent or a very small penetration in the surface of the material to be measured Its hardness, the various hardness tests differ in terms of the material used to effect the geometric penetration and the shear load. The selection of the hardness test depends on the material to be tested and the expected hardness. The dimensions of penetration (area, depth) are measured under the microscope and from the knowledge of the applied load and the resulting penetration, the hardness

can be known. Figure (2.6) shows the plastic deformation resulting from the effect of load on the hardness measurement[94].
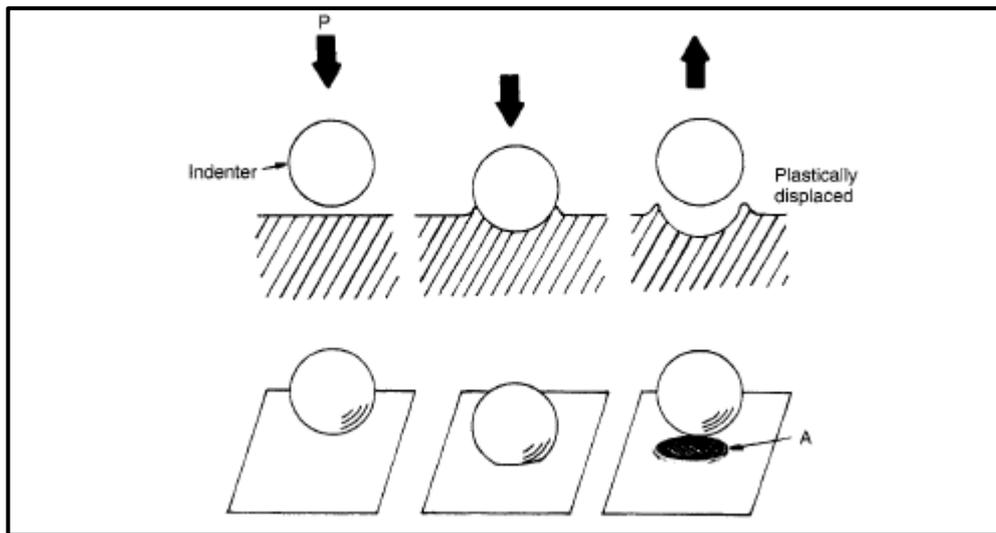
Figure (2.6): A: the area of plastic deformation, P: the applied load [105].

Hardness is measured in four main ways:

2.9.2.1 Brinell Hardness Test(BHT)

Is one of the oldest methods for testing the hardness of metals and alloys used in dentistry. This method depends on the dent caused by a small ball of steel or tungsten carbide with a diameter of (1.6 mm) and a load of (123 N). The load remains in place for a period of (30 sec), then the diameter of the dent is measured. The resulting number is known as Brinell Hardness Number (BHN) and is measured in (Kg/mm) units. Brinell Higher Number (BHN) indicates higher hardness. Brinell hardness is given by the following relationship[105]:

BHN= L /(π D/2)(D-(D^2 - d^2)$^{1/2}$)   (2.16)

whereas:

L: load (Kg)

D: Bug diameter (mm)

d: notch diameter (mm)

2.9.2.2 Knoop Hardness Test(KHT)

This method was developed to become a micro-testing method in which a pyramid-shaped diamond-shaped tool is used, through which the load is applied, and then the resulting penetration dimensions are measured, where Knob Hardness Number (KHN) represents the ratio between the applied load to the penetration area as in the equation [2]:

KHN=L / B^2 CP (2.17)

L: load shed (N)

B: the length of the resulting penetration dimension (mm).

CP: constant and its value is (0.07028).

KHN is measured in N/mm^2.

The area of the resulting dent changes according to the applied load and the nature of the material under test. One of the advantages of this method is that we can measure the hardness of materials with a large range of hardness by applying different loads. This method is used to measure the hardness of enamel and dentin in dentistry, but one of its drawbacks is that it needs a very smooth and flat surface. [106], and Figure (2.7) shows the dent produced when testing Knob's hardness.
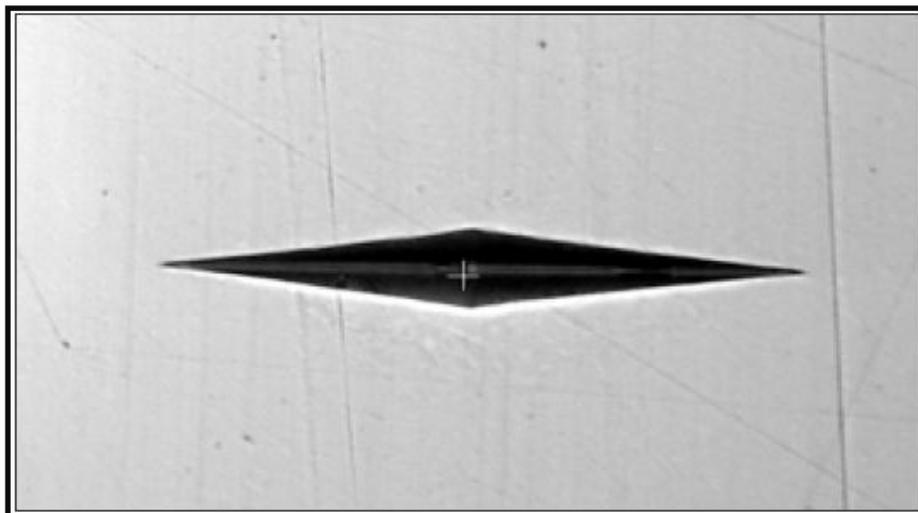
Figure: (2.7) The dent or penetration resulting from the Knoop test [96].

2.9.2.3 Rockwell Test Method

This method was developed to become a rapid hardness test method, where a ball-shaped or cone-shaped dent is used, and the resulting deformation is measured by a sensitive dialmicrometer, as the ball has different and multiple diameters, as well as the loads used. The test in this way is on groups and each group has a special (Rock) measurement (A - G) such as (RA, RB ... and so on) and in a special measurement called (Super Fical Rockwell) a light load (30 Kg) and a large diameter (12.7) are used. mm) to measure the hardness of plastic materials in dentistry [107].

2.9.2.4 Microhardness Test (Vickers):

Microhardness est (Vickers) the method of this test is similar to the Knob method by applying a load by means of a pyramid-shaped penetration material with an angle (136°) made of diamond on the material under test and the applied load range is N(1 - 10), this method is used to test the hardness of the visceral materials, as it is used to measure the hardness of materials with a small area and very hard materials [108], and the Vickers hardness is given by the following relationship:

VHN = 1.8544 *L /d^2 **(2.18)**

Where :

L: Load B (Kg).

d: average diameter (mm).

Figure (2.8) shows the dent produced when the Vickers hardness test.
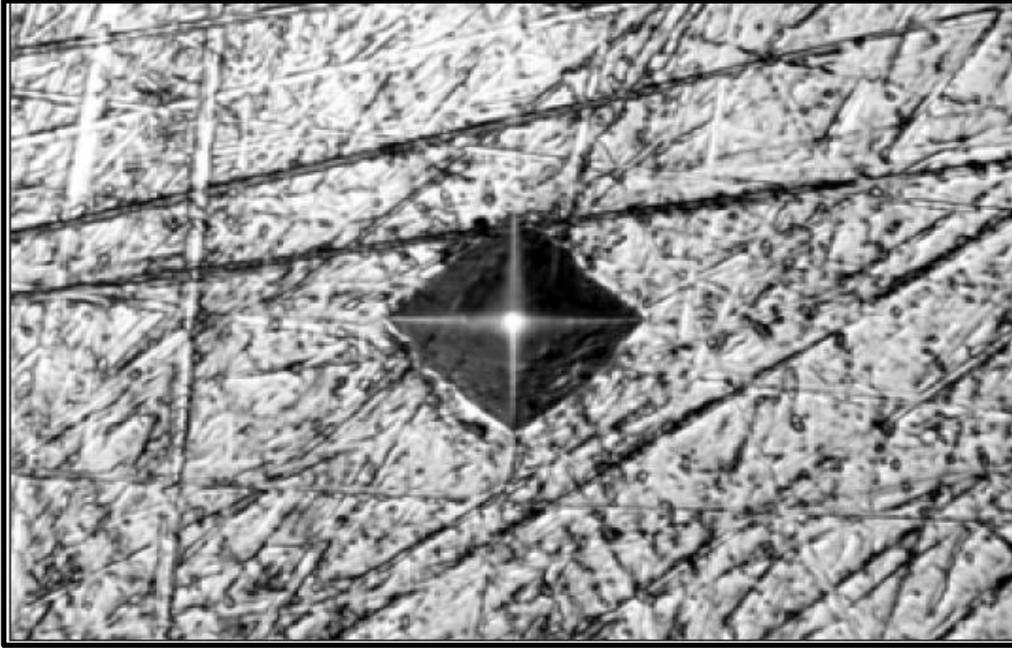
Figure (2.8) The resulting dent or penetration when tested (Vickers) [109].
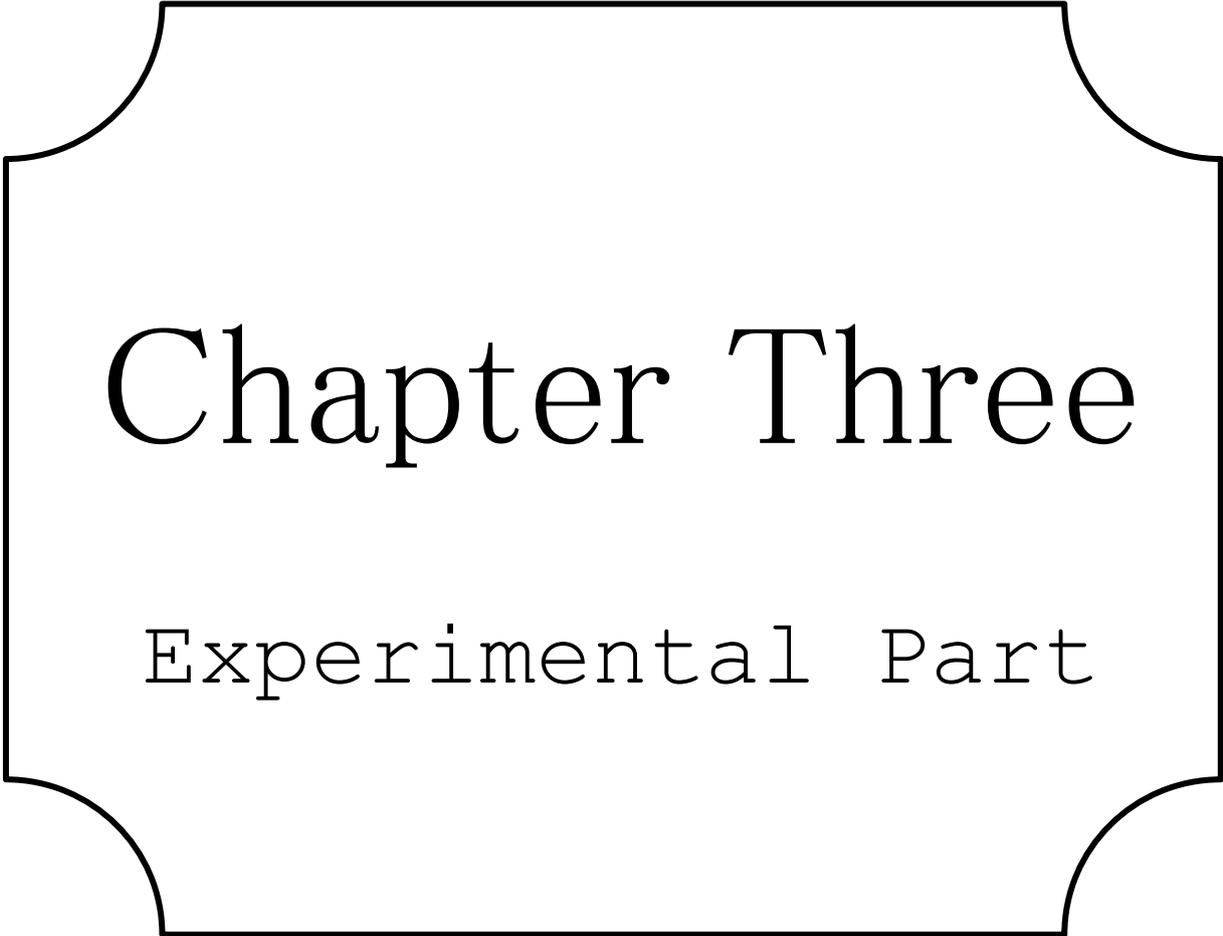
Chapter Three

Experimental Part

3.1 Introduction

This chapter involves the specimen preparation for (PMMA-ZnO-MgO) and (PMMA-ZnO-TiO$_2$) nanocomposites as dental fillings. Samples tests and measurements steps: Structural Properties (Atomic Force Microscope (AFM), Field Emission Scanning Electron Microscopy (FESEM), mechanical properties(Compressive strength, Polymerization shrinkage), antibacterial activity application measurements.

3.2 The materials used

3.2.1 Polymer

The polymer is used in this work:

Poly-Methyl-Methacrylate (PMMA): it was obtained as powder form and could be obtained from local markets with high purity (99.8)%. Keyuan manufacturer.

Figure: (3.1) Poly-Methyl-Methacrylate (PMMA).

3.2.2 Nanoparticles

1. **Zinc oxide nanoparticles (ZnO):** used as powder with particle diameter (20-30) nm from EPRUI. company and high purity (99.9)%.

Figure: (3.2) Zinc Oxide (ZnO).

2. **Titanium Dioxide nanoparticles (TiO$_2$):** used as powder with particle diameter (20-40) nm from EPRUI. company and high purity (99.9)%.

Figure: (3.3) Titanium Dioxide (TiO$_2$).

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3. Magnesium Oxide (MgO): used as powder with particle diameter (20-30) nm from EPRUI. company and high purity (99.9%).

Figure: (3.4) Magnesium Oxide

3.3 Preparation of (PMMA-ZnO-TiO2) and (PMMA-ZnO-MgO) Nanocomposites

The method of work depends on the two manufactured fillings on the base material, which is a polymer (PMMA).

Which is dissolved in Chloroform or Chloromethane, which is an organic compound with chemical formula $ChCl_3$, which is a colorless liquid that is easy to volatilize. It is also a very good solvent for various chemicals with a density of (1.49) g/cm^3. Where the polymer is dissolved in 30 ml of chloroform with continuous movement for 30 minutes. After dissolution, the oxides (Fillers) are added from (ZnO, TiO$_2$) to the first filling and (ZnO, MgO) to the second filling sequentially and by using magnetic stirrer to mix the polymer and nanoparticles 10 min to obtain

more homogeneous solution in room temperature. with different concentrations are (0, 2.5 , 5 and 7.5) wt.%. The casting method is used to prepare the samples of (PMMA- ZnO, TiO$_2$) and (PMMA- ZnO, MgO) nanocomposites in the template (petri dish has diameter 10 cm). The thickness of prepared samples was measured by using digital micrometer, the thickness range was (0.011-0.016) μm, and Figure (3.5) and Tables (3.1),(3.2) shows experimental work.

Table (3.1) Weight percentages for nanocomposites (PMMA- ZnO - TiO$_2$).

wt.%	PMMA gm	ZnO gm	TiO$_2$ gm	Weight of Sample
0	1	0	0	
2.5	0.975	0.0125	0.0125	1gm
5	0.95	0.025	0.025	
7.5	0.925	0.0375	0.0375	

Table(3.2) Weight percentages for nanocomposites (PMMA- ZnO - MgO) .

wt.%	PMMA gm	ZnO gm	MgO gm	Weight of Sample
0	1	0	0	
2.5	0.975	0.0125	0.0125	1gm
5	0.95	0.025	0.025	
7.5	0.925	0.0375	0.0375	
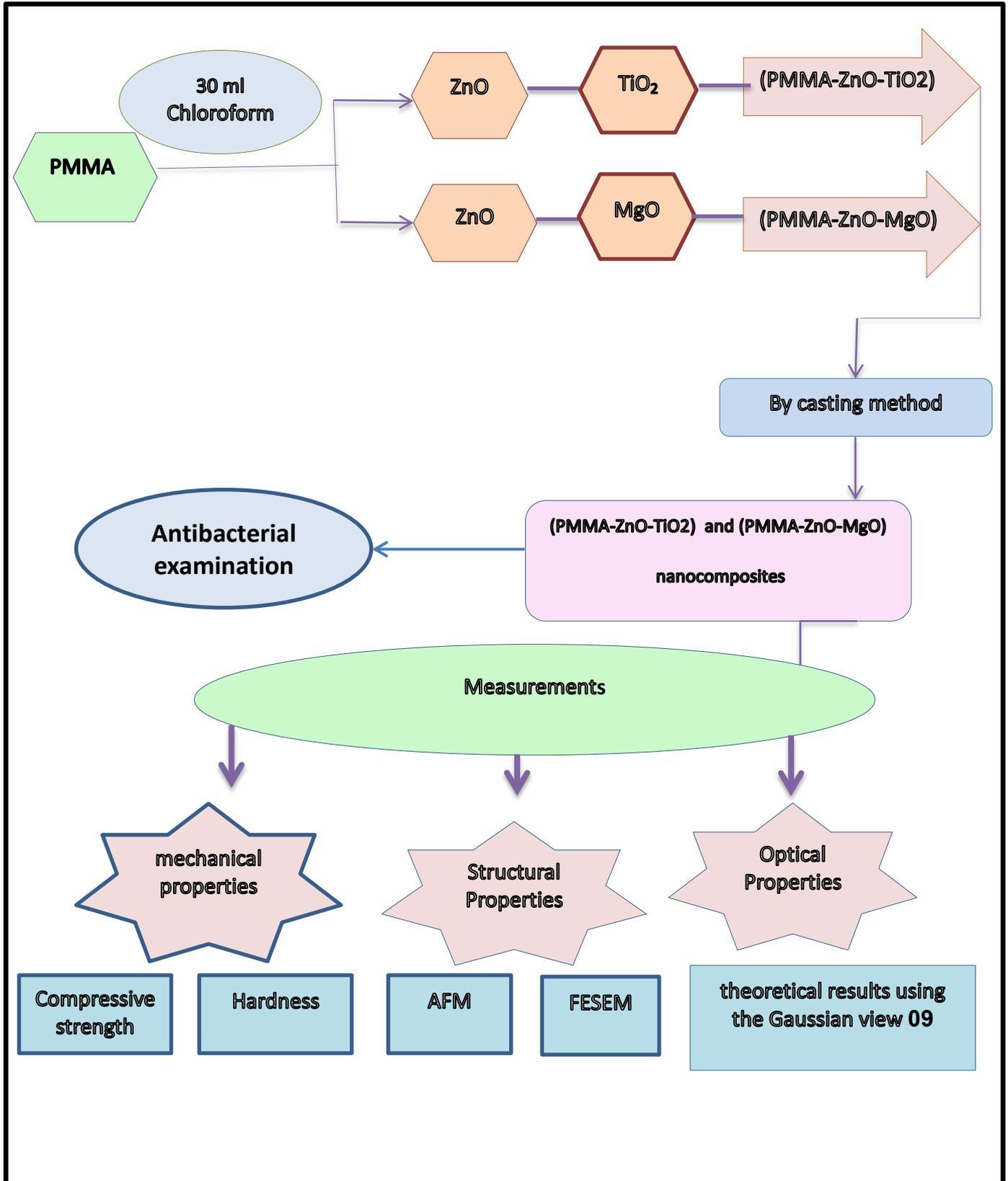
Figure (3.5) Diagram explains the main steps for procedure.

3.4 Use Devices

3.4.1 Sensor scale

It is a very sensitive device for weights and is used only in experiments that require very accurate weight. It is available within the laboratories of the College of Science - University of Babylon, as shown in Figure (3.6).

Figure (3.6) Sensitive Balance

3.4.2 Photosclerotherapy Device (Blue LED) .

It is one of the most important devices in dental fillings of materials in order to fix the composite material on the tooth. The materials used were self-hardening resins. These materials were mixed. This substance is first mixed and then placed in the tooth. It took about (20-30)seconds for it to fully cure itself. by using it, a lot of problems for the dentist were solved. One of these problems is that the dentist had no control over the speed of processing the material; The curing process begins as soon as the

blending begins. This resulted in the dentist applying the material to the tooth quickly and appropriately. If the material is not properly placed, it must then be excavated and the process started again. This offers new advantages for dentists: there is no need to be bound by time anymore and the dentist can now ensure the perfect fit and hardness of the material.Aphotopolymerization device manufactured by (WOODPECKER) was used with a luminous aperture of (6 mm) and an intensity of (400 MW / cm^2) with a wavelength (440-490 nm) located in the blue range of the visible spectrum[110], Figure (3.7) It shows the polymerization device used and the device is available within the laboratories of the Faculty of Dentistry - University of Babylon.

Figure: (3.7) Photosclerotherapy device

3.5 Structural Properties

3.5.1 Atomic Force Microscope (AFM)

Atomic Force Microscope (AFM) micrographs with digital instruments (Inc. BY2000) are taken to observe the surface roughness and topography of deposited thin films. Typical data had been taken from AFM height images include root mean square (RMS) roughness and grain size. It has three main modes of mapping topography: contact, non-contact and intermittent contact or tapping. The most important part of an AFM is the tip with its nanoscale radius of curvature. The tip is attached to a micron scale cantilever which reacts to the Van der Waals interaction and other forces between the tip and sample. This instrument is present in in Islamic Republic Iran- shahrood university of technology .The schematic of AFM microscope is shown in Figure (3.8).
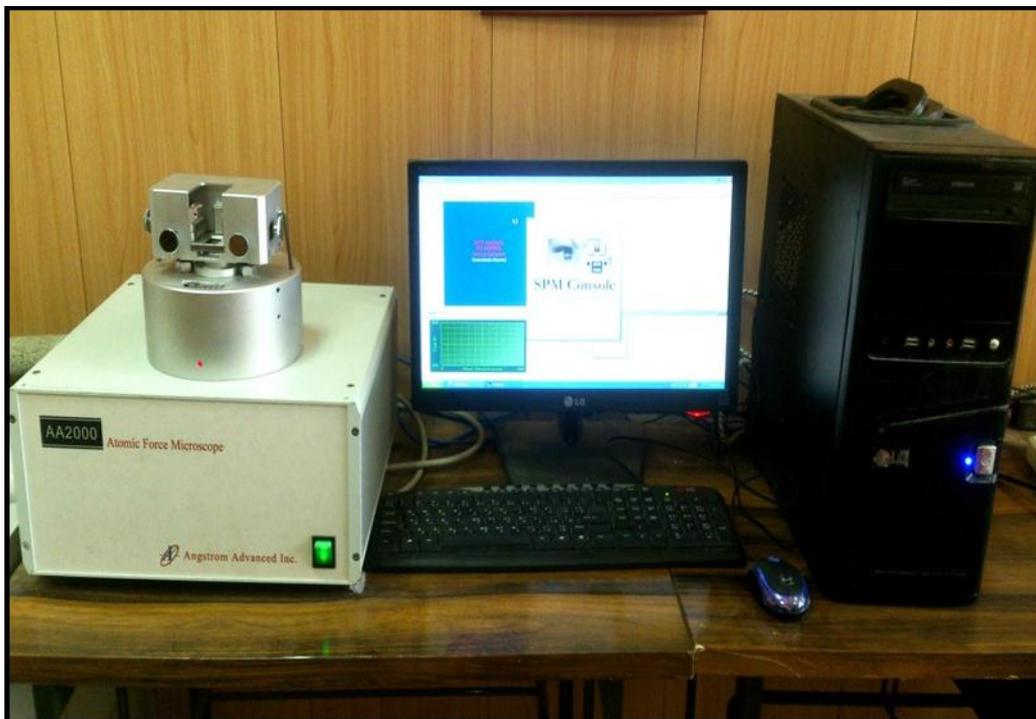
Figure (3.8): Photograph illustrates the AFM.

3.5.2. Field Emission Scanning Electron Microscopy (FESEM)

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX). The SEM study has been carried out by Inspect 550 scanning electron microscope equipped with energy dispersive X-ray (EDX) the magnification power 250000 The morphological properties of the pure (PMMA) and doped with fillers were investigated by FESEM (S-4300 of Ziss-Sigma-Germany) as in Figure (3.9), in Islamic Republic Iran- shahrood university of technology.
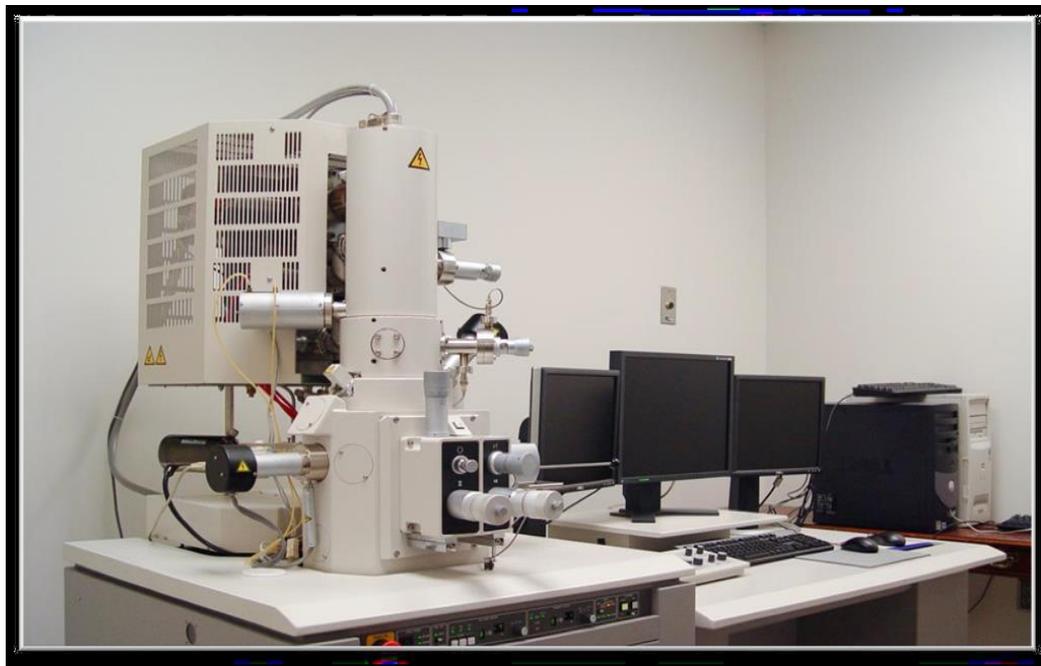
Figure (3.9): Field Emission Scanning Electron Microscopy (FESEM).

3.6 Mechanical properties

Two types of molds made of (Stainless Steel) were used in this study :

1. The first model is in the form of a cylindrical cavity with a diameter of (6 mm) and thickness (10 mm), with the use of an iron rod of diameter (6 mm) and thickness (8 mm) that is inserted into the cavity for the purpose of preparing samples with a thickness of (2 mm). This model is for preparing samples for hardness testing.

2. The two model is in the form of a cylindrical cavity with a diameter of (3mm) and a thickness of (6 mm), made in a similar way to the first model and used to prepare samples for testing the compressive strength.

3.6.1 Compressive Strength Testing

For the purpose of measuring the compressive strength, cylindrical samples with a diameter of (3 mm) and thickness of (6 mm) were prepared. This examination was carried out using a device of the type (Microcomputer Controlled Electronic Universal Testing Machine) with a capacity of (5KN). (Model WDW-56), a device of Chinese origin, (Ser NO.0536), the setting at University of Technology, as shown in Figure (3.10).

Figure (3.10): Compressive strength tester.
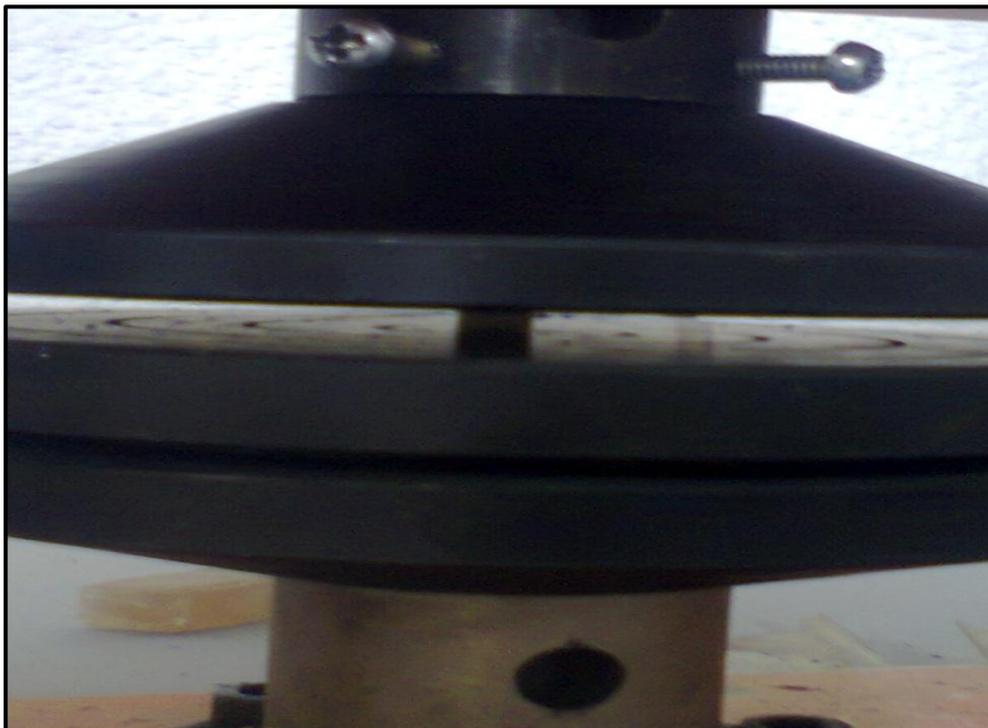
Figure (3.11): The sample during the compressive strength test.

Figure (3.12): The sample after conducting the compressive strength test.

3.6.2 Microhardness testing (Vickers)

For the purpose of measuring the microhardness by Vickers micro hardness method, samples of the material were used in the form of discs of diameter (6 mm) and thickness (2 mm), using a microhardness device that contains a diamond dent with an angle of 136◦, and a load of (5N). Where the load remains on the sample for a period of (10 sec), then it is lifted. After that, the hardness value in MPa units is taken from the digital screen installed on the device.and one of the specifications of this device is that it is of the type (TH-717 Digital Micro Hardness), the workplace at University of Technology , as shown in Figure (3.13).

Figure (3.13): Microhardness Apparatus (Vickers).

Figure (3.14): The sample before conducting the microhardness test.

Figure (3.15): The sample during the microhardness test.

3.6 Antibacterial Activity Application Measurements of for (PMMA – ZnO – TiO$_2$) and (PMMA – Zno – MgO) Nanocomposites

The study aimed to synthesize a new structure of nanocomposites to characterize them as anti-growth Streptococcus mutans isolated from human mouth and antibiotic resistance.This cross-sectional study included (60)patient subjects from (13-65) years old. These samples were obtained from the dental infectious patients and cultivated in plates containing antibiotics   amoxicillin, clindamycin, and moxifloxacin (concentrations of 16, 32 or 64 μg/ml). The Antibacterial susceptibility test for the compounds (PMMA-ZnO-TiO$_2$) and (PMMA-ZnO-MgO) was conducted using an agar disc. The tested sample of nanocomposites was determined using the disk propagation method . Antibacterial activities were performed with Gram-positive organisms (Streptococcus mutans) cultured in Muller-Hinton Medium.

Antimicrobial activity of the (PMMA-ZnO-TiO$_2$) and (PMMA-ZnO-MgO) nanocomposites tested specimen was determined using a disc diffusion method. The antibacterial activities were done by using gram positive organisms (Staphylococcus aureus) is a genus of gram-positive coccus (plural cocci) or spherical bacteria that belongs to the family Streptococcaceae, within the order Lactobacillales (lactic acid bacteria), in the phylum Bacillota. Cell division in streptococci occurs along a single axis, so as they grow, they tend to form pairs or chains that may appear bent or twisted,capable of growth both aerobically and anaerobically[111].

Bacteria (Staphylococcus aureus) was cultured in Muller-Hinton Medium. preparing samples for previous examinations, where a number of samples are prepared, with dimensions of (6 mm) and (2 mm) in thickness. Where the implantation process was for a type of bacteria present in the mouth, which is Streptococcus bacterium. It was obtained from the life sciences laboratories at the University of Babylon (Advanced Microbiology Laboratory).The disks of the(PMMA-ZnO-TiO$_2$) and (PMMA-ZnO-MgO) nanocomposites were placed over the media and incubated at (37) C^o for (24)hours. The inhibition zone diameter was measured.

Chapter Four

Results and Discussions

4.1 Introduction

In the current work the results and discussions of the electronic, structural and mechanical properties of the nanopolymer polymethacrylate (PMMA) and added oxides of Zinc Oxide (ZnO) and Titanium Dioxide (TiO_2) (PMMA-ZnO-TiO_2) for the first filling and the second filling includes polymer (PMMA), Zinc Oxide (ZnO) and Magnesium Oxide (MgO) (PMMA-ZnO-MgO) for the purpose of handling for dental filling applications.

Theoretically, the oxides were used for the purpose of improving the electronic properties of the nanopolymer to increase the efficiency of the two fillings, the particles were built with the best engineering optimization and the theoretical electronic properties were studied using density functional theory (DFT) using the (Gaussien 09) program .

Experimentally, it includes the results and discussions of the structural and mechanical measurements of the proposed pure PMMA and its nanocomposites. The effect of adding nano-oxides on the structural and mechanical properties of (PMMA-ZnO-TiO_2) and (PMMA-ZnO-MgO) nanocomposites is discussed in this chapter. The applications of the antibacterial activity of the polymer and its nanocomposites were also discussed.

4.2 Structural Properties of pure PMMA and its Nanocomposites.

4.2.1 Geometrical Properties

Several physical and chemical properties are limits by the geometry of a molecule. It is necessary to find the optimization of the molecule, in which the relaxed structure of the molecules at minimum energy. Initially, the suggested nanocomposites are designed by the Gauss View 5.0.8 program and then relaxed by using the three-parameter hybrid functional of (B3LYP) with density functional theory (DFT) together at the Gaussian 09 package of programs. The relaxed structures of the pure (PMMA), (PMMA-ZnO-TiO$_2$) and (PMMA-ZnO-MgO) nanocomposites , shown in Figures (4.1),(4.2) and (4.3).
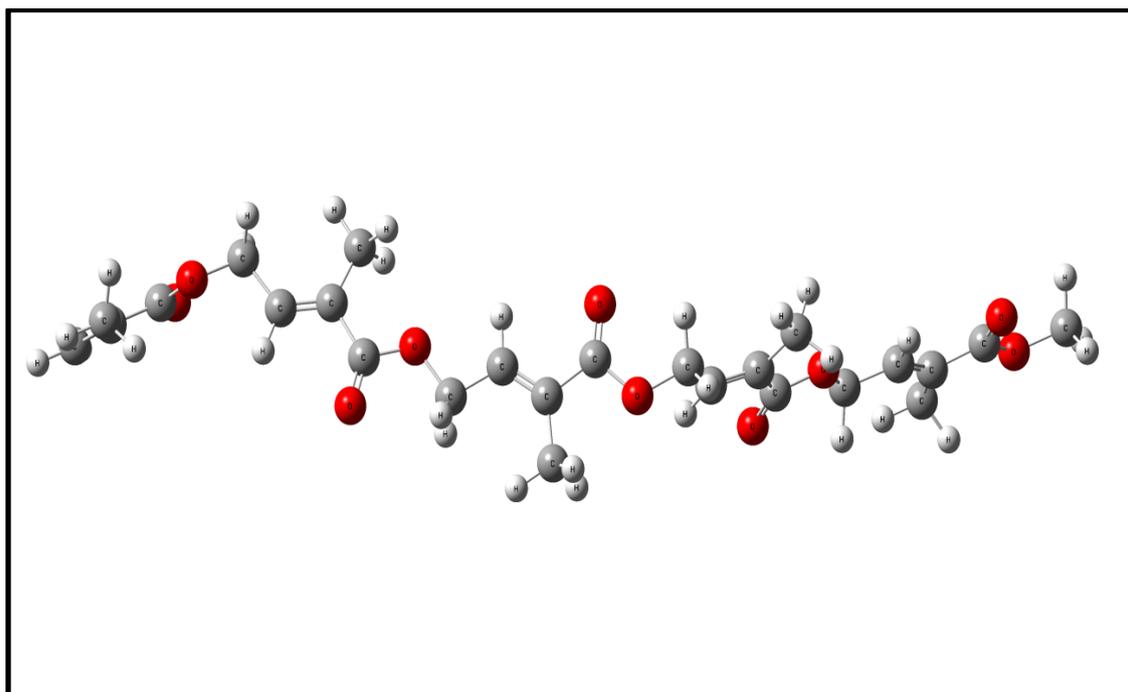
Figure (4.1): The relax structures of the pure (PMMA).
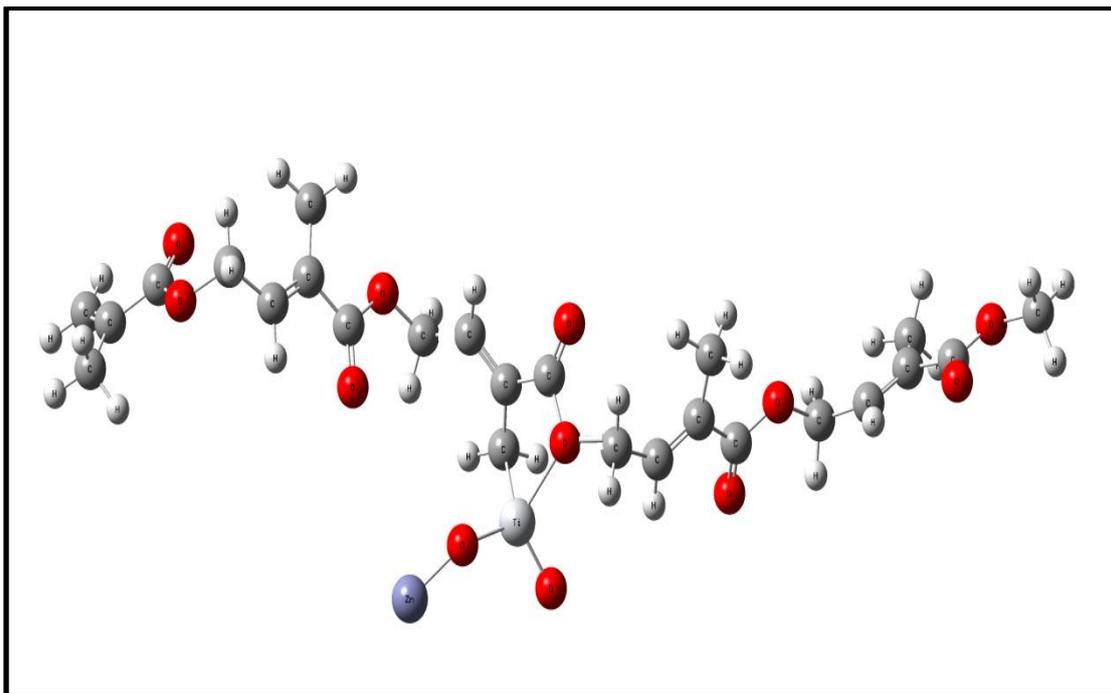
Figure(4.2): The relax structures of (PMMA-ZnO-TiO$_2$) nanocomposites.
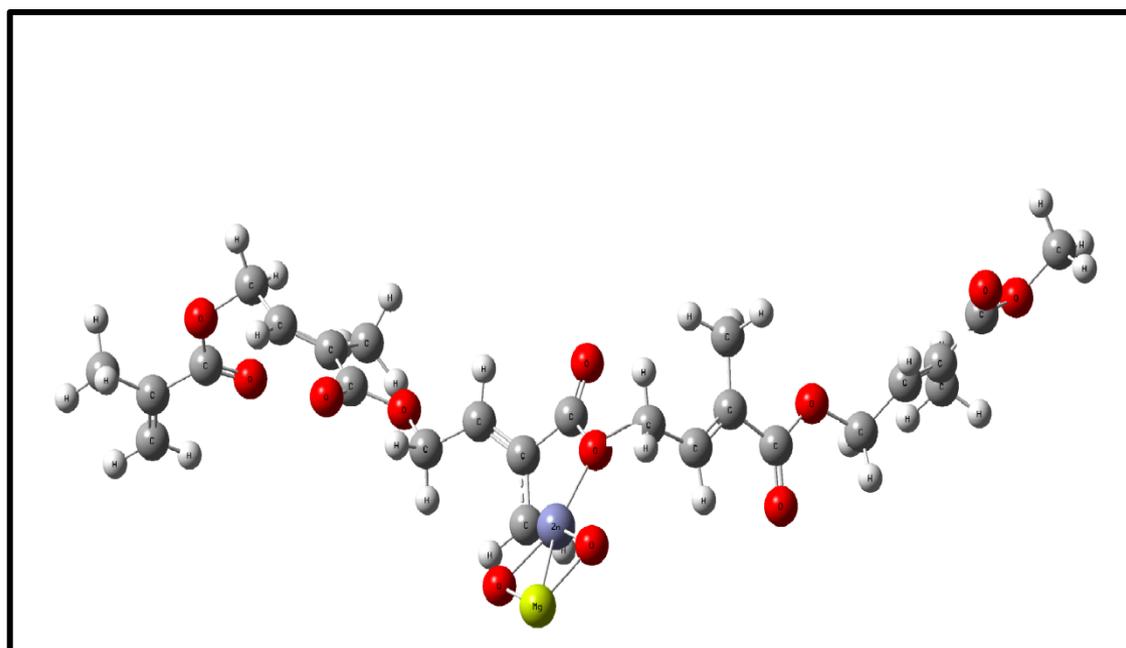
Figure (4.3): The relax structures of (PMMA-ZnO- MgO) nanocomposites.

Figures (4.4) , (4.5) and (4.6) illustrate the distribution of HOMO and LUMO shown the 3-D distribution of HOMOs and LUMOs of pure PMMA and its nanocomposites. From this figures notice, the distribution of pure PMMA is almost symmetrical but after adding nanoparticles leads

to change the map of HOMO and LUMO distribution, due to the linear combination atomic orbitals-molecular, this combination changes the symmetrical point group of the molecule, and therefore, the distribution of the HOMO and LUMO. for (PMMA), (PMMA-ZnO- TiO_2), and (PMMA-ZnO- MgO). Red color represents the positive charge and Green is the negative charge[112].

| HOMO | LUMO |
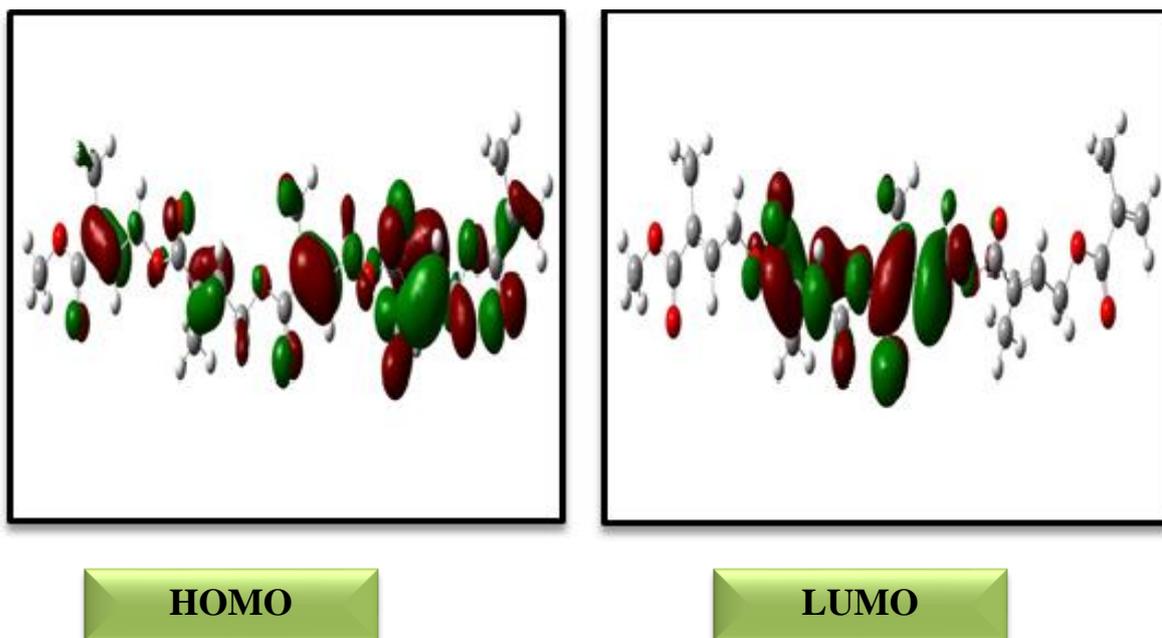
Figure (4.4): HOMO and LUMO distribution of (PMMA).

| HOMO | LUMO |
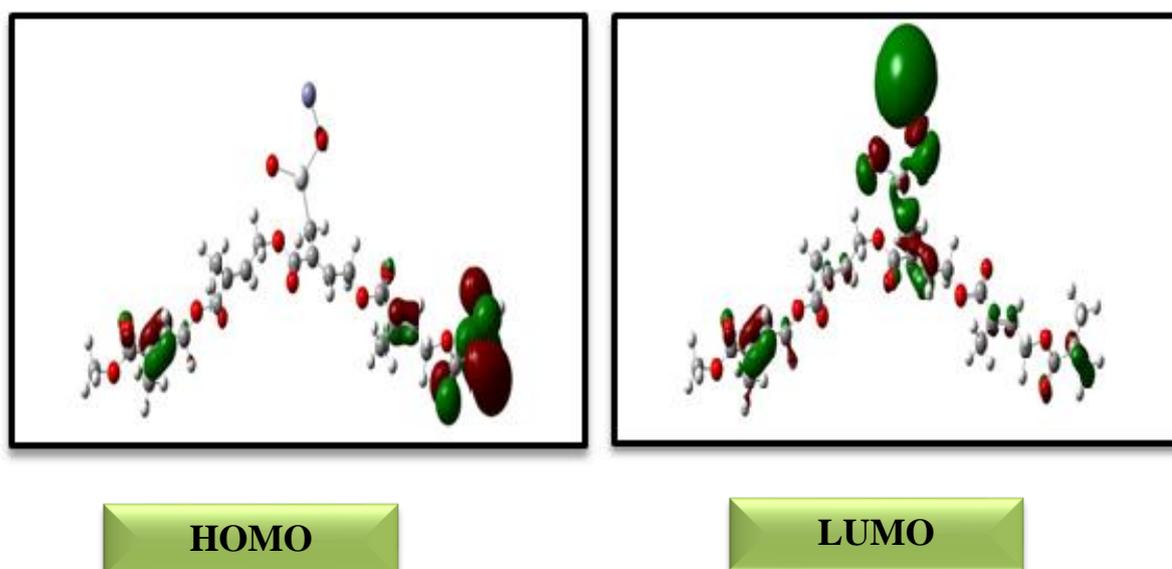
Figure (4.5):HOMO and LUMO distribution of (PMMA-ZnO-TiO_2).

| **H0MO** | **LUMO** |
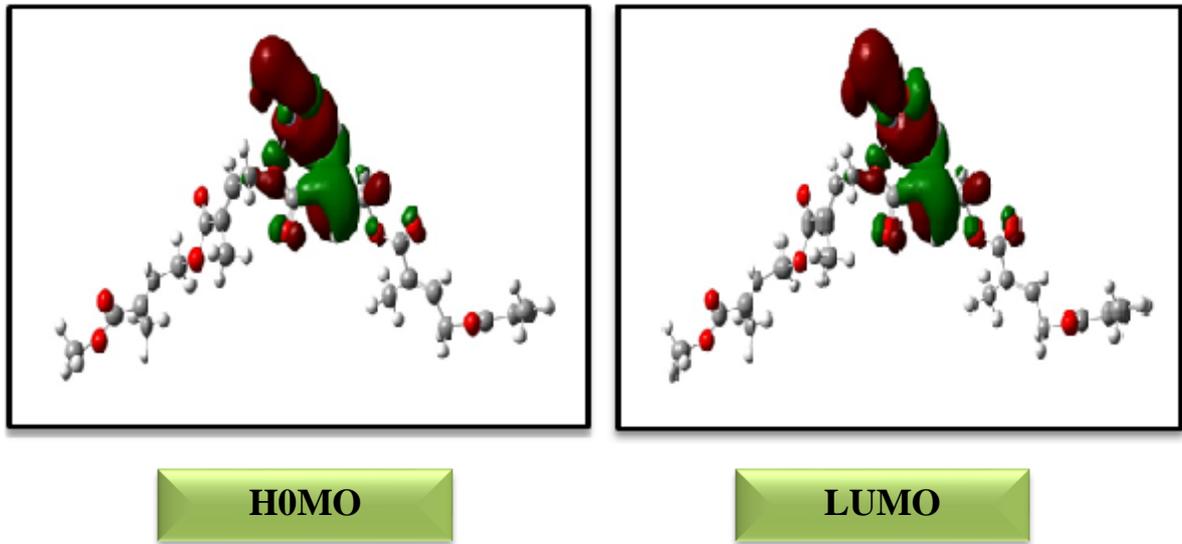
Figure (4.6):HOMO and LUMO distribution of (PMMA-ZnO-MgO).

4.2.2 Ultraviolet-Visible Spectra of pure PMMA and its Nanocomposites

The results of the study and analysis of ultraviolet visible (UV-Vis) spectra of pure (PMMA) nanoparticles and metal nanoparticles added to the nanopolymer showed that by time-dependent self-consistent field (TD-SCF) UV-Vis spectra of pure PMMA and metals added ,the results showed that the maximum peak in the ultraviolet region is at (225.38 nm) for pure (PMMA), but by adding minerals to form nano-fills, we notice an increase in the amount of absorbance for the two fillings, as it became in the first filling. (PMMA-ZnO-MgO) (920.33 nm) and for the second filling (PMMA-ZnO-TiO$_2$) (1240 nm), as the addition of nano-metals and due to the high absorption of nano-metals caused the red shift, as the absorption of the photon energy increased enough for the electron transfer Exciting it to move from a lower energy level to a higher energy level[113], shown in Figures (4.7),(4.8) and(4.9).
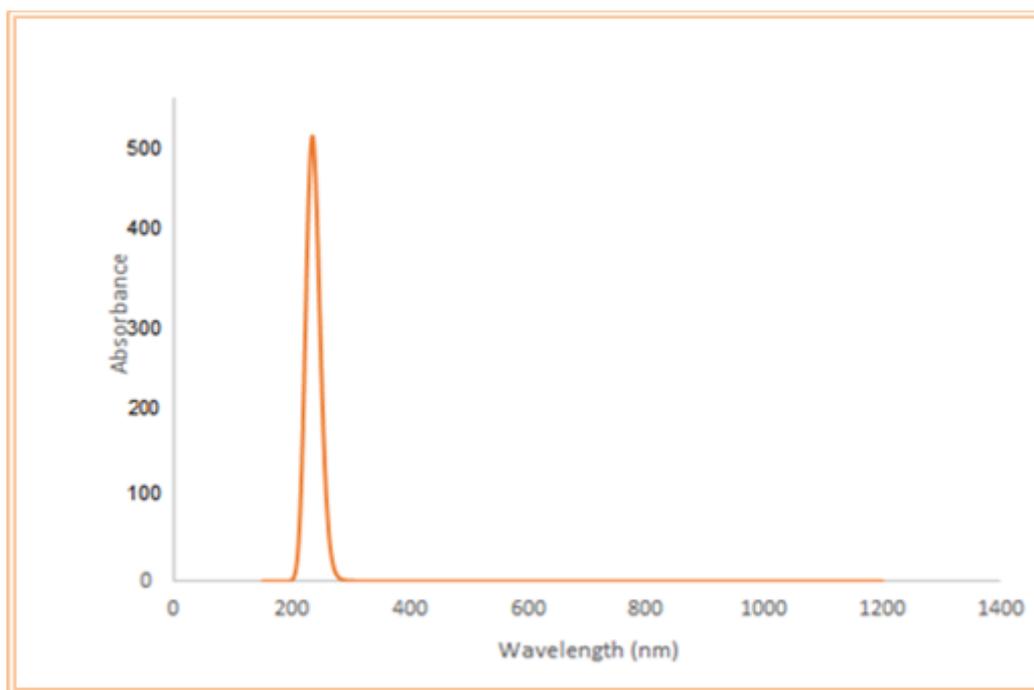
Figure (4.7): Ultraviolet-Visible spectrum for pure (PMMA).
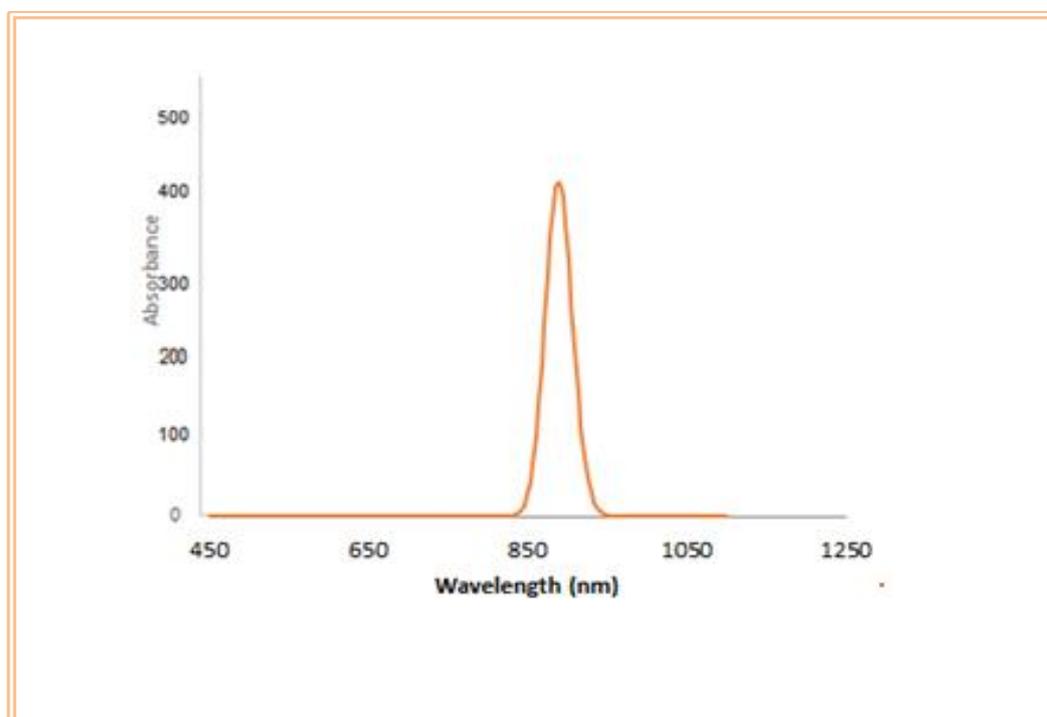
Figure(4.8): Ultraviolet-Visible spectrum for (PMMA-ZnO-MgO) nanocomposites.
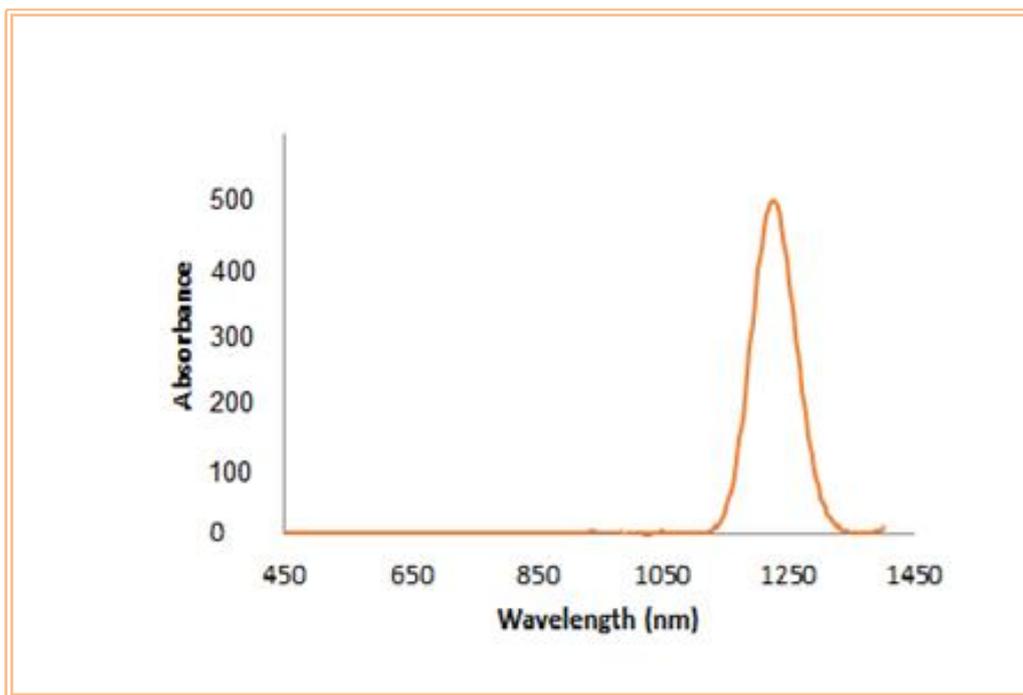
Figure (4.9): Ultraviolet-Visible spectrum for (PMMA-ZnO-TiO$_2$) nanocomposites.

4.3 The Electronic Properties of pure PMMA and its Nanocomposites

For the structures under study in this section, Table (4-3) shows the energy gap for these structures. For (PMMA) ,(PMMA-ZnO-MgO) and (PMMA-ZnO-TiO$_2$) molecule, the energy gap E$_g$ in Table (4.3) was calculated according to Koopmans theorem:

E$_g$ = E$_{LUMO}$ - E$_{HOMO}$

Which play a significant role for the reactant molecules in chemical reactions[114].

The energy gap of the studied nanocomposites is found from the interval LUMO-HOMO energy gap. The Eg values in Table (4.1) showed that the nanocomposites have different electronic properties, as it has an E$_g$ less than (5.73310 eV) of pure PMMA. In general, all nanocomposites have a lower energy gap than that of PMMA, but the nanocomposites (PMMA-ZnO-MgO) showed a decrease in energy gap to (3.89444) eV

compared to the pure polymer as observe in the nanocomposites of the second filler (PMMA-ZnO- TiO$_2$) had a lower energy gap, which reached (2.76421) eV when adding nanoscale titanium. The change in Eg of the structure is due to the changes in both the HOMO and LUMO energies, and the building of the molecular orbitals according to the linear combination of the LCAOs atomic orbitals.

This difference indicates that the energy gap depends on the nanoparticles added to the polymer. Figures (4. 4),(4.5) and (4.6) showed the 3D distribution of HOMOs and LUMOs of pure PMMA and its nanocomposites, the distribution of pure PMMA is almost symmetric but after addition of nanoparticles leads to change of the HOMO and LUMO distribution map, due to the linear combination of the molecular atomic orbitals.

As we can see in Table (4.1) the effect of adding nanoparticles on the HOMO and LUMO energies, the addition of nanoparticles has an effect on both the HOMO and LUMO energies, and it depends on the nanoparticles that were added to pure PMMA.

They show a decrease in the energy gap in the two materials Fillers compared to pure polymer, where show a change in the values of HOMO and LOMO as a result of the addition of nano oxides and the increase in chemical bonds, which leads to an increase in donor levels and an increase in the number of transferred electrons. The energy gap of the dental filling was measured to measure the sensitivity or the period of time required for the filling to remain well-functioning for a longer period of time, as the lower energy gap means that the filling lasts longer, as physics defines the energy gap as the energy required for the transmission of an electron from level to another.

This means that the decrease in the energy gap increases the permanence of the filling, i.e. its sensitivity is high, such as its sensitivity to heat and cold

Table (4.2): Electronic properties values in (eV) for the studied facilities. The values of the electronic properties of the pure polymer and the polymer after the addition of oxides to form the two nanocomposites, where an increase in the ionic potential appears, which leads to an increase in the stability of the studied system and an increase in electronic affinity as a result of the increase in the possibility of bonding with the added molecule Notice in Figure (4.11). An increase in electronegativity as a result of the different arrangement of the compounds, as we notice an increase in softness and a decrease in hardness. Notice in Figure (4.10) a decrease in hardness and an increase in softness when oxides are added and this explains the fact that the structures become less reluctant as the bonding and affinity between their molecules increase, so that the nanocomposite becomes unobstructed to the transfer of electrons and has a greater ability to attract the close electron [115].

Table (4.1) : The values of energy gap (eV) of the studied structures.

Sample	LOMO(eV)	HUMO(eV)	Eg(eV)
PMMA	-1.55213	-7.28522	5.73310
PMMA-ZnO-MgO	-4.41988	- 8.31432	3.89444
PMMA-ZnO-TiO$_2$	-6.88411	- 9.64832	2.76421

Table (4.2) : The values electronic properties in (eV) of the studied structures.

Sample	μ (eV)	X(eV)	S(eV)$^{-1}$	EA(eV)	IP(eV)
PMMA	2.86654	4.41867	0.17442	1.55213	7.28522
PMMA-ZnO-MgO	1.94722	6.36710	0.25677	4.41988	8.31432
PMMA-ZnO-TiO$_2$	1.38210	8.26621	0.36176	6.88411	9.64832
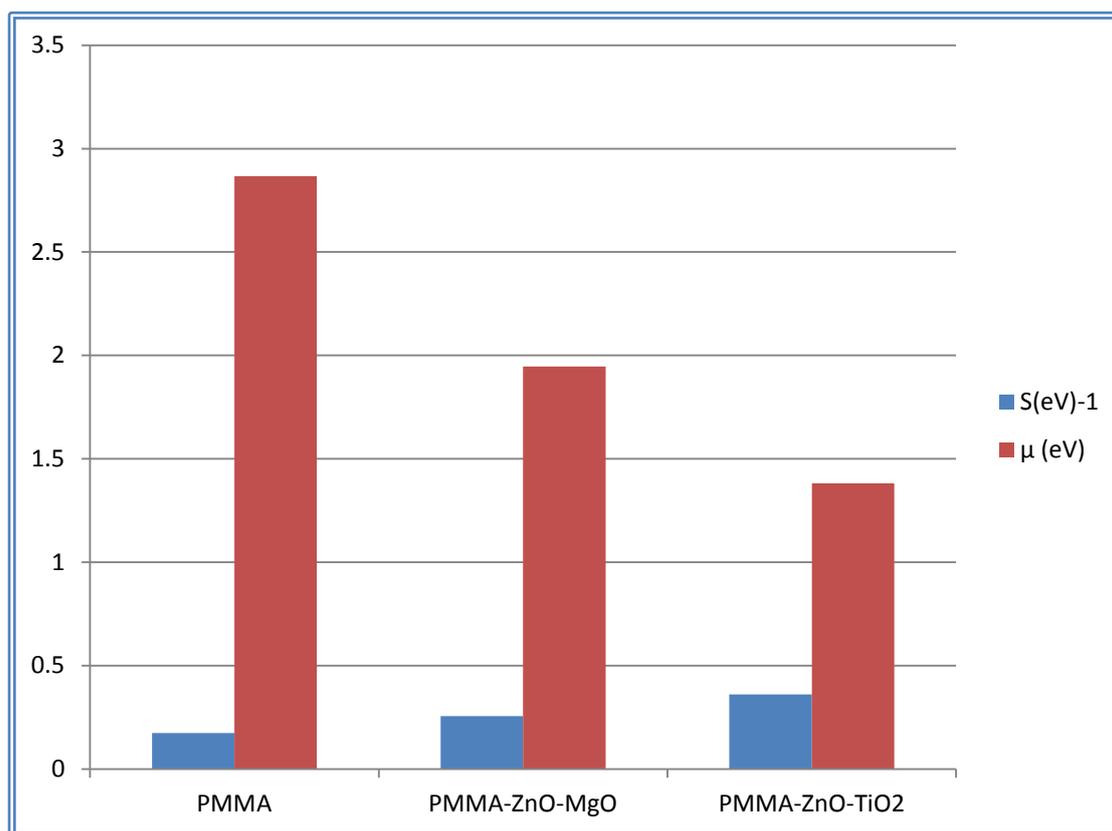
Figure (4.10): Chemical Hardness (μ)and Chemical Softness (S) in eV of pure PMMA and its nanocomposites.
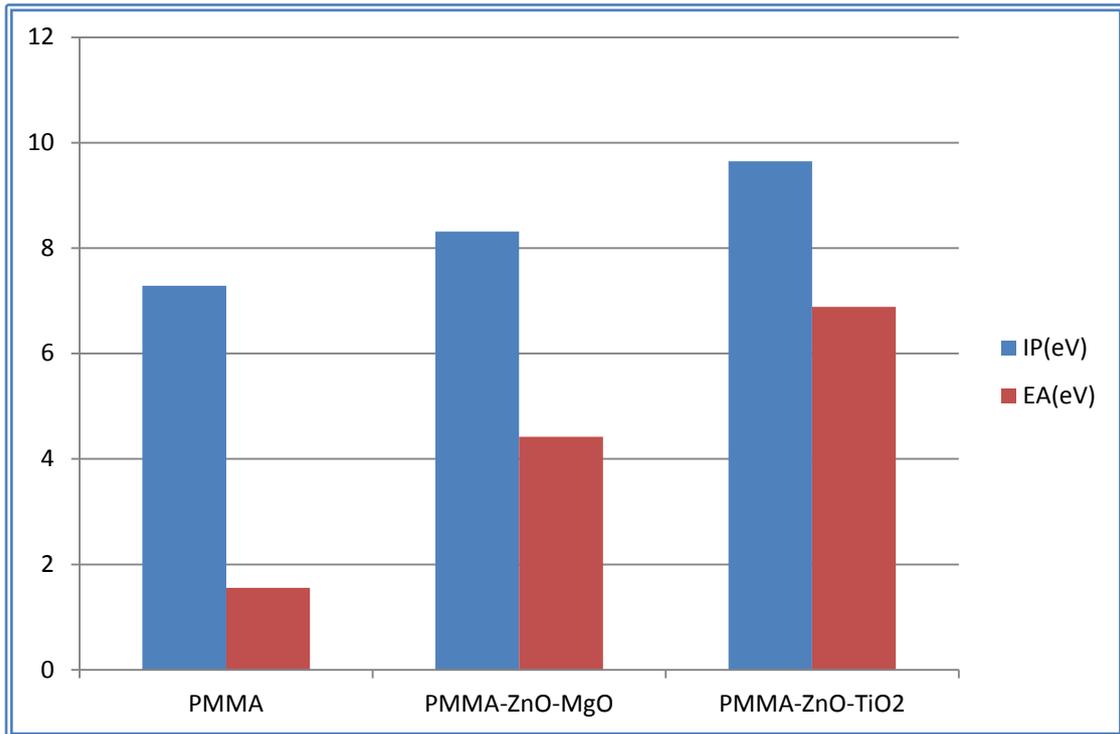
Figure (4.11): Ionization Potential (IP) and Electron Affinity (EA) in eV of pure PMMA and its nanocomposites.

4.4 Total Energy (E_T)

The total energy of the pure PMMA and the two proposed fillings was calculated, where notice a decrease in the amount of total energy after adding metals, as the total energy does not depend on the location, but depends on the number of electrons, where it is proportional inversely, meaning that adding metals led to a decrease In the amount of the total energy of for the two fillings and the total total energy is the sum of the potential energy and kinetic energy [116] .

Table(4.3) The total energy E_T for the pure PMMA and its nanocomposites.

Sample	Total energy(a.u.)
PMMA(pure)	-1634.13
PMMA-ZnO-MgO	-1422.74
PMMA-ZnO-TiO$_2$	-1086.52

4.5 Structural Properties of Nanocomposites

The structural properties of nanocomposites studied using techniques Field Emission Scanning Electron Microscope(FESEM) and Atomic Force (AFM).

4.5.1 Atomic Force Microscope (AFM)

Studying the surface topography of nanocomposites and the effect of the additive ratio of nanomaterials using atomic force microscopy (AFM) with the ability to image and analyze these surfaces with high resolution and evaluate the surface roughness based on the root mean square (RMS) through microscopy (AFM). Also study the effect of this on the filler properties to learn how the atoms are distributed and arranged on the surfaces and to identify differences, homogeneity properties, or features related to each individual atom. The study of the thin film surfaces of the prepared fillings by AFM microscopy is essential to give an illustrative picture and to calculate the surface roughness .

Surface roughness is important in describing dental composites because the surface composition and composition of the composites, in addition to the morphology of the fillings, have a significant impact on the properties of the filling, as it has been proven to be decisive factors in

both loading and strength of the filling [117]. As the higher the roughness percentage, the greater its ability to adhere to the tooth[117].

Results of (AFM) tests for the two fillings (PMMA- ZnO, TiO$_2$) and (PMMA- ZnO, MgO), where the topographic images consist of doped PMMA with different ratios (0, 2.5, 5, 7.5) wt.% by weight. The percentage of nanocomposites prepared by the polymer casting method is shown. The pure nanoparticles have a granular surface with few zigzags, as shown in Figures (4.12), (4.13).

The roughness increases with the increase in the percentage of doping in addition to the increase in the root mean (RMS), and the average grain diameter also shows the same behavior and increase, the regularity in the amount of increase and in the vertical arrangement on the crystal axis, where the increase in doping leads to Increasing the number of particles per unit volume, which leads to the loss of the energy of the particles in an amount sufficient to form molecular clusters, and these clusters reach the surface to form small grains that begin to grow, notice that the size of the grains increases with the increase in the added percentage.

Note that the roughness of the filling that contains a second Titanium Dioxide is higher than the filler containing magnesium oxide material as a result of the diameter and size of titanium dioxide (TiO$_2$) is higher than the diameter of the crystal size of magnesium oxide (MgO), and this result is consistent with the (FESEM) results. Table (4.4), (4.5) shows the roughness of (PMMA- ZnO- TiO$_2$) and (PMMA- ZnO- MgO), root mean square (RMS), where the results increase in roughness rate and root mean square RMS with increasing mixing ratios. It is clear that The surface is rough, and an increase in RMS leads to an increase in crystal growth. This indicates an improvement in the crystal structure with an

increase in the percentage of addition. However, the roughness of these surfaces remains less than (200) nm, which is the initial point for the accumulation of bacterial plaque and the risk of caries and gum infections, so it can be considered that these surfaces do not represent any danger, and this is agree with the researcher [118].
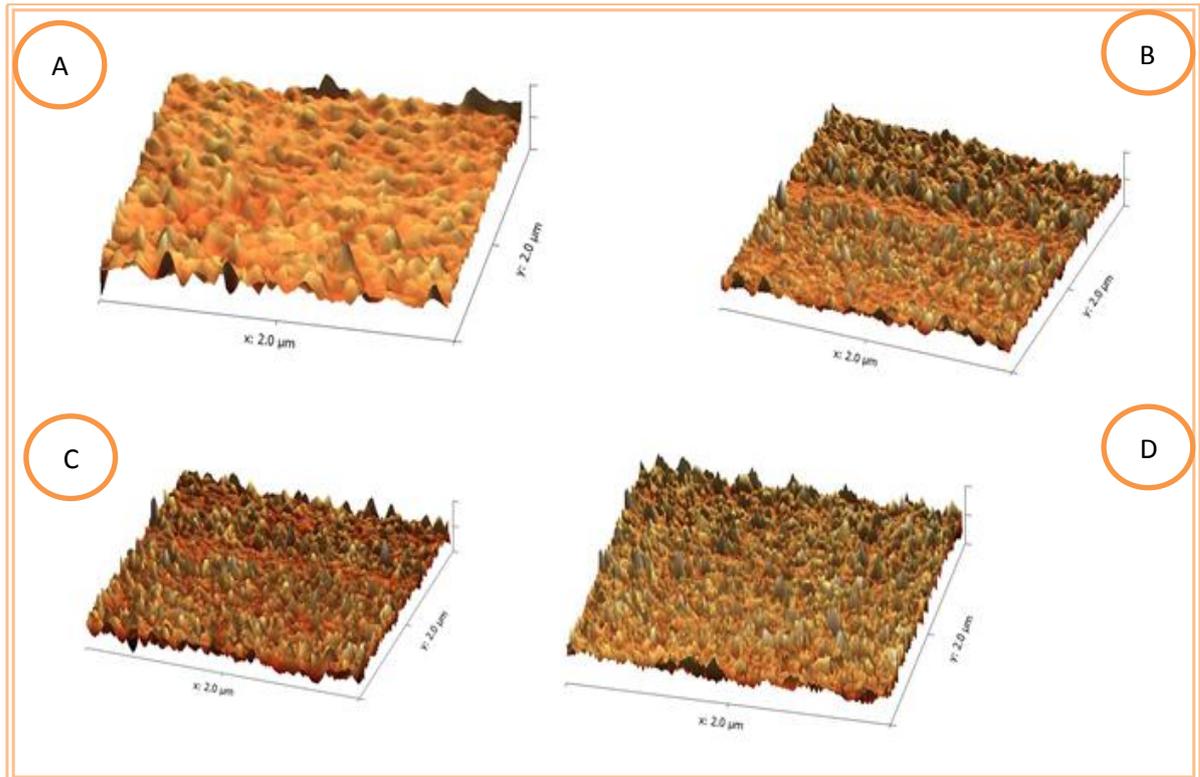
Figure(4.12): AFM images of (PMMA- ZnO - TiO$_2$) nanocomposites. (A) PMMA$_{pure}$,(B) (PMMA- ZnO - TiO$_2$) $_{2.5\ wt.\%}$, (C) (PMMA- ZnO - TiO$_2$) $_{5\ wt.\%}$, (D) (PMMA- ZnO - TiO$_2$) $_{7.5\ wt.\%}$.
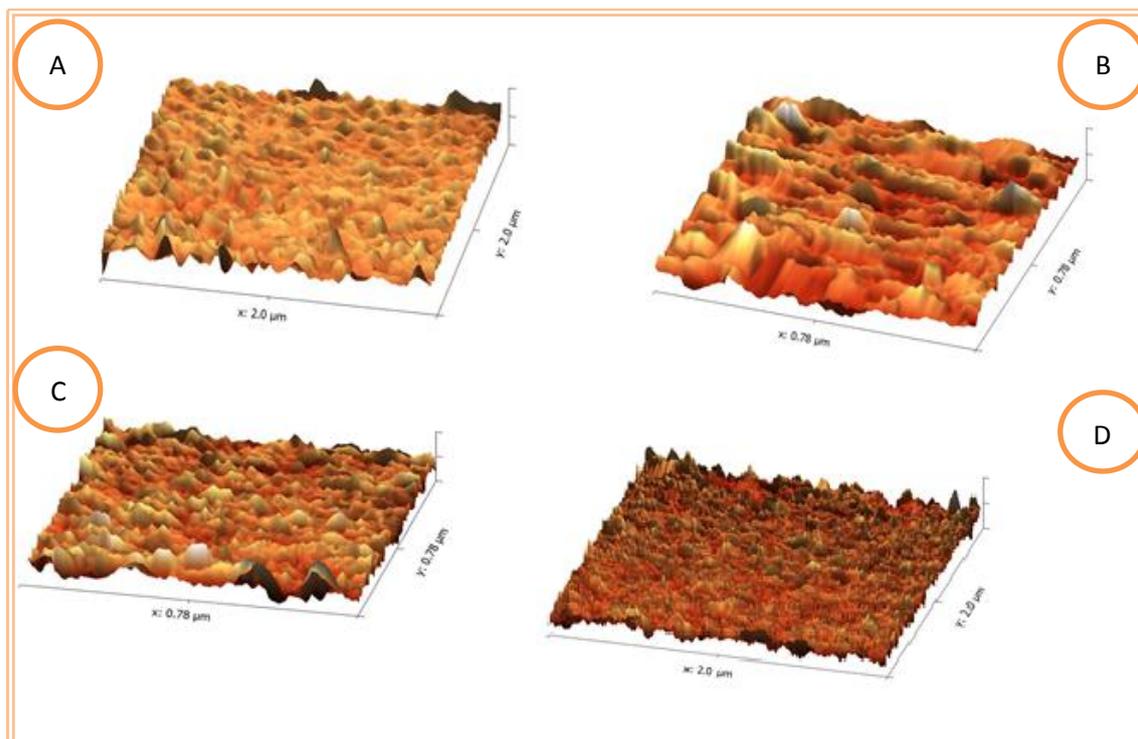
**Figure(4.13): AFM images of (PMMA- ZnO - MgO) nanocomposites. (A)
PMMA$_{pure}$,(B) (PMMA- ZnO - MgO) $_{2.5\ wt.\%}$, (C) (PMMA- ZnO - MgO) $_{5\ wt.\%}$,
(D) (PMMA- ZnO - MgO) $_{7.5\ wt.\%}$.**

Table (4.4): AFM parameters for (PMMA- ZnO – TiO$_2$) nanocomposites.

Sample	(wt%)	RMS (nm)	Roughness (nm)	Average Diameter (nm)
PMMA Pura	0	7.08	7.33	20.98
PMMA-ZnO-TiO$_2$	2.5	18.47	12.36	35.92
PMMA-ZnO-TiO$_2$	5	27.62	18.72	46.79
PMMA-ZnO-TiO$_2$	7.5	33.38	24.63	55.85

Table (4.5): AFM parameters for (PMMA- ZnO - MgO) nanocomposites.

Sample	(wt%)	RMS (nm)	Roughness (nm)	Average Diameter (nm)
PMMA Pura	0	7.08	7.33	20.98
PMMA-ZnO-MgO	2.5	12.67	7.80	26.92
PMMA-ZnO-MgO	5	20.31	9.63	32.79
PMMA-ZnO-MgO	7.5	25.55	14.72	40.85

4.5.2 Field Emission Scanning Electron Microscopy (FESEM)

The surface structure of the nanocomposites of (PMMA-ZnO-TiO_2) and (PMMA-ZnO-MgO) fillers can be photographed. The FESEM images visualize the surface structure of the nanocomposites with high clarity, showing the surface shapes of pure (PMMA) and nanocomposites (PMMA-ZnO-TiO_2) and (PMMA-ZnO-MgO), respectively, at (0, 2.5, 5 and 7.5) wt%. To study the morphology and arrangement of nanocomposites in greater depth. FESEM images show that in the first filling (TiO_2), the agglomerations are high, and the titanium material is well dispersed within the PMMA matrix with clear spherical shapes and this is evidence of the crystalline state of the material, and these agglomerations of molecules increase with increasing additive weight ratios[119]. as shown in Figures (4.14).
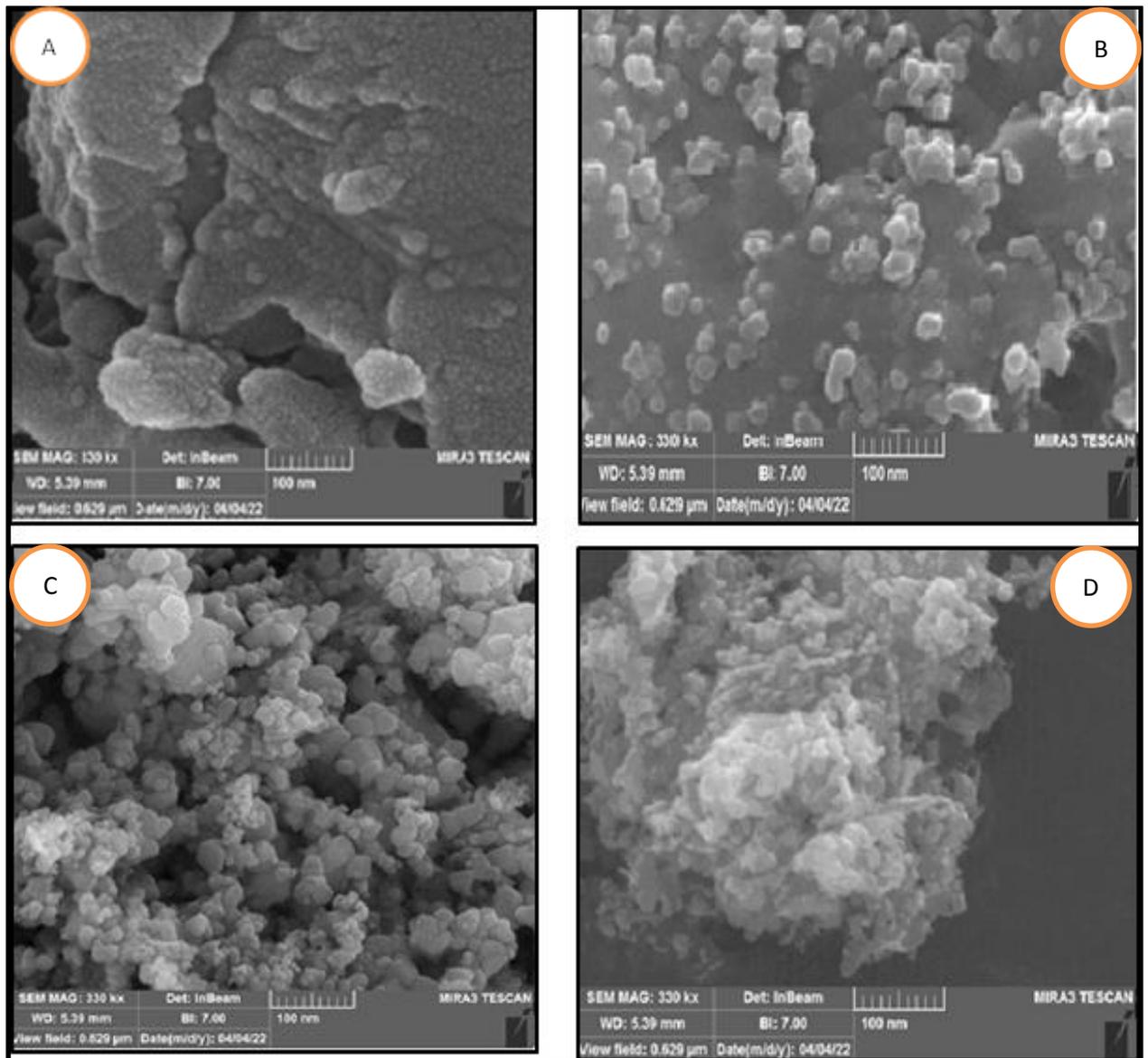
Figure(4.14):FSEM images of (PMMA- ZnO – TiO$_2$) nanocomposites. (A) PMMA$_{pure}$,(B) (PMMA- ZnO - TiO$_2$) $_{2.5\ wt.\%}$, (C) (PMMA- ZnO - TiO$_2$) $_{5\ wt.\%}$, (D) (PMMA- ZnO - TiO$_2$) $_{7.5\ wt.\%}$.

In the second filling (PMMA-ZnO-MgO), we also find high homogeneity and uniform distribution within the polymer matrix in the form of sheets and layers as a result of adding (MgO) to the second filling. As this homogeneity and agglomeration of the two fillings gives strength, hardness and increased compactness, which leads to obtaining improved properties, and this is consistent with the results of AFM. These

results are similar to what the researcher reached [120]. as shown in Figures (4.15)
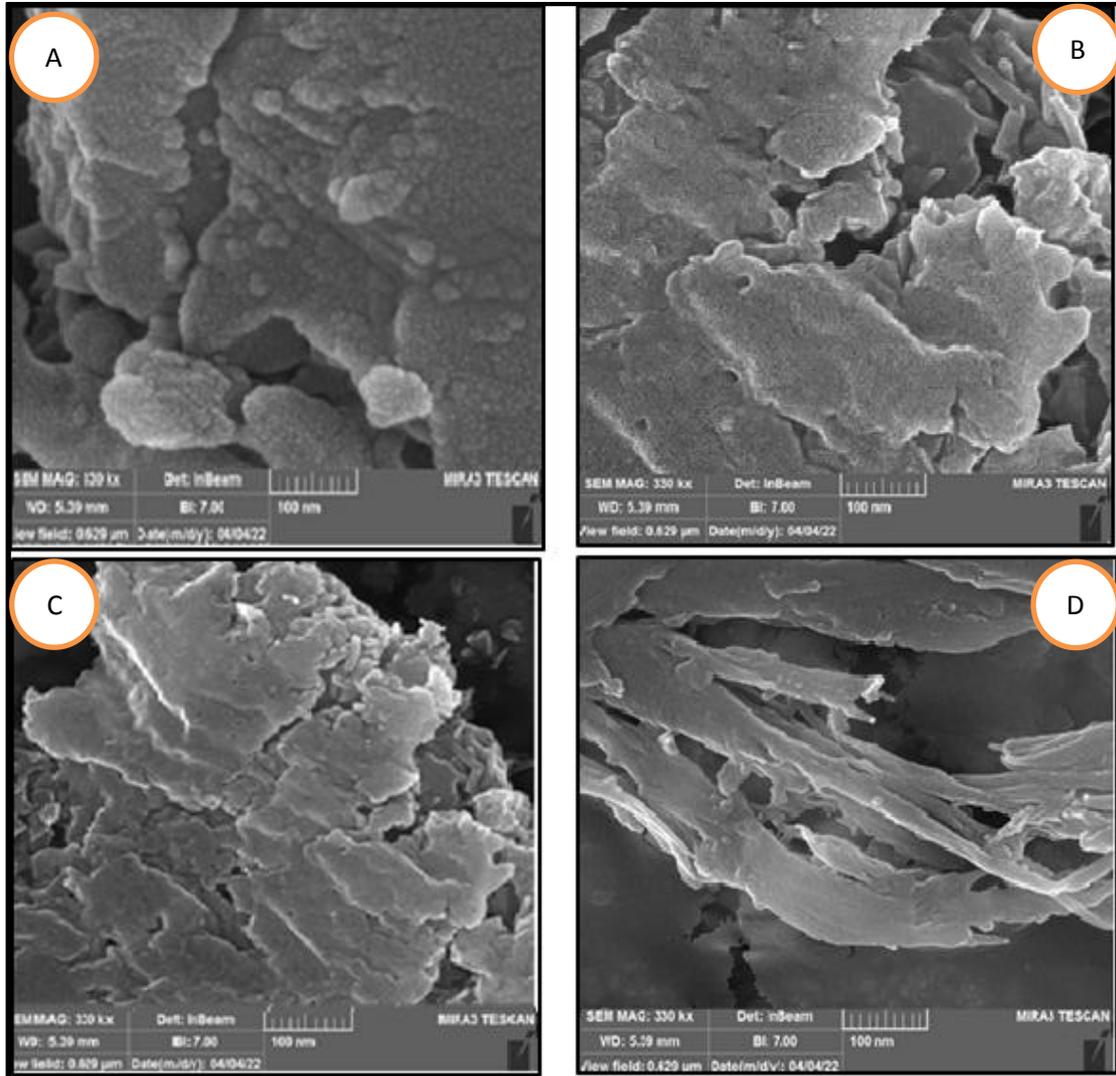
Figure(4.15):FESEM images of (PMMA- ZnO - MgO) nanocomposites. (a) PMMA$_{pure}$,(b) (PMMA- ZnO - MgO) $_{2.5 wt.\%}$, (c) (PMMA- ZnO - MgO) $_{5 wt.\%}$, (d) (PMMA- ZnO - MgO) $_{7.5 wt.\%}$.

4.6 Mechanical properties

Mechanical properties of nanocomposites studied using techniques Compressive strength and Hardness .

4.6.1 Compressive strength

Compressive strength (σ) is the most important feature of dental fillings. The compressive strength test is important in laboratory analyses, which are usually considered good indicators for simulating the forces experienced by fillings during chewing in the mouth [121]. Therefore, dental fillings must have a high value of compressive strength to withstand the external forces generated through chewing [122]. All samples are subject to the quality standard (ISO.9917). The ratio of length to diameter (2:1) used in these samples [123].

In this study, the compressive strength was calculated and the results of the compressive strength values for the fillings consisting of (PMMA-ZnO-TiO$_2$) (PMMA-ZnO-MgO) and the obtained compressive strength values are shown in Tables (4.6),(4.7). It turned out that the highest value of compressive strength for the fillings containing (TiO$_2$) was (235 MPa) at (7.5% g) at 20 (sec) and (345 MPa) at 30 (sec).

For fillings containing (PMMA-ZnO-MgO), the highest value of compressive strength was (160 MPa) at (7.5% g) at 20 (sec) and (211 MPa) at 30 (sec), where we notice the compressive strength increases with Increasing the time period of exposure, as the exposure led to the bonding of the filling with each other faster and its adhesion to the tooth, as the optical effectiveness is to connect a high-intensity beam, and the distance between the light source and the filling is very important. The compressive strength increases with the increase of nanomaterials. The high percentage of nanoparticles will increase the viscosity of the polymer[124]. These materials are able to form bonds with each other to

form a filling with high mechanical properties. This is consistent with the arrangement of the particles in the theoretical aspect, where the best engineering optimization has been obtained. As a result of the existing strong bonding properties that provide remarkable mechanical reinforcement to form the best filler structure. It is effective in enhancing the compressive strength of fillings.

It is interesting to note that the addition of (TiO_2) by (7.5% g) showed a significant improvement in compressive strength more than that of (MgO) because its molecules have strength and hardness resulting from its hexagonal crystal structure, where (TiO_2) is considered one of the strongest minerals with hardness The high quality and ability to withstand fracture and high load makes it highly efficient to withstand the force of chewing and the pressure that will occur on the tooth. As we can see from Table (4.6),(4.7) and Figure (4.16),(4.17), we notice that the pressure resistance is affected by the type of composite material and the type of filling. Therefore, the mechanical properties are improved by mixing the nanomaterials with the nanopolymer [124].

Table (4.6): Compressive strength(σ) parameters for (PMMA- ZnO - MgO) nanocomposites.

light period (sec)	σ (MPa)at 2.5% g	σ (MPa)at 5% g	σ (MPa)at 7.5% g
20	138	144	160
30	187	197	211
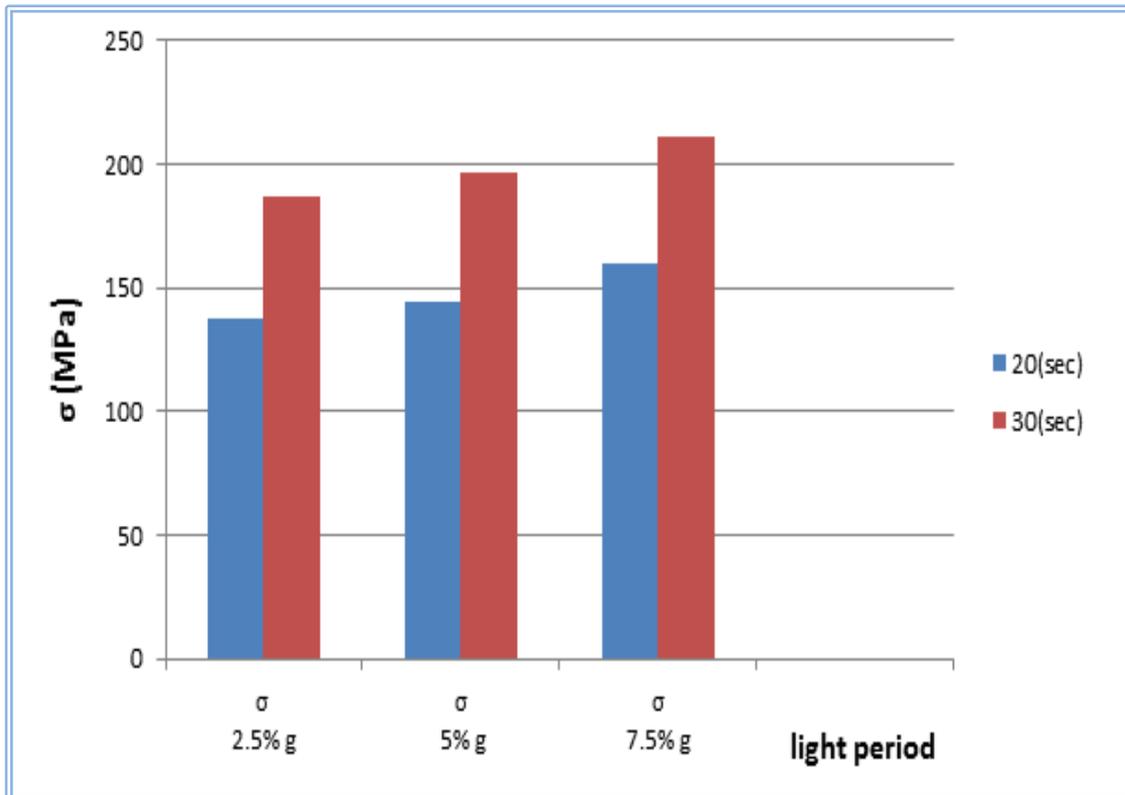
Figure(4.16):The effect of adding nanocomposites on the Compressive strength(σ) for (PMMA- ZnO – MgO) .

Table (4.7): Compressive strength(σ) parameters (PMMA- ZnO – TiO$_2$) nanocomposites.

light period (sec)	σ (MPa)at 2.5% g	σ (MPa)at 5% g	σ (MPa)at 7.5% g
20	186	213	235
30	287	304	345
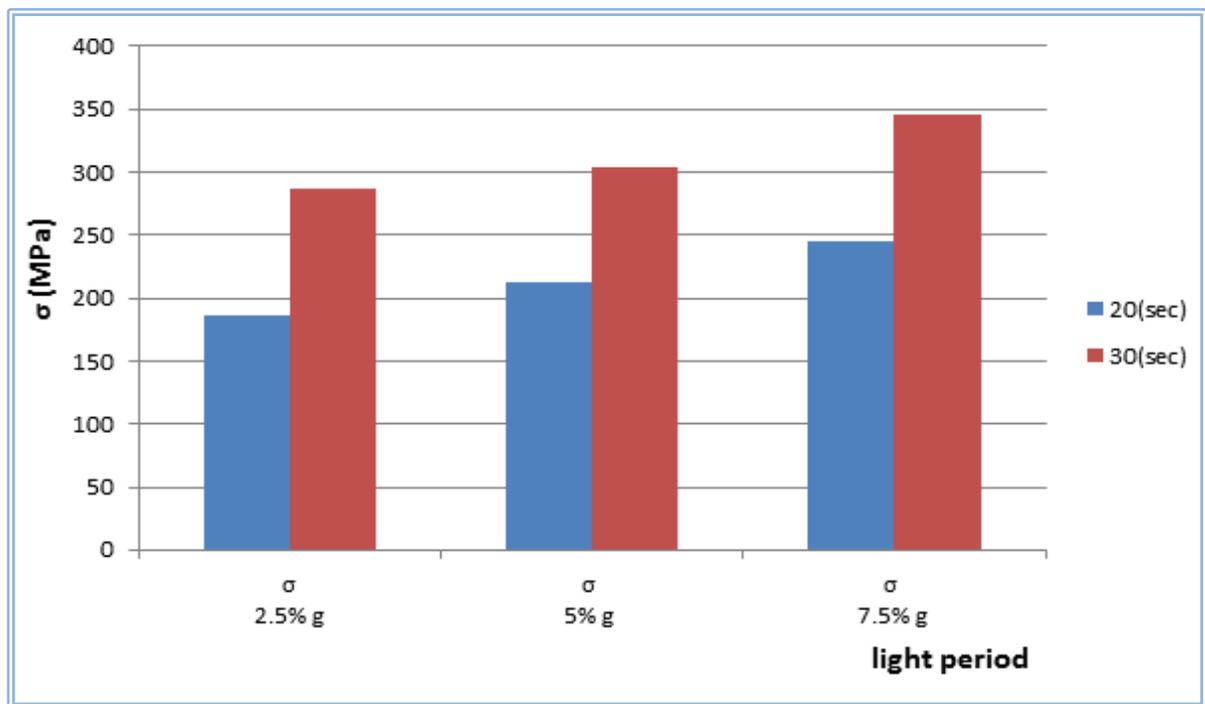
Figure(4.17):The effect of adding nanocomposites on the Compressive strength(σ) for (PMMA- ZnO – TiO$_2$) .

4.6.2 Hardness

Hardness is defined as a surface's resistance to scratching, cutting, and penetration. Table (4.8),(4.9) and Figure (4.18),(4.19) show the hardness values in units (Mpa) for the two prepared fillings. It can be seen that the surface hardness increases with the increase in the added percentage which leads to an increase in the hardness. There is a discrepancy in the stiffness values between the first and second fillers with increasing load due to the continuous shrinkage of the fillers in the initial spacings or the bonding and bonding between the filler particles. Therefore, the surface hardness depends on the type of nanomaterials and their proportion in the filler.

As in the case of pressure, we note that the filling containing Titanium Dioxide has a higher hardness than the filling containing Magnesium oxide, as Titanium dioxide has high strength and hardness and is malleable and ductile just like steel, as the filling containing (MgO) has a percentage of (7.5%) g was (86.8) MPa at 20 (sec) and (92.7) MPa at 30 (sec). While in the second filling containing TiO_2 the highest hardness was (7.5%) g was (94.8) MPa at 20 (sec). and (97.1) MPa at 30 (sec). Where the hexagonal crystal system, strong bonds, duration of exposure to light, type of nano-material and its percentage in the filler play a role in enhancing the strength and durability of the filler, as the increase in the addition ratio increases the surface hardness. Also, nanoscale fillers rarely have spaces between molecules. All experimental nanocomposites showed good ISO hardness values (above 50 MPa) [125].

On the other hand, although the fillers are similar in size, they contain nanoparticles that have unique and different properties and these properties are not only a matter of particle size, but also the qualities that these small sized particles cause of strength and durability. It has

reinforcing effects of the filler it contains, which makes the surface highly scratch-resistant as in[126,127].

Table (4.8): Hardness parameters for (PMMA- ZnO - MgO) .

light period (sec)	Hardness (MPa) at 2.5% g	Hardness (MPa) at 5% g	Hardness (MPa) at 7.5% g
20	84.3	85.4	86.8
30	90.2	91.6	92.7
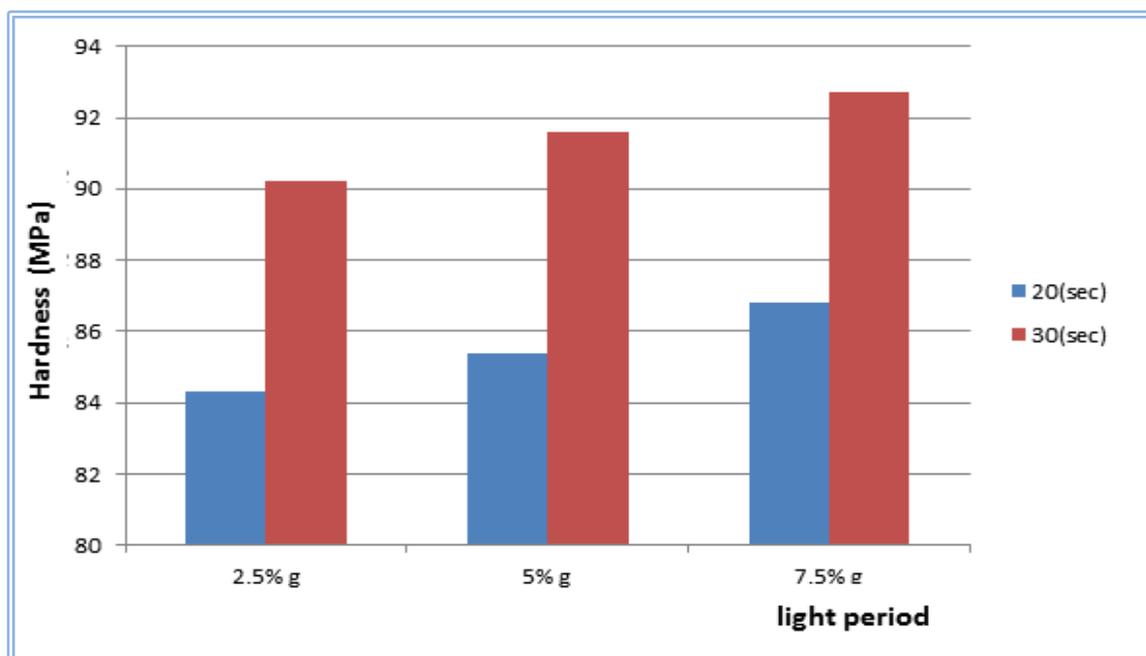
Figure(4.18):The effect of adding nanocomparticles on the hardness of nanopolymers for (PMMA- ZnO - MgO).

Table (4.9): Hardness parameters for (PMMA- ZnO – TiO$_2$) .

light period (sec)	Hardness (MPa) at 2.5% g	Hardness (MPa) at 5% g	Hardness (MPa) at 7.5% g
20	93.4	94	94.8
30	95.4	96.3	97.1
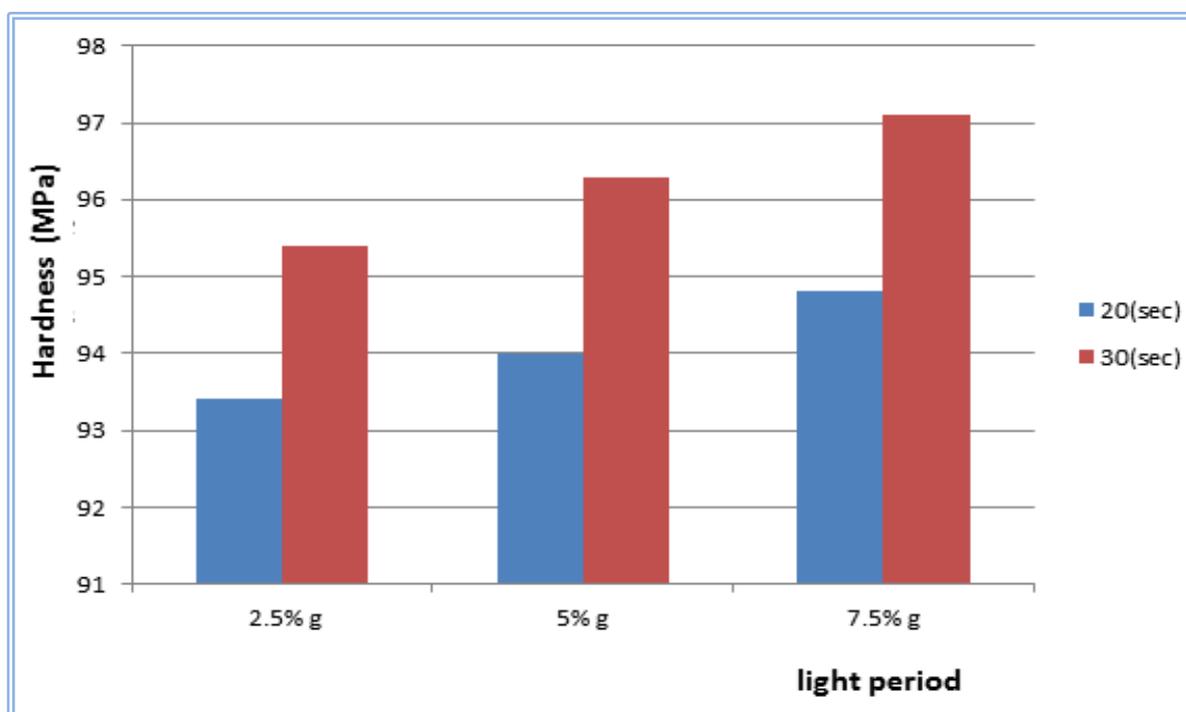
Figure(4.19):The effect of adding nanocomparticles on the hardness of nanopolymers for(PMMA- ZnO – TiO$_2$).

4.7 The Application of (PMMA-ZnO-TiO$_2$) and (PMMA-ZnO-MgO) Nanocomposites

The antibacterial activity of the(PMMA-ZnO-TiO2) and (PMMA-ZnO-MgO) Nanocomposites samples tested against results showed Gram-positive (Streptococcus bacterium) present in the mouth.This cross-sectional study included 60 patients subjects from thirteen to sixty-five years old. These samples were obtained from the dental infectious patients and cultivated in plates containing antibiotics amoxicillin, clindamycin, and moxifloxacin (concentrations of 16, 32 or 64 µg/ml). where we see that the addition of nanoparticles is an attractive option for antibiotics because it has an antibacterial effect, so it has been increasingly used to target bacteria as an alternative to antibiotics.

As the addition of nanomaterials to (PMMA) nanopolymer leads to the generation of antibacterial activity,and the obtained data are presented in Figures (4.20 - 4.21).

One of the most important nanomaterials added to the two fillings is

(ZnO), which is attributed to its ability to damage the cell wall of bacteria and disrupt DNA replication, and (TiO$_2$) were added to the first filling (PMMA-ZnO-TiO$_2$), as it showed that it has a high ability It generates small pores in the bacterial cell walls, which leads to increased permeability and cell death. It also has a high ability to reduce bacterial adhesion to the filling, thus preserving the tooth from bacterial activity The nanocomposite(PMMA-ZnO-TiO$_2$)showed high activity performance against S. mutans with the increase of (PMMA-ZnO-TiO$_2$). The inhibition zone values according to concentration, 2.5% .5% and 7,5% were (12mm, 15 mm, and 18mm), respectively for the anocomposite and zero activity for pure

PMMA which indicates that there is no antibacterial activity for the pure PMMA polymer [128].

As for the second filling, which is composed of (PMMA-ZnO-MgO), the results show that the addition of(MgO) is highly effective. In resisting bacteria and harming the bacterial membrane, it is considered one of the antibacterial substances in a large way, as it interacts with the bacterial surface and enters the inside of the bacteria to reduce its activity and inhibit it. It can also be decomposed and metabolized efficiently in the body, and the decomposition products emitted from Mg^{2+} and OH ions can be decomposed.

It is effectively eliminated from the body, because magnesium is an essential mineral for humans . The nanocomposite (PMMA-ZnO- MgO) showed high activity performance against S. mutans with the increase of(PMMA-ZnO- MgO). The inhibition zone values according to concentration, 2.5% .5% and 7,5% were (8 mm,   10mm, and 13 mm), respectively for the nanocomposite and zero activity for pure PMMA which indicates that there is no antibacterial activity for the pure PMMA polymer [129].

It was also noted that there is a discrepancy between the results of the two proposed fillings, where it was found that the filling containing (TiO_2) has a higher ability to inhibit bacteria due to its ability to destroy the cell wall more than(MgO), and that the cell wall of Gram-positive bacteria is thicker than the cell wall of Gram-negative bacteria, where it was proved that (TiO_2) has a higher ability to permeate the peptidoglycan layer than positive bacteria, the strength, high porosity and high ability to interact with the peptidoglycan layer made it a higher inhibitory region than the (MgO) containing filling[130]. .
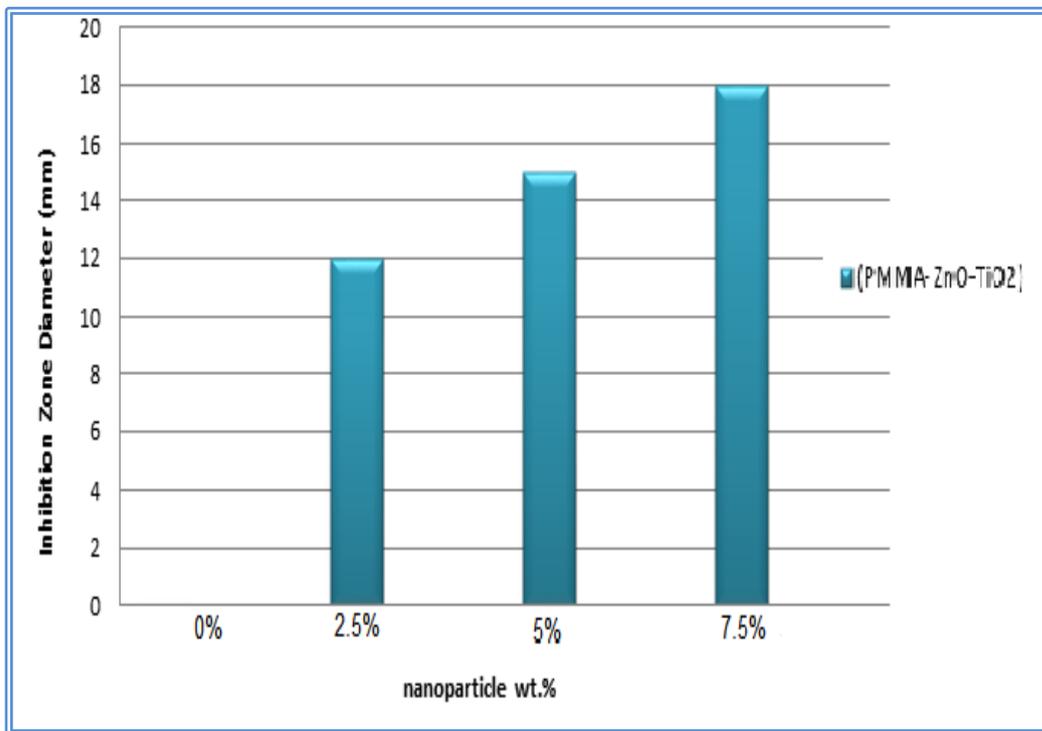

Figure (4.20) :Antibacterial application of (PMMA-ZnO-TiO$_2$)as a function of nanopartical concentrations against Streptococcus bacterium .
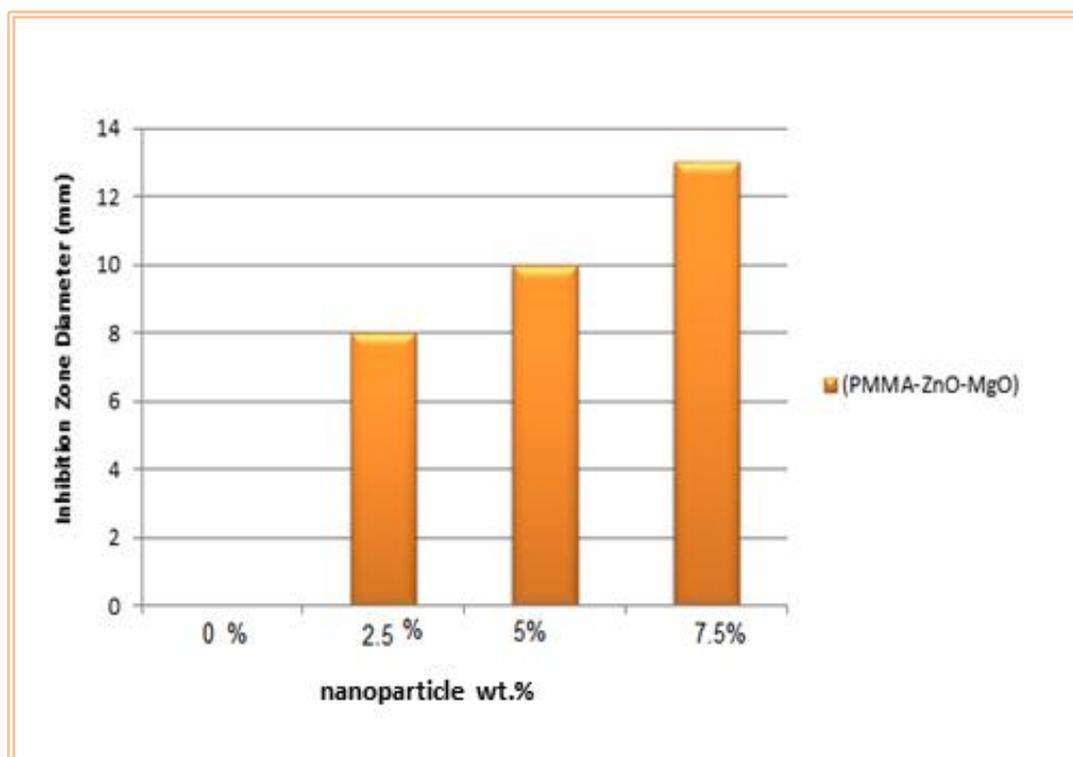
Figure (4.21) :Antibacterial application of (PMMA-ZnO-MgO)as a function of nanopartical concentrations against Streptococcus bacterium .

Chapter Five

Conclusions

and

Future works

5.1 Conclusions

There are many conclusions that can be summarized in the following points:

1. The geometrical optimization of pure PMMA was studied by B3LYP as well as the geometrical optimization of (PMMA-ZnO-TiO$_2$) and (PMMA-ZnO-MgO).

2. The result of HOMO, LUMO and energy gap of pure PMMA is obtained. The addition of nanoparticles to PMMA showed an effect on calculating two states (HOMO, LUMO).

3. The results of the study and analysis of ultraviolet visible (UV-Vis) spectra of pure (PMMA) nanoparticles and metal nanoparticles added to the nanopolymer showed that by time-dependent self-consistent field (TD-SCF) UV-Vis spectra of pure PMMA and metals added ,the results showed that the maximum peak in the ultraviolet region is at (225.38 nm) for pure (PMMA), but by adding minerals to form nano-fills, Increase in the amount of absorbance for the two fillings, as it became in the first filling. (PMMA-ZnO-MgO) (920.33 nm) and for the second filling (PMMA-ZnO-TiO$_2$) (1240 nm), as the addition of nano-metals and due to the high absorption of nano-metals caused the red shift.

4. The results show the charge distribution in HOMO and LUMO three-dimensional distribution of pure PMMA and its nanocomposites, the distribution of pure PMMA is almost the same but after addition of nanoparticles leads to change of HOMO and LUMO distribution map, due to the linear combination of molecular atomic orbitals.

5. One of the important results in this study is that the presence of nanoparticles reduces the energy gap of (PMMA-ZnO-TiO$_2$) nanoparticles have the smallest values of energy gap compared to

others, and the energy gap is small which means small excitation energies. Decrease in the energy gap from (5.73301) to (3.89444) eV in (PMMA-ZnO-MgO) and (2.76421) eV in (PMMA-ZnO-TiO$_2$).

6. An increase in the ionic potential, which leads to an increase in the stability of the studied system and an increase in electronic affinity due to the increase in the possibility of binding to the added molecule.

7. Nanofillers have low electrochemical hardness and high electronic softness. These results are the main receiver as an indication that the band gap becomes rather soft. The low electrochemical hardness and high electronic softness indicate the high activity of the nanocomposites in their interaction with surrounding species.

8. Pure (PMMA) has a lower electronegativity index than nanofillers. This indicates that the presence of the nanoparticles gives the structure the ability to accept an electron from the surrounding species.

9. The study show an increase in the roughness and grain size with the increase in the added percentage compared to the nanopolymer, as well as the increase in the doping percentage.

10. The study show the mechanical properties and proved that the (TiO$_2$)containing nano-filling has higher resistance to test the compressive strength and hardness than the (MgO)containing filling, and the reason is due to strength and hardness (TiO$_2$) and higher surface roughness than the surface roughness of(MgO) as shown by the atomic force microscopy (AFM) measurement.

11. Studying the effect of nano-fillings (PMMA-ZnO-MgO) and (PMMA-ZnO-TiO$_2$) nanoparticles on the antibacterial activity of Streptococcus, where the small size nanoparticles showed great

antibacterial activity, which caused weak bacterial resistance, due to the increase in nanoparticles that interact with the cell wall of bacteria and cause cell death or weakening.

12. At the time period of(30) seconds and with a concentration rate of (7.5)%, it is considered the best time period for the nanocomposite and the best results for the hardness and compressibility properties.

13. Filling (PMMA-ZnO-TiO$_2$) is better than filling (PMMA-ZnO-MgO) in all structural, mechanical and biological properties, such as resistance to bacteria (Streptococcus).

5.2 Future Works

1. Studying new physical and mechanical properties such as thermal conductivity, friction resistance, modulus of elasticity.
2. Studying the possibility of changing the added percentages.
3. Studying the effect of fillings on other types of bacteria existing in the mouth.
4. Practical study of the optical properties of (PMMA-ZnO-TiO$_2$) and (PMMA-ZnO-MgO).
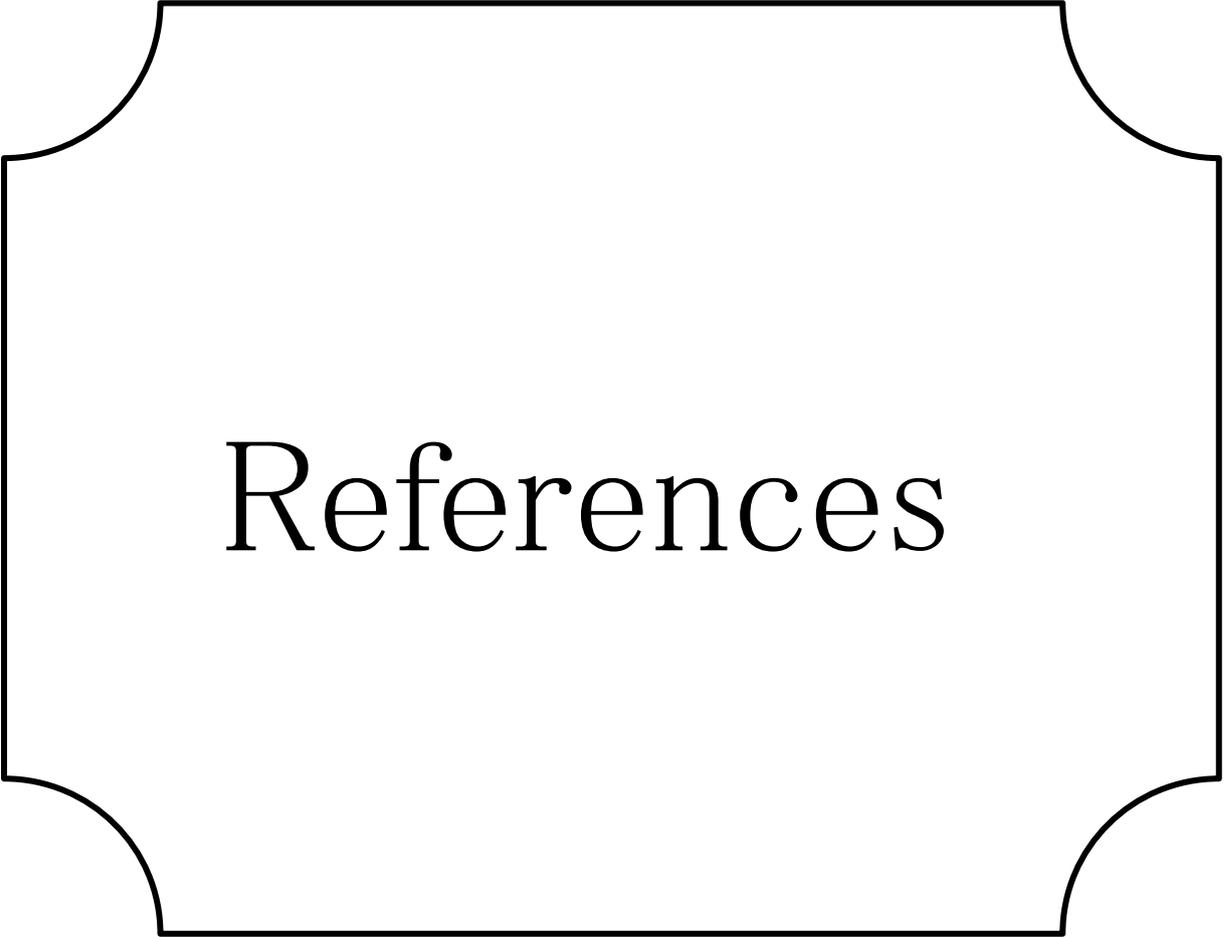
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