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Polymer Biomedical Films

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Abstract

Composite films of both Poly (vinyl alcohol)/nano silica-nano zinc oxide (PVA/SiO_2- ZnO) and Poly (methyl methacrylate) / nano silica-nano zinc oxide - chlorophyll (PMMA/SiO_2-ZnO-Ch) are prepared by using casting method and their medical applications are evaluated. In this study Nano, silica and Nano zinc oxide are used as filler with the following percentages of (1, 2 and 3) to improve the biological and mechanical properties of the composite films. Many tests are carried on the composite films such as Fourier transform infrared spectroscopy (FTIR), antibacterial activity, and tensile test. Their results show that zinc oxide has an excellent antibacterial activity and this activity increases in composite films with the increasing concentration of the zinc oxide .PMMA composite films show a better healing power than that of the PVA composite films. To avoid cracking on the produced PMMA film, chlorophyll as a bio natural pigment, is added it acts as a plasticizer and as a result it removes film stresses. All mechanical and physical tests show that the PVA composite has higher values than those of PMMA. This is due to the fact that PVA can build a hydrogen bond with ZnO or SiO_2 additives while PMMA has no tendency for H-bonding.

Keywords: Nano silica, Nano zinc oxide, Composite films. Antibacterial activity.

1. Introduction

Poly Vinyl Alcohol (PVA): is a non-toxic, synthetic polymer, soluble in water, slightly soluble in ethanol, but insoluble in other organic solvents. PVA has a relatively simple chemical structure with a pendant hydroxyl group. The monomer, vinyl alchol, does not exist in a stable form so it is rearranged to this tautomer, acetaldehyde. Therefore, PVA is produced by the polymerization of vinyl acetate to poly(vinyl acetate) (PVAc), followed by hydrolysis of PVAc to PVA. The physical characteristics and its specific functional uses depend on the degree of polymerization and the degree of hydrolysis [1] [2]

Commercial PMMA is an amorphous, relatively hard and transparent polymer which has a density of (1.15 to 1.195 g/cm^3) with a good resistance to dilute alkalis and other inorganic solutions. PMMA carries trade names such as Perspex and Plexiglass. Its stiffness is retained until it gets close to near its softening temperature (110ºC) [3][4] PMMA is best known for its exceptional light transparency (92% transmission) which is equal to that of clear glass, high refractive index (1.49) and good weathering properties. PMMA is one of the most biocompatible polymers [4].and it can be easily machined with conventional tools, molded, surface coated and plasma etched with glow or corona discharge. PMMA is one of the most widely explored biomedical materials because of its biocompatibility, and the recent

publications have shown an increasing interest in its applications as a drug carrier, blood pump and reservoir, membranes for blood dialyzer, in addition to its use in vitro diagnostics. Due to its excellent optical properties, PMMA is also found in contact lenses and implantable ocular lenses .It is also used in dentures, and maxillofacial prostheses due to its good physical and coloring properties. PMMA commonly known as bone cement is a widely used method of implant fixation; this technique has largely contributed to the success of modern joint replacement [4] [5] [6].

In recent years a number of studies have been made for the effect of Nano silica, Nano zinc oxide on composite films. Where In (2003), Lee and Rhee [7] reported the positive influence of silica in the bioactivity of PMMA composite. In (2008) the works of T. Yamaguchi [8] recorded the high proliferations of cells on silica nanofibers and they indicated that silica based materials are highly suited for many medical applications such as drug delivery, tissue engineering. They are also used as prosthetic material with a good bioactivity and an excellent biocompatibility. In (2003), S.H. Rhee et al, [7] showed that PMMA/ Silica hybrids exhibited better responses to cell attachment, proliferation and differentiation than the pure PMMA.

This research focuses on producing Nano composite films that have antibacterial activity to resolve the problems of non-antibacterial activity of thin medical films that used now in medical applications such as wound dressing. And reduce the hardness of the composite films of the PMMA by adding the chlorophyll pigment**.**

2. Experimental Part

2.1 Materials

The materials used in the preparation of the nanocomposites samples consist of polymer matrix from poly methyl methacrylate (PMMA), polyvinyl alcohol (PVA) and the reinforcement materials nano zinc oxide(ZnO),(nano silica(SiO_2) and Chlorophyll(Ch) are prepared in laboratory) .water glass used in the preparation of nano silica and medicago sativa used to extraction the bio natural pigment (chlorophyll)**.**

Table (1) the Properties of PMMA

Properties	Value
Light Transmission %	92
Hardness (Rockwell)	95
Specific Gravity	1.19
Vicat Softening Temp. ^oC	113
Heat Distortion Temp. ^oC	100

Table (2) the Properties of PVA

Properties	Value
Bulk density g/cm^3	0.68
Hardness (Shore D)	83.3
Melting point ^oC	220
Decomposition point ^oC	240

Table (3) the properties of water glass

Properties	Value
Gravity (degrees baume at 20 $\mathcal{C}$)	42
Specific gravity at 20 $\mathcal{C}$	1.408
Sodium oxide (wt % Na_2O)	9.01
Silica (wt % SiO_2)	29.49
Total solids (wt %)	38.50
%H_2O	61.5
Viscosity at 20 $\mathcal{C}$	0.33 pa.s

Table (4) the Properties of ZnO

Properties	Value
Purity %	95.7
Particles size (nm)	40
Specific surface area (m^2/g)	36
Melting point ^oC	2360
Density (g/cm3)	5.606

2.2 Extraction the chlorophyll (bio natural pigment)

There are at least five types of chlorophylls in plants, all with the same basic structure but which show variations in the nature of the aliphatic side chains attached to the Porphyrin nucleus, show in Figure (1). Thus, the structure of chlorophyll (b) only differs from that of (a) in having an aldehyde group instead of a methyl substituent attached to the top right – hand Porphyrin ring [9]**.**

Here, chlorophyll extracted from Medicago sativa by ethanol according to the following procedure.

1- Cleaning the Medicago sativa by distilled water to remove salts and impurities then dried at temperature 25°C and measured the weight of the dried Medicago sativa in sensitive balance with four digits, here its weight is (322.4 g) .
2- Cutting the dry Medicago sativa for smaller pieces to facilitate the extraction process by increasing the surface area exposed to the solvent. Then immersed in ethanol in the amount that covered all the Medicago sativa and covered the beaker to prevent the evaporation of the solvent for 5 days .
3- After 5 days, remove the remnants of extracted Medicago sativa and measured the weight of it then decantation the solution.
4- Evaporation of the solvent by heating without boiling the solution on a hot plate inside the hood until a dense dye obtained .
5- Evaporating the solvent completely by putting dense dye in a vacuum oven at 45°C for 15 hour, the extracted pigment weighs (18g) stored in the desiccator waiting to treat with polymer later .

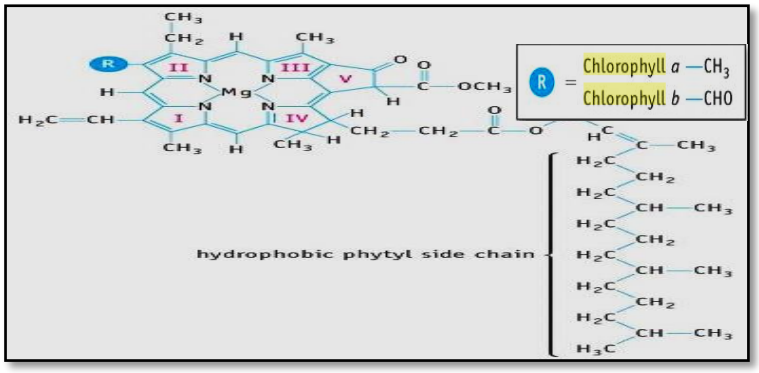


Figure 1 The chemical formula of chlorophyll (a) and (b)[10]

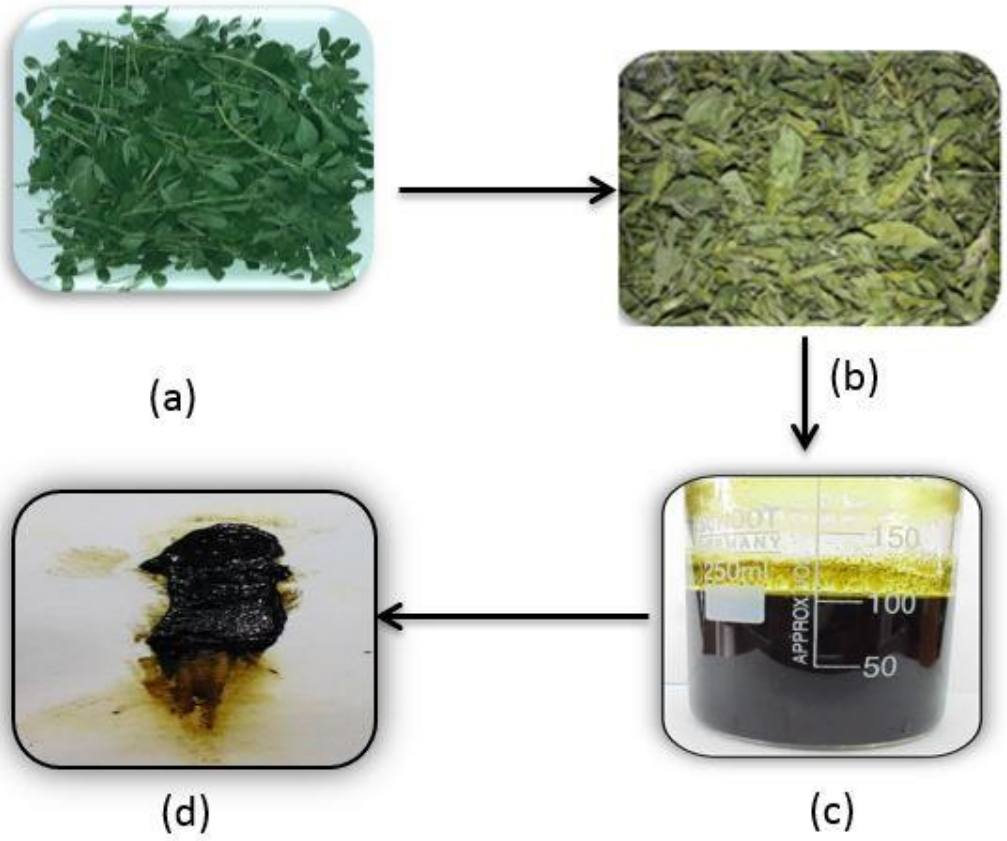


Figure 2 Procedure of chlorophyll extraction (a) Medicago sativa, (b) the remnants of Medicago sativa and (c) extracted chlorophyll solution, (d) dense chlorophyll pigment.

2.3 Preparation of Nano silica (SiO_2): The silica powder of 0.2817 g/cm^3 density and particle size ranges (72-89) nm, with a purity of 99.90% was prepared by precipitation method as in the following steps:

1. Mixing: Silica was prepared, using 400g of water glass and an addition of 36% hydrochloric acid (HCl). Added drops wise until silica deposited**.**

2. Washing and (decantation): Precipitated silica is washed with hot distilled water to remove the formed sodium chloride and retain acid, until no acid remains by checking the pH**.**

3. Evaporation of water: At this stage, the excess water is removed by evaporation on a hot plate, then drying in vacuum oven at temperature 110 oC for 2 hours.

4. **Ignition**: After evaporation of water,the material was weighed. The weight of the resulting silica was 209 g. At this stage, the silica has been weighing are ignited at 900 °C for a period of one hour to get rid of a moisture completely and more pure silica. Then, silica was weighed again. The weight was187g.

5. Milling and sieving: The resulting silica is ground manually with a steel mortar to fragment clustered and assembled particles, and crushed well for an hour. Then sifts the milled particles by using a sieve with holes size 75-90 μm to pass fine particles only. Now, the sample is ready to determine the particle size.

2.4 Preparation of Polymer Thin Film

Nanoparticles of (SiO_2, ZnO) with each polymer matrix of poly (methyl methacrylate) (PMMA) and poly (vinyl alcohol) (PVA)) are used in the preparation of polymer nanocomposite film. Some addition percents of both nanoparticles used in the films are (1, 2, and 3) wt% of each ($SiO_2$and ZnO) for both types of polymers .

Two types of polymeric films are prepared (the PVA/SiO2, ZnO and PMMA/ SiO2, ZnO, Ch) according to the following procedure:-

Table (5) Chemical Composition of Biofilms

	Additives		
Polymer PMMA	SiO_2	ZnO	chlorophyll
Sample 1	0	0	0
Sample 2	1%	1%	1%
Sample 3	2%	2%	2%
Sample 4	3%	3%	3%
Polymer PVA			
Sample 1	0	0	0
Sample 2	1%	1%	0
Sample 3	2%	2%	0
Sample 4	3%	3%	0

- Dissolve Poly (vinyl alcohol) (PVA) in distilled water at the concentration (0,05 wt%) using the magnetic stirrer at 70 oC for 30 min. First disperse each of the (SiO2, ZnO) nanoparticles in distilled water using ultrasonic device at 40 oC for 90 min , then add the dissolved solution at concentration (1, 2, and 3) wt% to the polymer solution and use the magnetic stirrer for 60 min to obtain a good distribution of the nanoparticles. Afterwards, cast the polymer solution into a brittle dish and leave it in the air for 48 hours and then put it in a vacuum at 40 Co for 4 hours to complete the drying process. After all these steps, that polymeric film is obtained.
- Dissolve Poly(methyl methacrylate) PMMA in acetone solvent at concentration (0,05 wt%) using the magnetic stirrer at 25 oC for 30 min. Add chlorophyll to the polymer solution at the same concentration of nanoparticles and used magnetic stirrer for 30 min. First disperse each of the (SiO2, ZnO) nanoparticles in acetone solvent using ultrasonic device at 40 oC for 90 min and then added the dissolved

solution at concentration (1, 2, and 3) wt% to the polymer solution and use the magnetic stirrer for 60 min to obtain a good distribution of the nanoparticles. Then cast the polymer solution into brittle dish and leave it at the air for 24 hours and then put it in a vacuum at 20 Co for 5 hours to complete the drying process. After the end of these steps, the polymeric film is obtained .In this film chlorophyll is used to avoid cracking in the produced biofilm. Chlorophyll is a biomolecule, which is both cheap and very good plasticizer.

3. Characterization

3.1 Antibacterial Test: Agar well diffusion method is widely used to evaluate the antimicrobial activity of plants or microbial extracts [11].As it is the case with to the procedure used in disk-diffusion method, the agar plate surface is inoculated by spreading a volume of the two type of microbial (E.coli and S. Aureus) inoculum over the entire agar surface. Then, a hole with a diameter of 6 to 8 mm is punched aseptically with a sterile cork borer or a tip, and a volume of (20–100 µL) of the antimicrobial agent or an extract solution at a desired concentration is introduced into the well. Then, agar plates are incubated under suitable conditions depending upon the test microorganism. The antimicrobial agent diffuses in the agar medium and inhibits the growth of the microbial strain tested [11].

3.2 Fourier Transforms Spectrophotometer (FTIR): was used to characterization of very complex mixtures by FTIR analysis instrument Type (IR Affinity-1) made in (Kyoto Japan). In order to measure a sample, calibrate the device using the KBr, and then prepare the powder of the sample to be examined, and mixed with KBr (mixing ratio 99% KBr). The mixing process achieved thoroughly then pressed as tablet-shaped semi-transparent to the possibility of penetrating radiation.

3.3 Scanning Electron Microscope(SEM): was used to examine the morphology of polymer blends. The sample used in the testing was cut into small pieces(1x1 cm) to fit into the device. To achieve a good electric conductivity, all samples were first sputtered with gold has been made from the surface along the edge.

3.4 Tensile Test: tensile properties, including elastic modulus, toughness, maximum tensile strength and elongation were measured by a means of Universal Tensile Strength test in the Department of Polymers Engineering and Petrochemical Industries Faculty of Materials Engineering.

3.5 Viscosity: The Viscosity of polymer solution is tested by DV-lll ULTRA (BROOKFIELD) in Rheology Laboratory in the Department of Polymers Engineering and Petrochemical Industries Faculty of Materials Engineering.

3.6 Density Test: was performed using high precision density tester type GP-120 S, made in Matsu haku, which contain water at room temperature.

4. Results and Discussion

4.1 Anti-Bacterial results

Figure 3 shows the antibacterial activity of PVA/SiO2-ZnO Nano composite films that were prepared by the casting method versus two types of bacterial: (a) E. colie as a negative type and (b) S. aureus as a positive type. See Table (5).

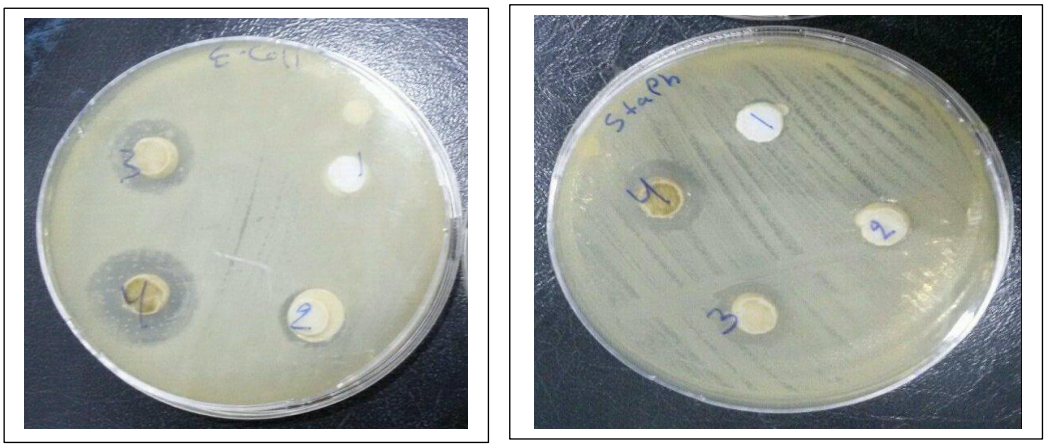


Figure 3 Antibacterial Activity of Nano Composite (PVA/SiO_2, ZnO) Versus *S. Aureus* and *E. Coli* .

Figure 4 shows the antibacterial activity of *PMMA*/SiO_2-ZnO-Ch Nano composite film .versus two types of bacterial: (a) *E. coli* as a negative type and (b) *S. Aureus* as a positive type .

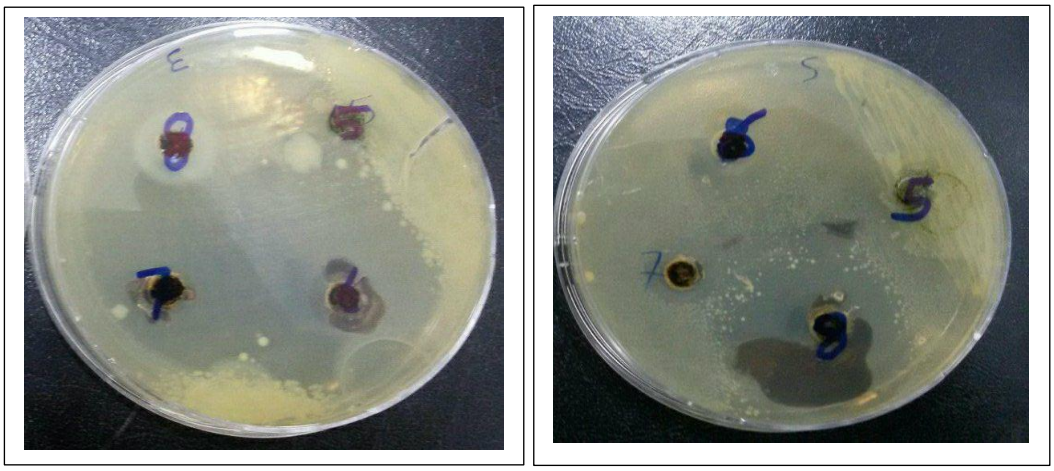
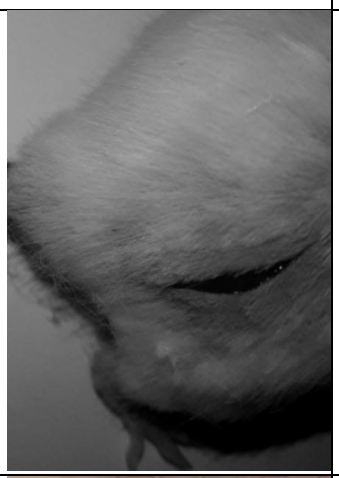
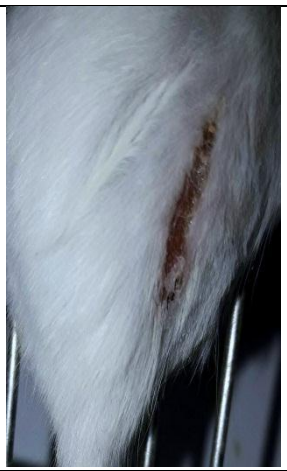
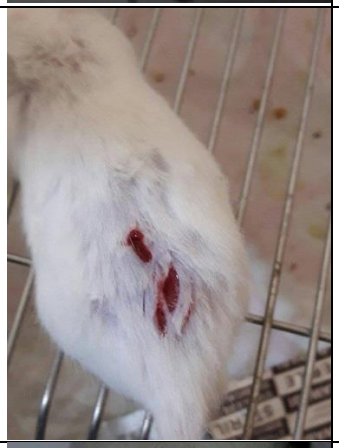
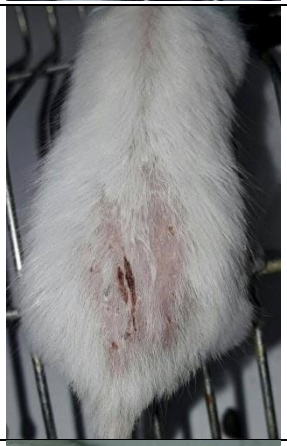
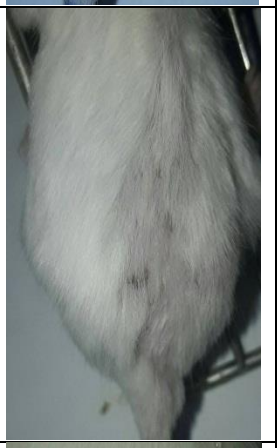
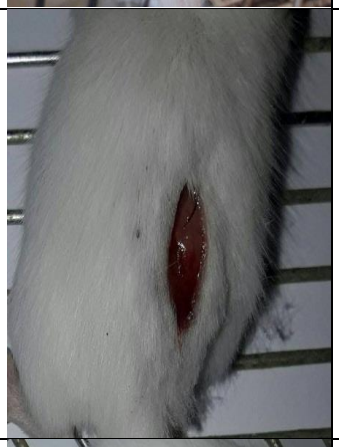
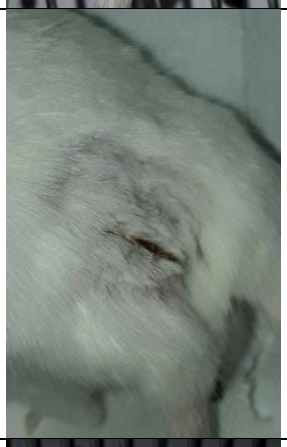
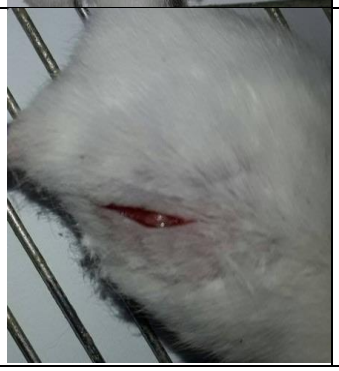
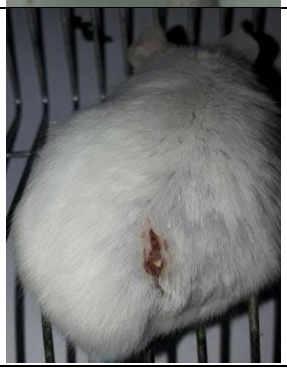
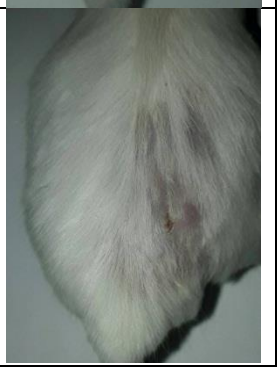


Figure 4 antibacterial activity of Nano composite (PMMA,SiO2,ZnO, Ch) versus *S. aureus* and *E. Coli* .

Figure 3 show increase of the antibacterial activity of PVA composite films with increasing the concentration of the additives. Figure 4 show that antibacterial activity of PMMA composite films is higher than those of PVA composite films. And its activity increase with increasing the concentration of the additives.

Through a practical examination in the laboratory for each concentration on the wound of the mouse, it was found that the contribution of PMAM composite films in the healing process was higher than that of PVA composite films. This is due to its high anti - bacterial effectiveness.

Samples	Day 1	Day 3	Day 6
PMMA + 1% of each (SiO2,ZnO, Ch)			
PMMA + 2% of each (SiO2,ZnO, Ch)			
PMMA +3% of each (SiO2,ZnO, Ch)			
PVA+1% of each (SiO2, ZnO)			

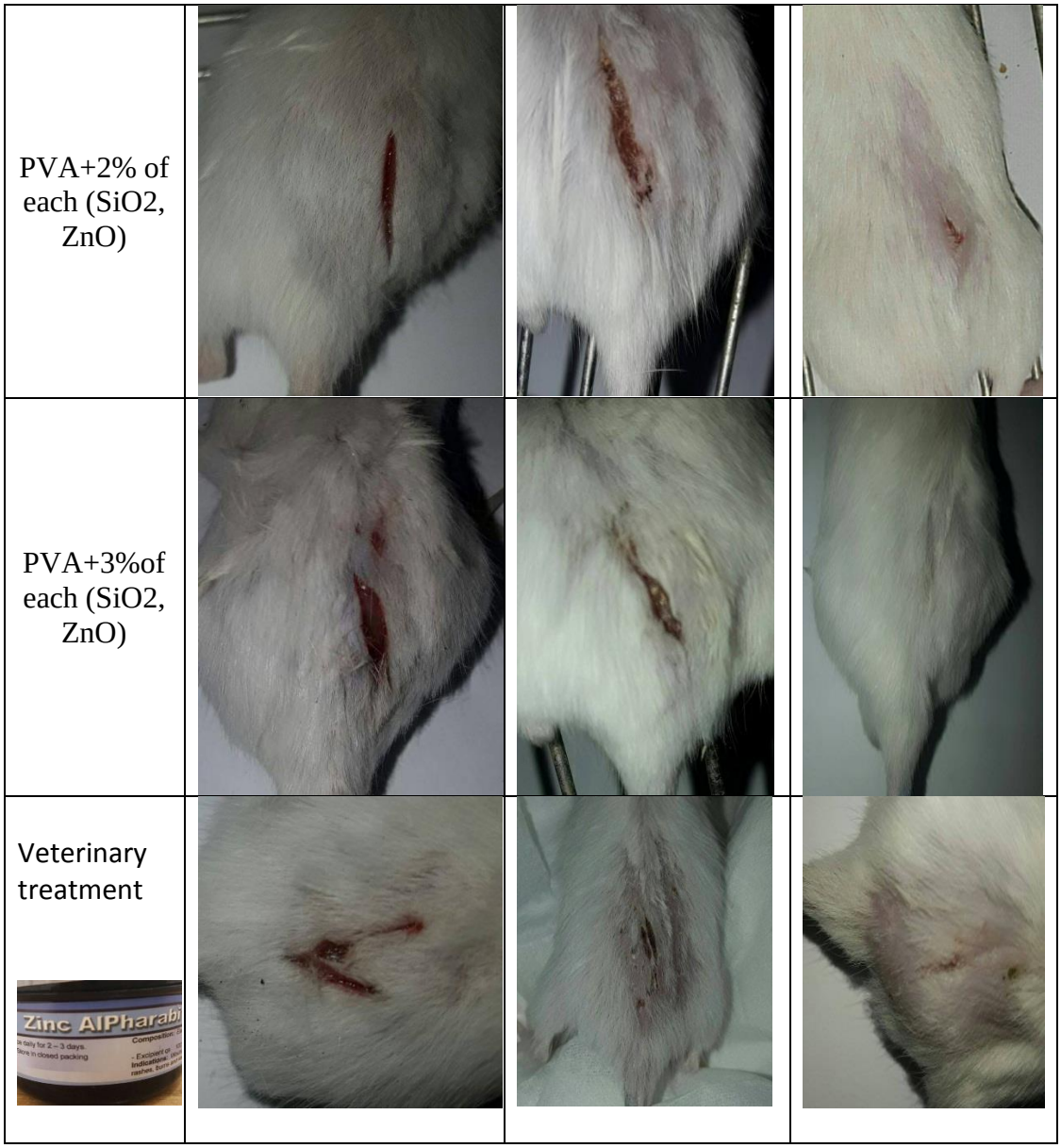


Figure 5 the laboratory test on mouse

The practical examination as shown in figure (5) shows that healing power of both PMMA and PVA composite films increase with increasing the concentration of the additives and the best healing power at the concentration 3% .

4-2 FTIR Analysis Results

FTIR is usually used to know the special function group and find the chemical structure of materials depending on IR spectrum. Figure (6) shows FTIR spectrum of composite films (pure PMMA and PMMA with the same concentration of each of the different additions (1,2 and 3)wt% (SiO_2, ZnO and Ch) , Figure (7) shows FTIR spectrum of composite films (pure PVA and PVA with the same concentration of each different additions (1,2 and 3)wt% (SiO_2, ZnO) in the range between 500 and 4000cm-1.

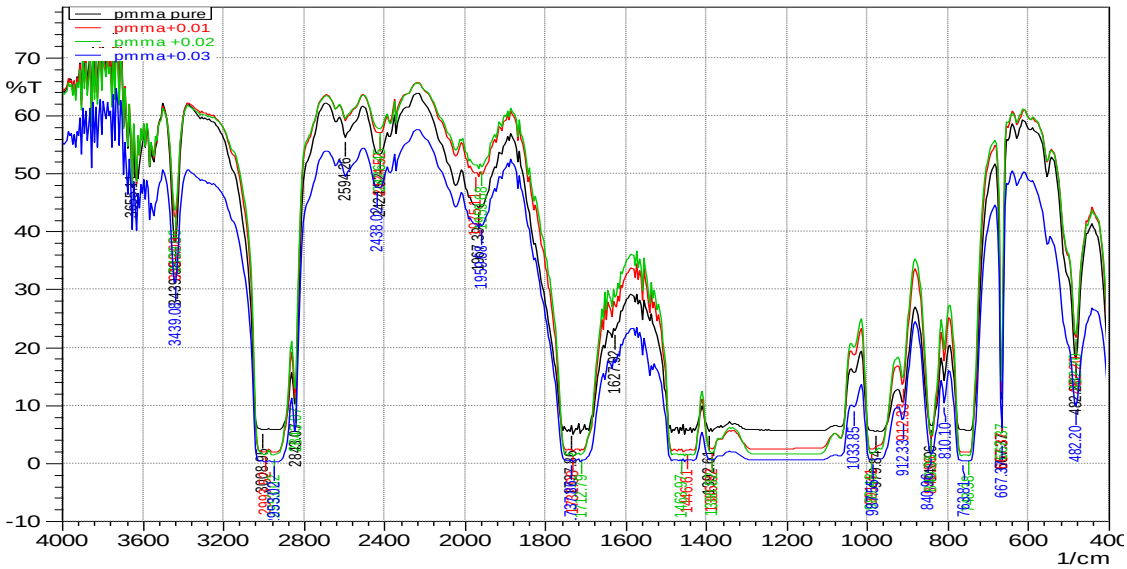


Figure 6 FTIR Spectra of Nanocomposite Films (PMMA,SiO2,ZnO, Ch)

Generally, all these variation can be attributed to the interaction between the addition material and the base one. Such interaction is a physical interaction. So its effect is mainly on the secondary engineering bond not on the primary bond. Hence the FTIR spectrum shows small effect on the absorption band, which indicates clearly no effect on the primary bonds .

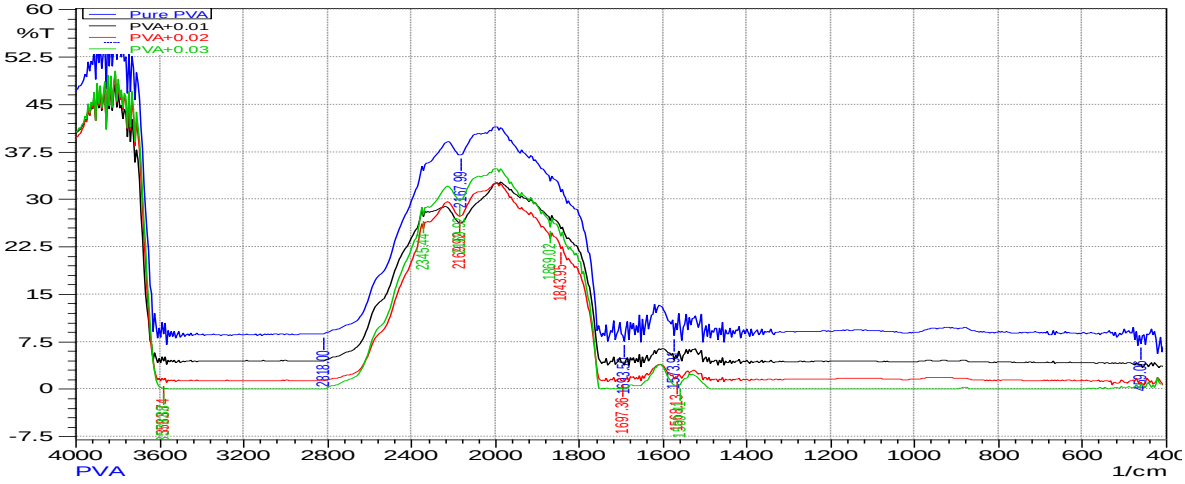


Figure 7 FTIR Spectra of Nanocomposite Films (PVA,SiO_2,ZnO)

4-3 Scanning Electron Microscopy (SEM) :

Figure (8) shows different magnifications of silica surface that micro particles and nanoparticles measure. The results of this analyses showed that the diameters of spherical nanoparticles in the range of (72-89) nm and, (highly agglomeration).

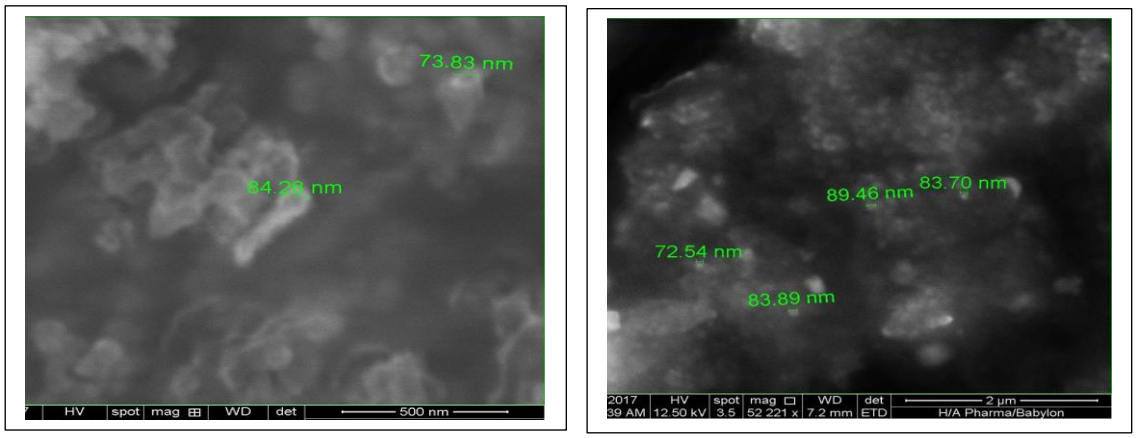


Figure (8) SEM Micrographs Images of Precipitated SiO_2

4-4 Tensile Test

Figure (9) shows the effect of SiO_2, ZnO and SiO_2, ZnO ,Ch content on the tensile strength of PVA or PMMA composite films respectively . The tensile strength of PVA/SiO_2, ZnO increases as the additives ratio increases. This increase in tensile strength is due to the good interfacial adhesion between addition and PVA. That indicates a good distribution of nanoparticles in the polymer matrix and a transfer of the load from the polymer matrix to the nanoparticles.

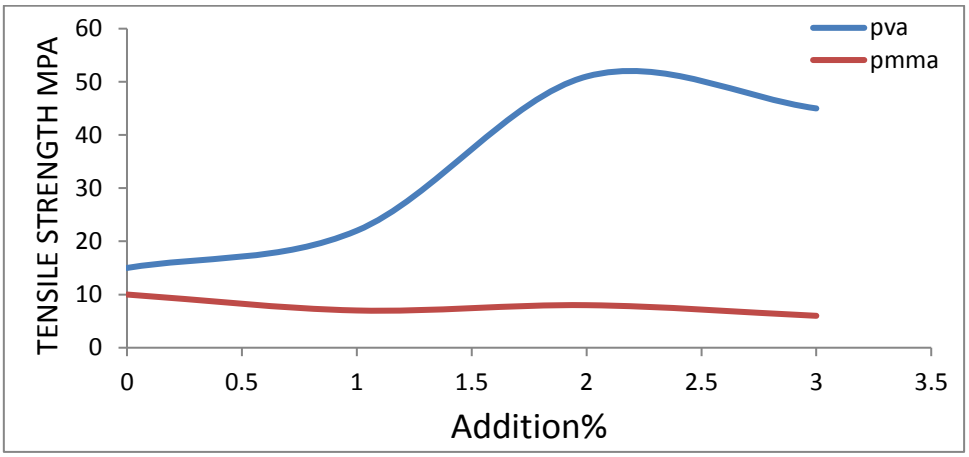


Figure (9) Effect of Additive Content on the Tensile Strength of PVA,PMMA Composite Films (Mpa)

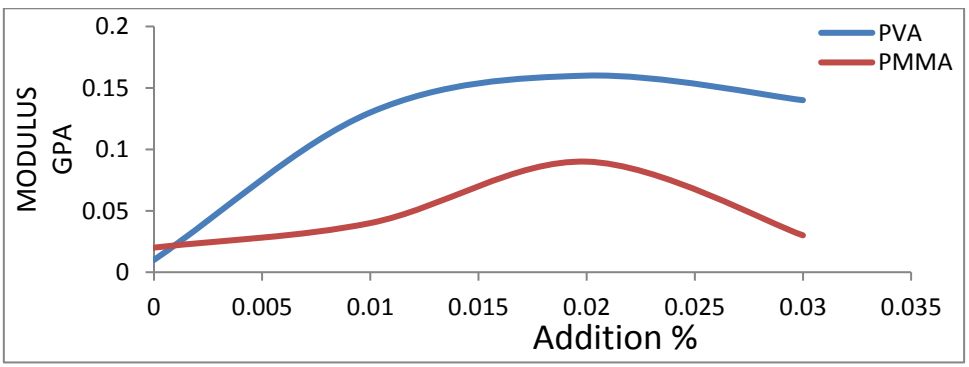


Figure 10 Variation of Young Modulus of PVA, PMMA Composite Films (Gpa).

4-5 Viscosity Test

Figure (11) shows that viscosity of the solution of composite films of (PVA) increases as the additives increases. The increases of (SiO_2, ZnO) concentration are directly proportional to the particles sizes and viscosity is related to the agglomeration.

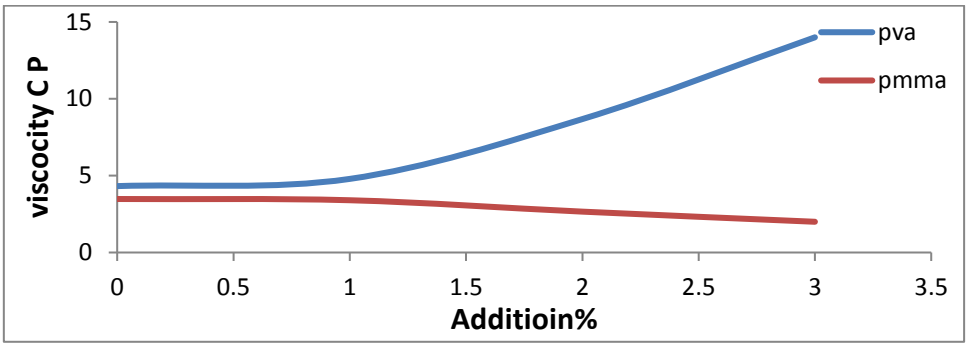


Figure (11) Viscosity of the Solution of Composite Film of (PVA) or (PMMA)

4-6 Density Test

Figure (12) shows the density of PVA/ SiO_2, ZnO and PMMA SiO_2, ZnO, Ch samples. The density of PVA/ SiO_2, ZnO composite film increases with increasing ratio of (SiO_2, ZnO) .

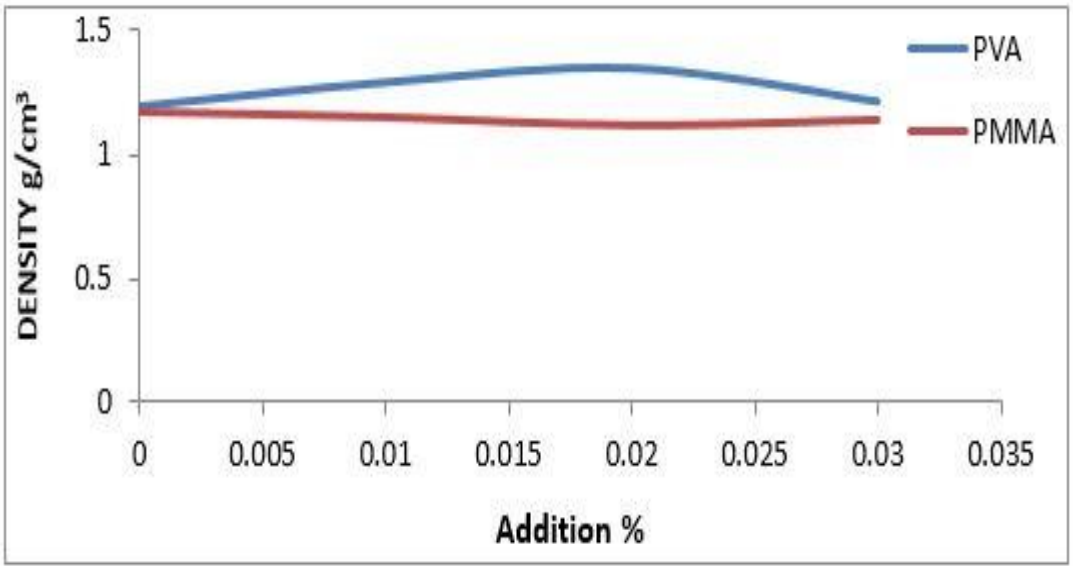


Figure 12 Density of PMMA and PVA Composite Film

5- Conclusions:

PMAM composite films shows excellent Antibacterial activity higher than those of PVA do. And its activity in thin medical films increasing with increasing additives concentration. To avoid cracking on produced PMMA film, chlorophyll as bio natural pigment is added which acts as plasticizer and remove film stresses as the result shows that. FTIR spectrums of polymers with pigment show slightly effect on the absorption band, which indicates that there is no effect on primary bonds. But on secondary bond only by physical interactions.

6- References

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الخلاصة

الافلام المركبة لكل من بولي فنيل الكحول مع السليكا النانوية – اوكسيد الزنك النانوي. بولي مثيل ميثا اكريليت مع السليكا النانوية – اوكسيد الزنك النانوي– الكلوروفيل يتم تحضيرها باستخدام طريقة الصب ويتم تقييم تطبيقاتها الطبية. في هذه الدراسة السليكا النانوية واوكسيد الزنك النانوي تستخدم كماده ماله لتحسين الخواص البيولوجية والميكانيكه للأفلام المركبة. يتم اجراء العديد من الاختبارات على الافلام المركبة مثل مطياف الأشعة تحت الحمراء والفعالية المضادة للبكتريا واختبار الشد. اضهرت النتائج أن أوكسيد الزنك لديه نشاط مضاد للجراثيم ممتاز وهذا النشاط يزداد في الأفلام المركبة مع زيادة تركيز اوكسيد الزنك. الافلام المركبة البولي مثيل ميثا اكريليت اضهرت قوة شفاء أفضل من لأفلام المركبة لبولي فنيل الكحول. ولتجنب الشقوق على افلام بولي مثل ميثا اكريلت المنتجة، الكلوروفيل كصبغه طبيعية حيوية تضاف حيث انها تعمل كملدن وبذالك تزال الشقوق من الافلام المركبة. جميع الاختبارات الميكانيكية والفيزيائية تظهر ان لأفلام المركبة لبولي فنيل الكحول لها قيم اعلى من قيم الافلام المركبة البولي مثيل ميثا اكريليت وهذا يرجع الى حقيقة ان بولي فنيل الكحول يمكن ان يبني اواصر هيدروجينية مع اضافات اوكسيد الزنك النانوي او السليكا النانوية بينما بولي مثيل ميثا اكريليت لا يمتلك ميل لعمل اواصر هيدروجينية.

الكلمات المفتاحية: ـ نانو سليكا، اوكسيد الزنك النانوي، افلام مركبة، الفعالية المضاده للبكتريا.