Journal of Engineering and Applied Sciences 13 (15): 6232-6237, 2018
ISSN: 1816-949X

PMMA/SiO_2, ZnO, Ch) Biomedical Films

Jaleel Kareem Ahmed, Nizar Jawad Hadi and Salah Mahdi Abdullah
Department of Polymer and Petrochemical Industries,
College of Engineering Material, University of Babylon, Babylon, Iraq

Abstract: Composite films of Poly (Methyl Methacrylate) (PMMA)/SiO_2-ZnO-Ch are prepared by casting method and evaluated for medical application. Nano silica was prepared from water glass by precipitation method, chlorophyll (Bio natural pigment) extraction from medicago sativa and use as plasticizer. In this study, nano silica and nano zinc oxide are used as filler to improve the biological and mechanical properties of composite films. Where nano silica has good mechanical properties and nano zinc oxide has excellent antibacterial activity (SiO_2-ZnO and Ch) are used with a following percentages (1-3) wt.% to the polymer. Many tests are carried on composite films such as antibacterial activity, Fourier Transform Infrared spectroscopy (FTIR) and tensile test. The result shown that zinc oxide has excellent antibacterial activity. And its activity in composite films increasing with increasing its concentration.

Key words: Composite films, antibacterial activity, nano silica, nano zinc oxide, concentration, FTIR

INTRODUCTION

In this research two type of nano filler are used to prepared nanocomposites films with excellent biological and mechanical properties. And to avoid cracking on produced PMMA film, Chlorophyll (Ch) as Bio natural pigment is added which acts as plasticizer and remove film stresses as the result shows that Casting method have been widely used for prepared nano composite films. casting method have become very popular recently due to the their low processing temperatures and possibility of controlling the size.

Commercial PMMA is an amorphous, relatively hard and transparent polymer has density (1.15-1.195 g/cm^3) with good resistance to dilute alkalis and other inorganic solutions. PMMA, carrying trade names such as Perspex and Plexiglass. Its stiffness is retained until near its softening temperature (110°C) (Ahmed *et al*., 2014).

PMMA 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 recent publications have shown an increasing interest in its applications as a drug carrier, blood pump and reservoir, membranes for blood dialyzer and in vitro diagnostics. It is also, found in contact lenses and implantable ocular lenses due to excellent optical properties, dentures and maxillofacial prostheses due to good physical and coloring properties. And 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 (Peterson and Bronzino, 2007; Bettencourt and Almeida, 2012).

PMMA is widely used in the medical field for prosthetic applications. It is known to be biocompatible with good mechanical and physical properties suitable for application in orthopedics and ophthalmology (Ramakrishna *et al*., 2001).

In recent years a number of studies have been made for prepared composite films of PMMA/Silica (Rhee *et al*., 2003) showed that PMMA/Silica hybrids exhibited better responses to cell attachment, proliferation and differentiation than pure PMMA. The researches by Yamaguchi *et al*. (2008) showed high proliferations of cells on silica nanofibers. Indicating that silica based materials are highly suited for many medical applications such as drug delivery, tissue engineering and as prosthetic material with good bioactivity and excellent biocompatibility. This research focuses on producing thin flexible biomedical 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 etc.

MATERIALS AND METHODS

Poly (Methyl Methacrylate) Powder (PMMA): Poly (Methyl Methacrylate) (PMMA) powder was obtained

Corresponding Author: Jaleel Kareem Ahmed, Department of Polymer and Petrochemical Industries, College of Engineering Material, University of Babylon, Babylon, Iraq

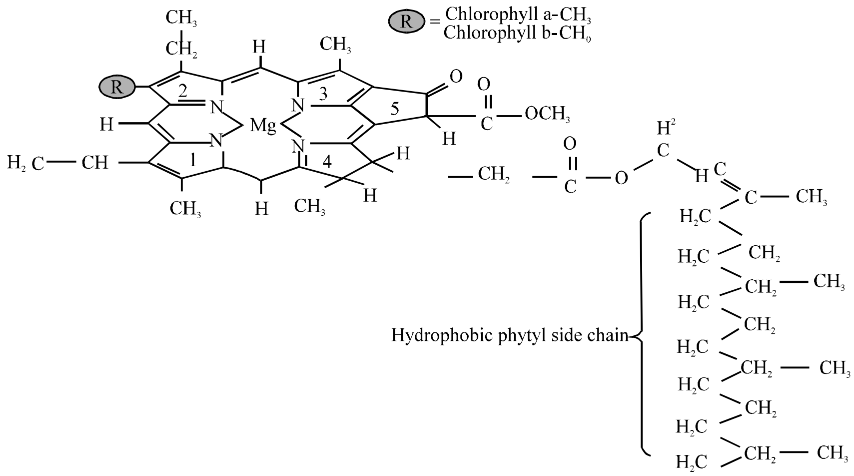

Fig. 1: The chemical formula of chlorophyll a and b (Kotz *et al*., 2012)

from Yonghui chemical Holdings Limited Company, China. This type is a good biocompatible materials, therefore, it was used in medical field.

Zinc Oxide (ZnO): Zinc Oxide (ZnO) powder was obtained from Yonghui Chemical Holdings Limited Company, China.

Nano silica prepared in laboratory: 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.

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

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.

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

Ignition: After evaporation of water, material was weighed. The weight of the resulting silica was 169 g. At this stage, the silica has been weighing are ignited at 900°C for a period of 1 h to get rid of a moisture completely and more pure silica. Then, silica was weighed again. The weight was147g.

Milling and sieving: The resulting silica is grind 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.

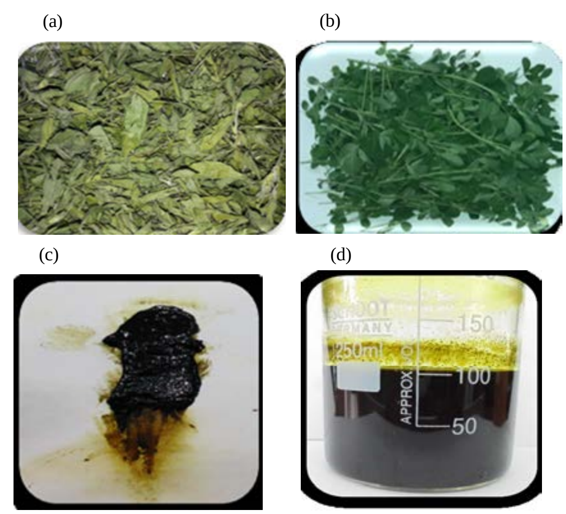

Fig. 2: Procedure of chlorophyll extraction: a) *Medicago sativa*; b) The remnants of *Medicago sativa*; c) Extracted chlorophyll solution and d) Dense chlorophyll pigment

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 Fig. 1 and 2. Thus, the structure of chlorophyll only differs from that of in having an aldehyde group instead of a methyl substituent attached to the top right hand Porphyrin ring (Harbone, 1984). Here, chlorophyll extracted from *Medicago sativa* by ethanol according to the following procedure as shown in Fig. 2. Cleaning the *Medicago sativa* by distiled 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 (393.3 g). Cutting the dry *Medicago sativa* for smaller pieces to facilitate the extraction process by increasing the surface area exposed to the solvent. Then immersing in ethanol in amount that covered all the *Medicago sativa* and covered the beaker to prevent the evaporation of the solvent for 5 days.

After 5 days, remove the remnants of extracted *Medicago sativa* and measured the weight of it then decantation the solution. Evaporation of the solvent by heating without boiling the solution on a hot plate inside the hood until a dense dye obtained. Evaporating the solvent completely by putting dense dye in a vacuum oven at 45°C for 15 h, the extracted pigment weighs (21 g) stored in the desiccator waiting to treat with polymer later.

Preparation of polymer thin film: Dissolve poly (methyl methacrylate) PMMA in acetone solvent at concentration (0.05 Wt.%) using the magnetic stirrer at 25°C 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 (SiO_2, ZnO) nanoparticles in acetone solvent using ultrasonic device at 40°C for 90 min and then added the dissolved solution at concentration (1-3) 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 h and then put it in a vacuum at 20°C for 5 h 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.

Characterization

Antibacterial test: Agar well diffusion method is widely used to evaluate the antimicrobial activity of plants or microbial extracts (Balouiri *et al*., 2016). Similarly 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 6-8 mm is punched aseptically with a sterile cork borer or a tip and a volume (20-10 μL) of the antimicrobial agent or extract solution at 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 (Balouiri *et al*., 2016).

Fourier transforms spectrophotometer (FTIR): It 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 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.

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

Tensile test: Tensile properties including elastic modulus, toughness, maximum tensile strength and elongation were measured by a device universal tensile test in strength of strength of materials laboratory in the Department of Polymers Engineering and Petrochemical Industries, Faculty of Materials Engineering.

Atomic Force Microscopy (AFM): The morphological studies of nano composite film are conducted by tapping mode AFM (AA3000) in the Ministry of Science and Technology. The particle size distributions of prepared film is test by AFM.

RESULTS AND DISCUSSION

Anti-bacterial results: Figure 3a, b shows the antibacterial activity of PMMA/SiO_2,ZnO,Ch nano composite films that were prepared by casting method at this work versus two types of bacterial *S. aureus* as a positive type and *E. colie* as a negative type".

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 4 show FTIR spectrum of composite films (pure PMMA and with different additions (1-3) Wt.% of the same concentration in each addition from (SiO_2, ZnO and Ch (in the range

(a) (b)

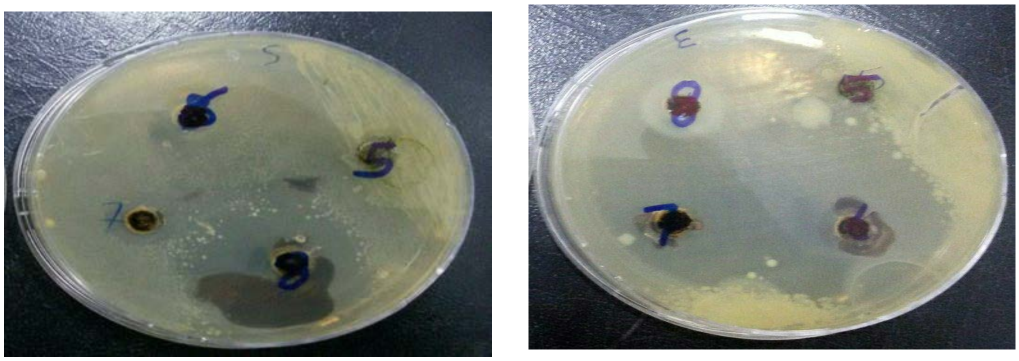

Fig. 3: a) Antibacterial activity of nano composite (PMMA, SiO_2, ZnO, Ch) versus *S. aureus* and b) Antibacterial activity of Nano composite (PMMA, SiO_2, ZnO, Ch) *E. coli*

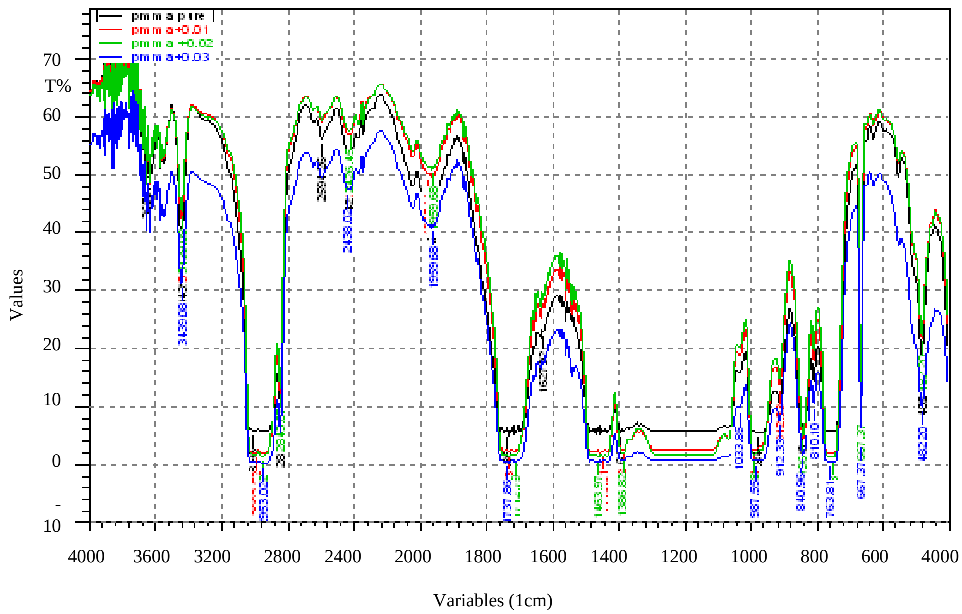

Fig. 4: FTIR spectra of nanocomposite films (PMMA, SiO_2, ZnO, Ch)

between 500 and 4000 cm. Generally, all these variation can be attributed to the interaction between the addition material and base one such interaction is physical interaction. So, its mainly on the secondary engineering bond not on the primary bond. Thus, the FTIR spectrum shows small effect on the absorption band which indicate clearly no effect on the primary bonds.

Scanning Electron Microscopy (SEM): Figure 5 shows different magnifications of silica surface that micro particles and nanoparticles are measured. The results of this analyses showed that the diameters of spherical nanoparticles in the range of 72-89 nm and highly agglomeration are observed by this examination. This agree with the results of research (Music *et al*., 2011).

(a) (b)

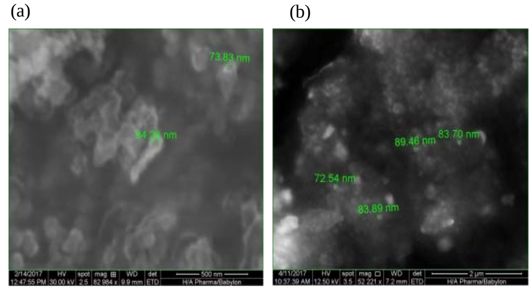

Fig. 5: SEM micrographs images of precipitated SiO_2

Tensile test: Figure 6-8 show the effect of SiO_2, ZnO, Ch content on the tensile strength of PMMA composite films. The tensile strength of PMMA/SiO_2, ZnO, Ch decreasing as additive ratio increases.

Atomic Force Microscopy (AFM): AFM is usually used for determining the size of the nanoparticles and its morphology in two and three dimensions. The principle of AFM is based on mechanical contact between the sample and tip therefore, the measurement of particles in nanometer scale is strongly affected by sample-tip interaction (Fig. 9 and 10).

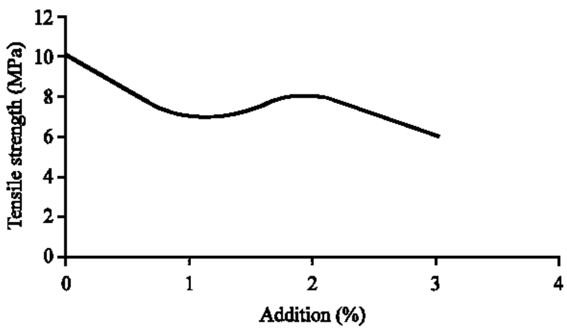

Fig. 6: Effect of additive content on the tensile strength of PMMA composite films (MPa)

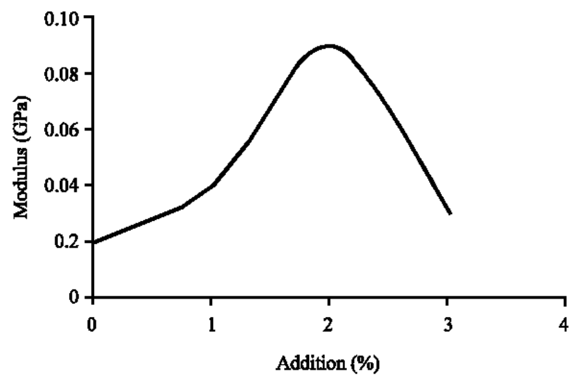

Fig. 7: Variation of young modulus of PMMA composite films (Gpa)

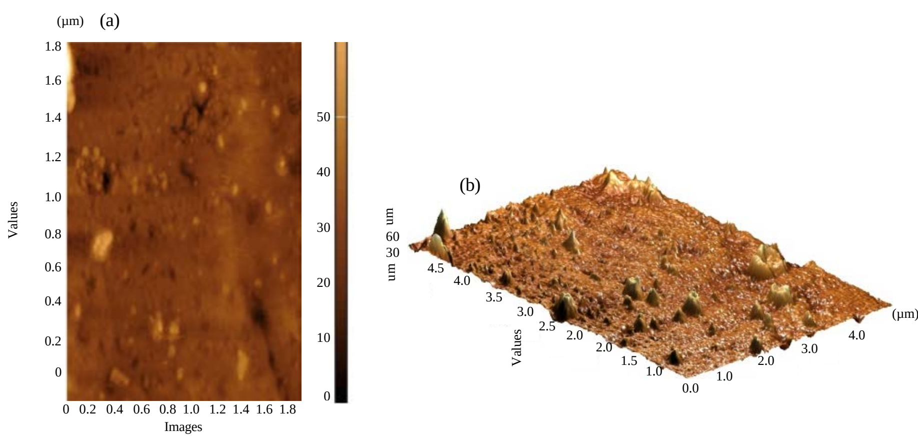

Fig. 8: AFM images of the composite film of 1% (SiO_2, ZnO, Ch)/PMMA: a) 2-D particles size and b) 3-D particle size

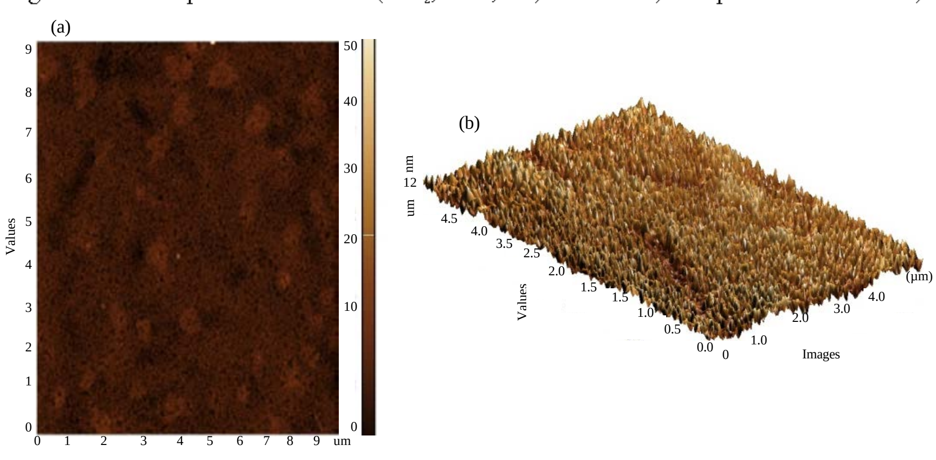

Fig. 9: AFM images of the composite film of 2% (SiO_2, ZnO, Ch)/PMMA: a) 2-D particles size and b) 3-D particle size

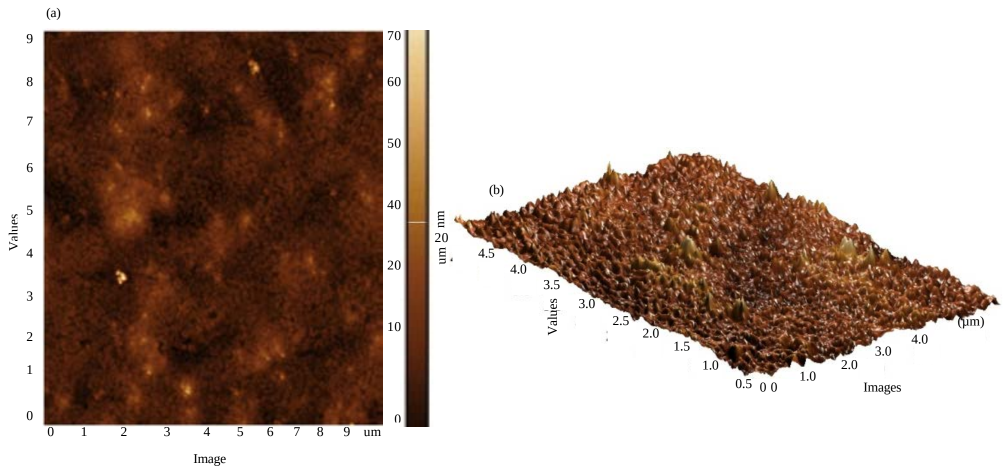

Fig. 10: AFM images of the composite film of 3% (SiO_2, ZnO, Ch)/PMMA: a) 2-D particles size and b) 3-D particle size

CONCLUSION

Zinc oxide shows excellent antibacterial activity. And its activity in thin medical films increasing with increasing its concentration. The composite films possess the best healing power when concentrating 3 wt.%. 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.

REFERENCES

Ahmed, J.K., Z.J.A. Amer and M.J.M. Al-Bahate, 2014. Effect of chlorophyll and anthocyanin on the secondary bonds of Poly Methyl Methacrylate (PMMA). Intl. J. Tech. Res. Appl., 2: 73-80.

Balouiri, M., M. Sadiki and S.K. Ibnsouda, 2016. Methods for In vitro evaluating antimicrobial activity: A review. J. Pharm. Anal., 6: 71-79.

Bettencourt, A. and A.J. Almeida, 2012. Poly (Methyl Methacrylate) particulate carriers in drug delivery. J. Microencapsulation, 29: 353-367.

Harbone, J.B., 1984. Phytochemical Methods. 2nd Edn., Champion and Hall Publishers, London, UK., pp: 84-196.

Kotz, J.C., P.M. Treichel and J. Townsend, 2012. Chemistry and Chemical Reactivity. 8th Edn., Cengage, Boston, Massachusetts, USA.,.

Music, S., N. Filipovic-Vincekovic and L. Sekovanic, 2011. Precipitation of amorphous SiO2 particles and their properties. Braz. J. Chem. Eng., 28: 89-94.

Peterson, D.R. and J.D. Bronzino, 2007. Biomechanics: Principles and Applications. CRC Press, Boca Raton, Florida, USA., ISBN:9781420040029, Pages: 312.

Ramakrishna, S., J. Mayer, E. Wintermantel and K.W. Leong, 2001. Biomedical applications of polymer-composite materials: A review. Compos. Sci. Technol., 61: 1189-1224.

Rhee, S.H., M.H. Hwang, H.J. Si and J.Y. Choi, 2003. Biological activities of osteoblasts on poly (methyl methacrylate)/silica hybrid containing calcium salt. Biomater., 24: 901-906.

Yamaguchi, T., S. Sakai and K. Kawakami, 2008. Application of silicate electrospun nanofibers for cell culture. J. Sol Gel Sci. Technol., 48: 350-355.