Engineering and Technology Journal

Journal homepage: engtechjournal.org

Preparation and Characterization of Polymer Blend and Nano Composite Materials Based on PMMA Used for Bone Tissue Regeneration

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A B S T R A C T

As the elderly population increases, the need for bone loss treatments is increasing. Vital substances used in such treatments are required to continue for a longer period and work more effectively. The particularly important biological material is poly methyl methacrylate (PMMA) bone cement, which is widely used in damaged bone replacement surgery. So, this study focused on the role of added some nanoparticles consist of zirconia (ZrO_2), and magnesia (MgO) on the binary polymeric blend (Acrylic bone cement: 15% PMMA) for a bone scaffold. Where, ZrO_2 and MgO nanoparticle was added with selected weight percentages (0, 0.5, 1, 1.5 and 2 wt.%), which were added to the polymer blend matrix. Some mechanical properties were studied including the tensile strength and young modulus for all the prepared samples. The chemical bonding of nanoparticles and synthetic binary polymeric blend composites was evaluated by Fourier Transform Infrared (FTIR) spectroscopy. Tensile strength and young modulus of binary polymeric blend reinforced with 1.5 wt.% ZrO_2, and 1 wt.% MgO, significantly increased. The surface morphology of the fracture surface of tensile specimens was examined by Scanning electron microscope (SEM). The SEM images confirmed that the homogenous distribution of nanoparticles (ZrO_2, and MgO) within the polymeric blend matrix.

1. Introduction

Bones play a key role in our bodies, allowing daily tasks to be performed. They are also important for storing minerals and producing red blood cells. If bones fail to repair due to significant injury or

disease, replacement surgery may be conducted to replace the bone tumor with a bone repair (i.e., Bone, as a functionally smart tissue, is capable of healing and remodeling in the case of limited bone defects) [1, 2].

In the manufacturing of scaffolds, both natural and synthetic biomaterials are used. Systems for bone tissue engineering include bone regeneration following tissue loss owing to degenerative surgical procedures. In the condition of disease with degeneration risk, the therapy requires the surgical removal of the tumor bone tissue and the bone defect can be filled with bone graft material in the second phase [3].

Polymethyl methacrylate (PMMA) is a non-adhesive acrylic polymer, widely used as bone cement for implants in orthopedics. Chanley introduced orthopedic use of PMMA cement in the early 1960s and this was the first cement to be used in spine applications. PMMA has been extensively studied as bone cement for over 40 years and widely suitable are many injectable PMMA cement formulations engineered for vertebral body applications. Because of its desirable features, PMMA bone cement occupied an uncomfortable room for several centuries, such as appropriate strength to provide mechanical stability, moldable to fill complicated flaws, low cost and authorized by Food and Drug Administration (FDA) [4, 5]. A polymer mixture is a component of a material category where two or more polymers are combined to form a fresh material with distinct physical characteristics. They combine the characteristics of the alloy subsystems in a beneficial way. In some instances the properties of the polymer blends are superior to those of their components. Polymer blending is a technological way to provide materials with a complete set of desired special properties at the lowest price, such as a combination of toughness and strength, and solvent resistance.

One of the most common methods for developing new polymeric materials is blending polymer [6]. In tissue engineering, biopolymer composites are of excellent importance for medical applications because they provide a favorable environment for cell growth and differentiation [7]. Recently, due to its excellent biocompatibility, Nano ZrO_2 has received great attention. ZrO_2 classification as a filler was based on this filler's characteristics, which can enhance the mechanical characteristics of acrylic resins. ZrO_2 has a range of useful characteristics, including great toughness and mechanical strength, resistance to abrasion and corrosion, and biocompatibility. Nano ZrO_2 has good mechanical characteristics that enable it to resist the propagation of cracks, and it is known to have the greatest oxide hardness [8]. Magnesia (MgO) is also another bioactive material and an appropriate additive to PMMA since the adhesion of osteoblasts to cement involving magnesium oxide was significantly greater than the adhesion to PMMA alone (P<0.001) without significant changes in mechanical strength [9].

A review by Karageorgiou and Kapalan [10] revealed different types of bone with their required mechanical properties. Cortical (mid-femoral), depending on the direction and type of load, has a strength ranging from 33-193 MPa with elasticity modulus from 3 to 17 GPa, while trabecular (Proximal femoral) has 6.8 MPa and 0.441 GPa of strength and modulus, respectively. Salih et. al. (2016) [11] developed a PMMA reinforced with (0, 0.5, 1, and 1.5 vol. %) of MgO. A remarkable improvement of tensile strength and modulus of elasticity was recorded. The mechanical properties increased with an increase in volume fractions of MgO in the PMMA matrix .

Gad et. al. (2018) [12] added a silanized ZrO_2 (40 nm) in size to PMMA base materials with (2.5, 5 and 7.5 wt.%). Tensile strength and SEM tests were investigated. The results demonstrated that there is an increase in the tensile strength with an increase in wt.% of ZrO_2. The SEM micrographs viewed good surface characteristics with the different ZrO_2 concentrations .

The main objective of this study was to improve the mechanical properties of the polymeric blend that's reinforced with nanoparticle (ZrO_2, and MgO) according to the standards of bone tissue engineering.

2. Materials and Methods

I. Materials used

Acrylic bone cement for bone scaffold, as resin material manufactured by (the company of Re-Acromed) which was supply from UAE. Acrylic bone cement comprises two parts, one is powder and the other is a liquid. The powder is composed of (PMMA), and the liquid composition is (methyl methacrylate, dimethylparatoluidine, and ethylene glycoldi methacrylate). Self-Curing Polymethyl methacrylate (PMMA) is another type of acrylic resin manufactured by (ORT-365) was supply from Ankara. It comprises two parts, one of them is a transparent viscous liquid and the other is a paste.

The transparent viscous liquid is composed of (MMA) and a paste is composed of (DIBENZOYL). Tables 1 and Table 2 show the technical information of acrylic bone cement and PMMA respectively, according to the product company.

Table 1: Technical information on acrylic bone cement according to the product company

	Molding Consistency
Mixing Ratio	5 wt. powders, 3.5 wt. liquid
Mixing Time	Approximately 30 seconds
Working Time	Ends after about 2 minutes
Curing Time	Approximately 14 minutes

Table 2: Technical information on PMMA according to the product company

Viscosity at 20 ℃	300/350 mPa.s
Resin/ Hardener	100/2
Time for Work at 20 ℃	8-10 min.
Working Time	15 min
Hardness shore D	80-85

Two types of nanoparticles as reinforcement materials have been used. These nanoparticles are the zirconium oxide (ZrO_2), which was obtained from Honwu Nanometer material company in china with purity (99.9%) has a white color, with an average diameter (50.65 nm). It is a type of yttria (Y_2O_3) stabilized zirconia and MgO powder, which was obtained from Beijing DK Nanotechnology Company in China with purity (99.9%) has a white color, with an average diameter (68.83 nm).

II. Preparation of polymer blends and composite samples

To prepare polymer, blends were down by hand lay-up molding by using two different types of PMMA material. Acrylic bone cement specimens were prepared by (5 wt.) of powders with (3.5 wt.) of the liquid part of methyl methacrylate monomer. According to the manufacturer instructions of the second material (PMMA), the mixing ratio of acrylic resin and hardener is (100/2). So on, the control group was prepared by the weighed amount of acrylic bone cement as a basic substance and blended with PMMA at 15% weight percentage, and were mixed manually until the mixture gets in homogenous form. To get the final standardized samples, the blend was poured into the mold. Then, the mixture was left in the mold at room temperature for 48 hours to solidify. After that, the casting sample is placed inside an oven at 50 ℃ for 3 hours. Finally, to complete polymerization, it was left for 72 hours at room temperature.

III. Prepared composites

The weights of the reinforcement components depend on the appropriate selection ratio of the weight fractions of the strengthening materials (Zirconia, and magnesia) as the nanoparticle's powders were calculated by utilizing electronic sensitive balance, depending on the matrix material's total weight (binary polymeric blend) which is contained on (Acrylic bone cement: 15% PMMA). The reinforcement materials (Zirconia, or magnesia) were mixed in individual form with a binary polymer blend material according to the selection ratio of reinforcement materials followed by heat treatment at 55 °C for 3 hours to accomplish polymerization and to remove any residual stress resulting from de-molding of the samples into the cavity of the metal mold.

3. Test Methods

I. Fourier transform infrared radiation (FTIR) spectroscopy test

According to the international standard (ASTM E1252-98) [13], the Fourier Transform Infrared Radiation (FTIR) spectroscopy test was carried out by test instrument, manufactured by (Bruker Company in Germany), kind (TENSOR-27). It is equipped with a room temperature DTGS detector, mid- Infrared spectrum was used within a range of (4000 to 400) cm^{-1} and a KBr beam splitter.

II. Mechanical tests

The tension test was performed according to ASTM D638 [14, 15]. The sample length used is (165 mm) and (7 mm thickness). A universal testing machine (UTM) performed the tensile test with a load capability of 50 KN and a cross-head velocity of (5 mm/min). Through tensile, evaluation and comparison of modulus of elasticity (Young's modulus) and ultimate strength were made for materials with different fillers weight fractions.

4. Results and Discussion

Figures 1, a and b, illustrates the infrared spectra of neat acrylic bone cement and type PMMA, respectively. The wide peak of 4000-2900 cm^{-1} is assigned to the appearance of stretching vibration, where the peak of 2961.29 cm^{-1} belongs to the methyl group's C–H stretch (CH$_3$). Due to the presence of ester carbonyl group stretching vibration, C=O stretching, PMMA's main characteristic vibration bands are sharp intense peak at 1745.87 cm^{-1}[13]. Because of the C-O (ester bond) stretching vibration, the 1457.16 cm^{-1} and 1280.78 cm^{-1} band are associated with C – H symmetric and asymmetric stretching modes respectively, the wide peak ranging from 1488-1000 cm^{-1} can be explained. The peak at 1280.78 cm-1 relates to the torsion of the methylene group CH$_2$ and the peak at 1195 cm^{-1} belongs to –O-CH$_3$ stretching vibrations [17] and the peak at 864.21 cm^{-1} corresponds to the C-C stretching band [18].

The infrared spectrum of the binary polymer blend (Acrylic bone cement: 15 % PMMA) as optimal samples is shown in Figure 1, c. From this figure, it was observed that all the characteristics vibration bands of the acrylic bone cement shown in Figure 1-a, are presented in the FTIR spectrum of a binary polymer blend. Also, it was found from this spectrum that the peak at 2920.07 cm^{-1} corresponds to the methyl group's C – H stretching band (CH$_3$). The main characteristic vibration bands of acrylic bone cement appear at 1722.57 cm^{-1} of stretching vibration C=O band, and the peak at 1434.69 cm^{-1} for stretching vibration ester bond C–O and at 1386.51 cm^{-1} are associated with symmetric and asymmetric stretching modes of C–H band respectively. The peak at 1239.41 cm^{-1} is appointed to the methylene group torsion band (CH$_2$), while the stretching band C–C is at (986.85 and 840.58) cm^{-1}[17].
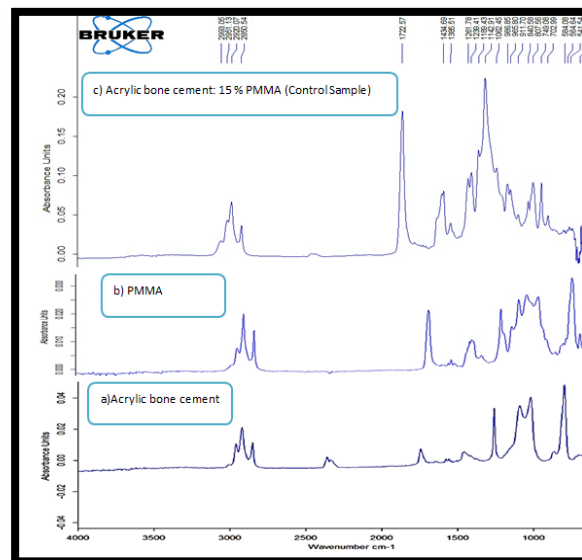

Figure 1: The infrared spectrum for a: Neat acrylic bone cement, b: Neat PMMA, and c: Polymer blend (Acrylic bone cement: 15% PMMA)

The infrared spectra of (control sample) binary polymer blend (Acrylic bone cement: 15 % PMMA), and polymer blend composites reinforced with different ratios of ZrO$_2$ nanoparticles are shown in Figure 2. All the features of polymer blend vibration bands of (control sample), shown in Figure 1, are presented in infrared spectra of ((Acrylic bone cement: 15 % PMMA): X % ZrO$_2$) composites specimens (Figure 2). PMMA principal vibration band characteristics appear at C = O band 1723.97 cm^{1} and fingerprint peaks at C – O band 1434.69 cm^{-1}. The existence of ZrO$_2$ particles in PMMA led the bands given to Zr – O and O – Zr – O bands in ZrO$_2$ to weaken and probably disappear [18].

In infrared spectra for ((Acrylic bone cement: 15% PMMA): X% ZrO_2) composites specimens no new peaks or peak shifts were observed. This is due to having to find a physical bond and absent any cross-linking in these specimens. There is a clear decrease in peak intensity for all the characteristic peaks at 0.5 wt. % ZrO_2 and then increase again with further increase in ZrO_2 content in PMMA composites specimens.
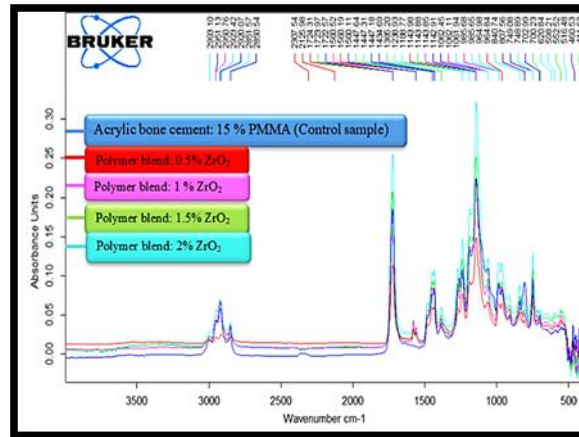

Figure 2: The infrared spectra for the first group bio-composites ((Acrylic bone cement: 15 % PMMA): X% ZrO_2), as a variable of the composite content of ZrO_2 nanoparticles

The infrared spectrum of binary polymer blend (Acrylic bone cement: 15 % PMMA) and its polymer blend composites reinforced with different ratio of MgO nanoparticles content in the composite are shown in Figure 3. All the vibration bands features of polymer blend as a control sample, shown in Figure 1, are presented in (Acrylic bone cement: 15% PMMA): X% MgO) composite samples are comparable to the FTIR range of neat acrylic bone cement discussed previously in Figure 1, a, the main attributes of the acrylic bone cement vibration band is the C= O band appearing at 1722.57 cm^{-1} and the fingerprint peak appearing at 1434.69 cm^{-1} for C–O band vibration. The existence of MgO nanoparticles in polymer mixture (Acrylic bone cement: 15% PMMA) resulted in the weakening of the bands ascribed to Mg–O, and Mg–O–Mg compound in the range of cm^{-1} (661.01–511.18) as a wide band [19].
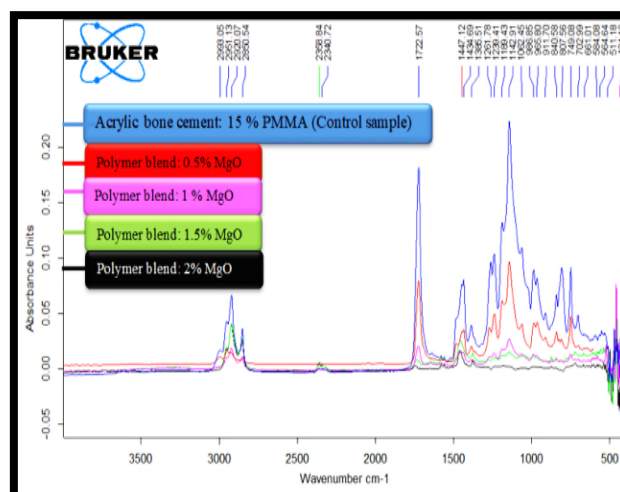

Figure 3: The infrared spectra for the second group biocomposites ((Acrylic bone cement: 15 % PMMA): X % MgO), as a variable of the composite content of MgO nanoparticles

Figures 4 and 5 show a stress-strain behaviour of composite materials consist of the polymeric blend (Acrylic bone cement: 15 % PMMA) reinforced with three types of nanoparticles of ZrO_2 and MgO individually at the selected weight fractions, which are (0.5, 1, 1.5 and 2 wt.%), respectively.
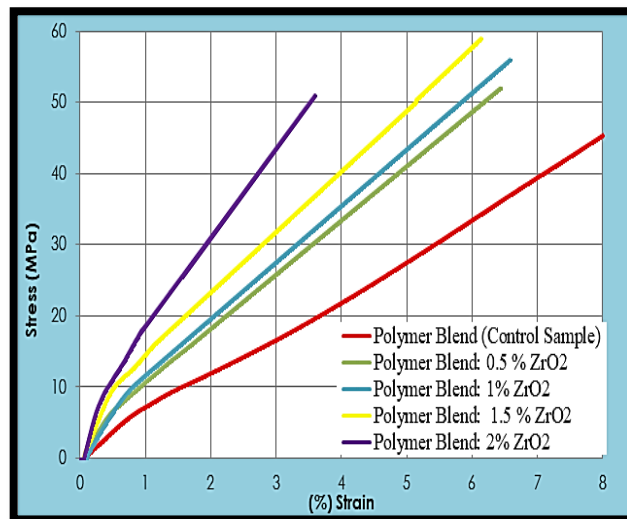
Figure 4: Stress-strain curve for the bio composite ((Acrylic bone cement: 15 % PMMA): X% ZrO$_2$), as a variable of the composite content of ZrO$_2$ nanoparticles
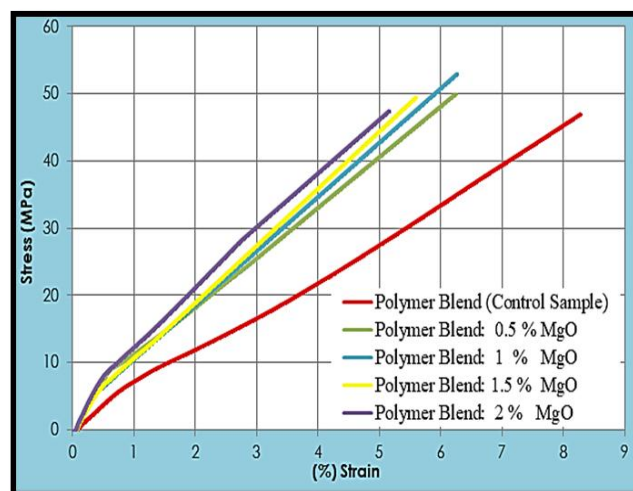

Figure 5: Stress-strain curve for the biocomposite ((Acrylic bone cement: 15 % PMMA): X % MgO), as a variable of the composite content of MgO nanoparticles

Figures 6, and 7 show the fracture strength, and modulus of elasticity for three groups of hybrids Nano composite samples ((Acrylic bone cement: 15 % PMMA): X% nanoparticles) respectively as a function of nanoparticle (ZrO$_2$ and MgO) content in the blend. It can be noticed from these figures, that tensile strength was enhanced, as compared with the polymeric blend, by increasing the weight fraction of ZrO$_2$ up to 1.5 wt.% with (26 %), and (12%) enhancement for 1 wt.% MgO, respectively, in strength respectively. The strengthening resulting from the existence of uniformly distributed harder and stronger particulates in the matrix can explain this enhancement in strength. Also, the large surface area of nanoparticles offers more points of contact between polymer blends and Nano additives thereby enhancing mechanical interlocking and enabling a shift in the characteristics of polymer mixture with (1.5 wt.% ZrO$_2$) and (1 wt.% MgO) supplied by plastic deformation in the polymer matrix ductility. As well as, the nanoparticles already well spread transfer stress from the matrix to the strong Nano fillers.

Finally, polymeric blend reinforced with 1.5 wt.% ZrO$_2$ show good mechanical properties and contribute to the improvement of the mechanical properties by ZrO$_2$ nanoparticles added to the polymeric blend. This could be attributed to the inherent strength of ZrO$_2$ as compared with other nanoparticles.

However, from Figure 7, it was noticed that the polymeric blend composites samples with 1.5 wt.% ZrO$_2$, and 1 wt.% MgO nanoparticles exhibited higher values of young's modulus. Moreover, from this figure, the polymeric blends reinforced by ZrO$_2$ nanoparticles have a high elastic modulus in comparison with their counterparts of the other groups' composites samples. This behaviour may be

attributed to the inherent characteristic of ZrO_2 which has high mechanical strength which improves the mechanical properties of acrylic blend based composites [20].

When further addition of the nanoparticles (ZrO_2, and MgO) increases, seems to reduce the interfacial adhesion between the components, and a non-homogenous distribution led to composites with lower elastic modulus.
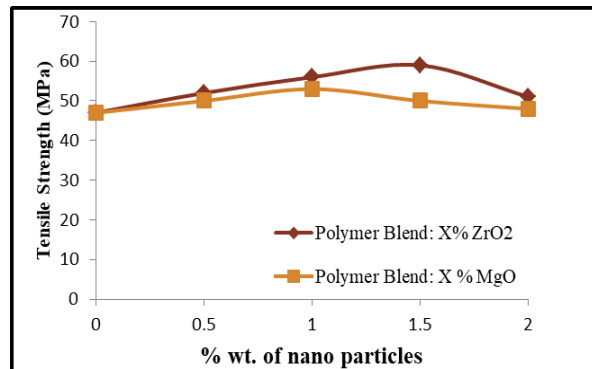

Figure 6: Tensile strength for the bio composite ((Acrylic bone cement: 15 % PMMA): X% nanoparticles), as a variable of a Nano fillers (ZrO_2, and MgO) content in the blend
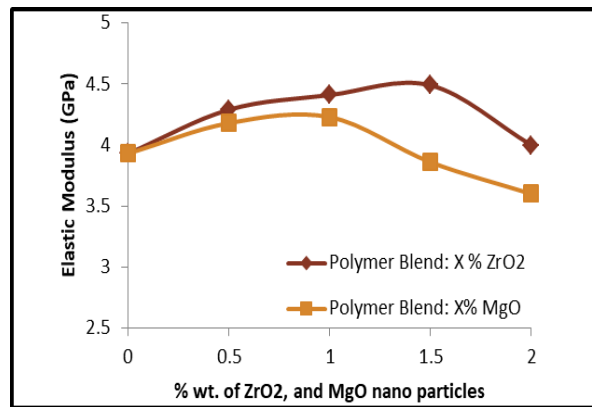

Figure 7: Modulus of elasticity for the bio composite ((Acrylic bone cement: 15% PMMA): X% nanoparticles), as a variable of a Nano fillers (ZrO_2 and MgO) content in the blend

Regarding, the Nano hybrid composites, the addition of the filler of (2 wt.% ZrO_2), and (<1.5 wt.% MgO) caused a reduction in tensile strength. This reduction was due to the presence of particle-matrix interfacial defects and the presence of Vander Waals forces causes the dispersion process to be ineffective. Furthermore, the existence of agglomerated fillers that form loosely connected clusters that affect the crack propagation mode decreases the tensile strength [21].

The size, amount and dispersion of the reinforcement phase and interfacial bonding between the components of composite influence the mechanical and physical properties directly. They have influence on the microstructure morphology of composites as well. Thus, in an attempt to correlate the mechanical characteristics of polymer blending samples with their microstructural morphologies, the scanning of electron microscopy (SEM) micrograph analyses were conducted on the fracture surfaces (at magnification 1000X). The fracture surface morphology for binary polymer mixing (control sample) and for polymer Nano composite of ((Acrylic bone cement: 15% PMMA):1.5 % ZrO_2), and ((Acrylic bone cement: 15% PMMA): 1 % MgO), were characterized. Homogenous morphologies were observed, all microstructural morphologies showed up as co-continuous structures, making it more difficult to distinguish between individual polymers in the composites of these polymeric blends. These fracture surface morphologies, shown in Figures 8 a, b, and c, show stronger interfacial adherence between composite specimen components with additional nano-sized reinforcing materials (1.5% ZrO_2 and 1% MgO) to binary polymeric blend respectively. However, the fracture surface of polymeric composites was rough and uneven with ductile dimples pattern. Also, the morphology of fracture surface exhibited lamellar steps with relatively homogenous size and distribution, characteristics of ductile fracture [22]. Besides, there was no wide agglomeration of

these nanoparticles showing the uniform distribution of particles. It was also observed that the microscopic structure of the fracture surface morphology for most of the nanoparticles are embedded inside the matrix material as an integral part of the base material structure, indicating good compatibility between the matrix material and leads to the formation of strong physical bonding (strong interfacial regions) between the nanoparticles and polymeric blending matrix [3, 23].

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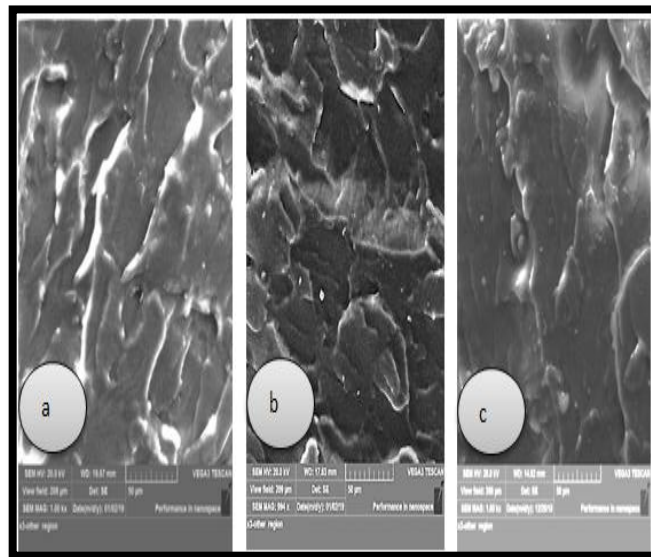

Figure 8: SEM images for (a): Binary polymeric blend ((Acrylic bone cement: 15% PMMA (control sample)), (b): ((Acrylic bone cement: 15% PMMA): 1.5% ZrO$_2$), and (c): ((Acrylic bone cement: 15% PMMA): 1% MgO)

5. Conclusions

The following comments could be taken from this study :

The addition of ZrO$_2$ nanoparticles to polymer blend (Acrylic bone cement: 15% PMMA) gave better mechanical properties (tensile strength and young modulus) as compared with other reinforcement nanoparticle materials (MgO) used in this study. Also, when the nanoparticles added to a certain limit (1.5 wt.% ZrO$_2$), and (1 wt.% MgO) enhanced the tensile strength and Young modulus of polymeric blend Nano composites samples. Finally, when the nanoparticle added more than this a certain limit in composite led to a reduction in the mechanical properties, but they retained in these properties better than they are in the polymer blend as a base material. So, these samples may be from the promising materials to achieve the properties required for bone scaffold applications.

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