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Article

A Study on the Effect of Nano Alumina Particles on Fracture Behavior of PMMA

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Abstract: In the current research, the role of nano-sized alumina on deformation and fracture mechanism of Poly Methyl Methacrylate (PMMA) was investigated. For this purpose, PMMA matrix nanocomposite reinforced with different wt% of alumina (*i.e.*, 5, 10 and 15) were fabricated using the compression molding technique. Tensile properties of produced nanocomposites were studied using Zwick Z250 apparatus at cross head speed of about 5 mm/min. In order to specify the role of alumina nanoparticles on deformation and fracture mechanism of PMMA, microscopic evaluation was performed using scanning electron microscope (SEM). The achieved results prove that tensile properties of PMMA depend on alumina wt%. For example, addition of 15 wt% alumina to PMMA causes an increase of about 25% modulus of elasticity. Micrographs taken from the fracture surface of PMMA and its nanocomposites show deformation and fracture mechanism of PMMA changes as alumina is added to it.

Keywords: PMMA; nanocomposite; alumina; fracture mechanism

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1. Introduction

Acrylic bone cement, based on Poly Methyl Methacrylate, has been widely used in dentistry and orthopedic surgery [1–7]. The most frequent complication in cemented orthoplastry is the loosening of cemented prosthesis due to mechanical failure of acrylic bone cement [7,8]. Similar to brittle materials, bone cement can tolerate the compression loading unlike tensile conditions. For this reason, it is clear that bone cement has been implicated as one of the factors that cause aseptic loosening [9]. The addition of reinforcement may improve the fracture properties of bone cement [7–9]. It is known that mechanical properties depend on the type, concentration, size and shape of reinforcement. Other important factors that affect the mechanical behavior of filled systems are the strength of the adhesive bond between phases, the type of dispersion and the kind of agglomeration [10]. Very few studies have examined the enhancement of mechanical properties of bone cements using reinforcement. Serbetci *et al.* [3] studied the thermal and mechanical properties of hydroxyapatite (HA) impregnated acrylic bone cements. Their results showed that addition of HA into bone cement caused an increase in both compressive strength and compressive elastic modulus unlike tensile strength. Kotha *et al.* [8] investigated the changes in the fracture properties by the addition of 316L stainless steel fibers to bone cement and found that increasing the volume fraction of the steel fibers resulted in significant increases in the fracture toughness of the steel-fiber-reinforced composite. The physical and mechanical properties of metal-filled acrylic resin have been studied by Marei *et al.* [11]. It was found that addition of 5% metal powders by volume caused to 2.5% increase in compressive strength. Vallo [12] indicated that addition of up to 50 wt% glass particles to acrylic bone cement could increase flexural modulus and fracture toughness of these composite significantly. Based on the literature survey done by the authors, in spite of importance of deformation and fracture mechanism of PMMA and its composite, this subject has not been under attention by other investigators in more details and only the authors concentrated on the generation method. For example, H. Liu *et al.* synthesize superfine alumina (Al_2O_3) encapsulated with (PMMA) by *in situ* emulsion polymerization [13]. Poly methyl methacrylate (PMMA)/Al_2O_3 composites have also been prepared by the sol gel method [14]. For this purpose, in the current research we will try to clarify the role of Al_2O_3 content on deformation and fracture mechanism of PMMA.

2. Experimental Procedure

2.1. Materials

Cold-cure Acrylic powder (Acropars, Marlic) and Methyl Methacrylate (Acropars, Marlic) were used to produce PMMA as the polymeric base of composite. Al_2O_3 nano powder was used as reinforcement phase. The details of used materials are summarized in Table 1.

Table 1. The specifications of used materials.

MMA Monomer			**Al_2O_3**
Density (gm/cc)	**Boiling Point (°C)**	**Percent Volatile (214° F and 760 mmHg)**	**Purity of Al_2O_3 Nano Powders**
0.94	101	100%	99.7%

2.2. Sample Preparation

In order to decrease the agglomeration and obtain a uniform mixture of PMMA powders and alumina nanoparticles, all tests were accomplished in different frequencies and mixing times. According to our research, the best condition was 10 min with frequency of about 28 s^{-1}. For this reason the nanocomposite was prepared by mechanical milling of PMMA and Al_2O_3 powders in a mixer mill (Retsich MM400, Germany) for 10 min with frequency of about 28 s^{-p}. Both PMMA and Al_2O_3 powders were mechanically mixed firstly to achieve PMMA matrix nanocomposite with different Al_2O_3 content (*i.e.*, 0, 5, 10 and 15 wt%). After mixer milling, the same ratio of the solid/liquid components were used in the preparation of compositions. The solid part consisted of the mixed PMMA and Al_2O_3 powders and the liquid part consisted of the PMMA monomer, the inhibitor and the catalyst. The weight ratio of the solid/liquid components was kept 5/3.5 in all samples. For the cement dough preparation, the powder and the liquid parts were manually mixed together for 30 s at temperature of about 25 °C. The obtained homogeneous dough was kept for 2–4 min (depending on the sample) to reach a sticky state. In this step, the dough was inserted in to the mold and shaped by a compression molding method to get a standard sample. Table 2 presents the details of fabricated nanocomposites.

Table 2. The details of fabricated composites.

Samples Code	Nanocomposites	Al_2O_3 (wt%)
P	PMMA	0
P/5A	PMMA/5% Al_2O_3	5
P/10A	PMMA/10% Al_2O_3	10
P/15A	PMMA/15% Al_2O_3	15

2.3. Microscopic Evaluation

To elucidate the role of alumina content on deformation and fracture behavior of PMMA, the surface fracture of some samples were evaluated using SEM (LEO 1450). Also TEM (LEO 919 AB) was used to find out the morphology of nano-sized Al_2O_3. Figure 1 shows transmission electron microscope micrograph taken from the nano-sized Al_2O_3.

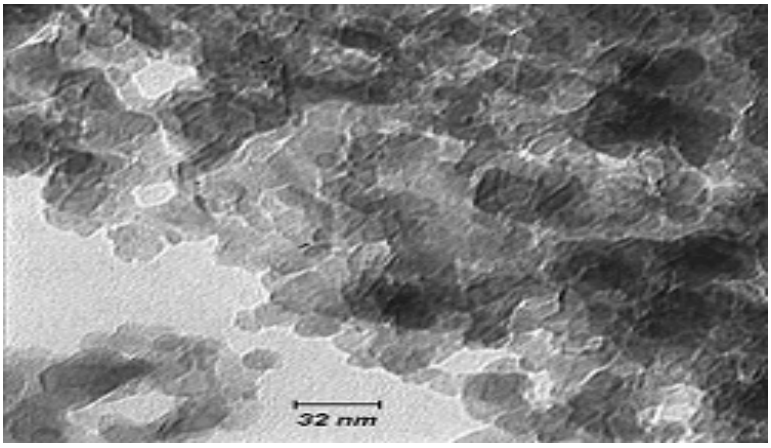

Figure 1. TEM micrograph of nano- sized Alumina.

2.4. Tensile Properties

Tensile tests were performed using Zwick Z250 apparatus with a 20 N capacity load cell. Specimens were fabricated using the mold, as described in ASTM D638 type 2. Five specimens of each group tested at room temperature and under a cross head speed about 5 mm/min. Tensile tests were performed at room temperature.

3. Results and Discussions

The values of tensile strength (MPa), elongation at break (%), tensile modulus (GPa) of the samples are given in Table 3. The results show that the addition of Al_2O_3 particles causes to increase the tensile modulus unlike the tensile strength and elongation at break of PMMA.

Table 3. Dependency of tensile properties of Poly Methyl Methacrylate (PMMA) on Alumina content.

Elongation (%)	Tensile Strength (MPa)	Young's Modulus (GPa)	Sample Code
2.4	44.7	2.4	P
1.8	40.9	2.7	P/5A
1.6	39.8	2.9	P/10A
1.4	37.0	3.0	P/15A

The exact reason for this variation can be attributed to the fact that alumina particles play like stress concentrators, and this role is promoted as particles lead to be agglomerated. Thus, during tensile loading, the magnitude of stress increases drastically near the agglomerated nanoparticles and making the debonding between PMMA and alumina. The values of agglomeration of filler particles play an important role in creation of stress concentration and cause cracks propagate faster so fracture occurs immediately [15]. The authors believe that alumina content affects on wettability of Methyl Methacrylate monomer. The evidence of this role will be shown using SEM micrographs and appears in the following. This result is similar to what proposed by other investigators, for example Kurtz *et al.* [1] studied on static and fatigue mechanical behavior of bone cement with elevated barium sulfate content. They hypothesize that agglomerations of barium sulfate particles in the clinical formulation acted as local stress concentrations or fatigue crack initiation sites, and were likely responsible for the lower tensile and fatigue properties, relative to neat bone cement. Kwon *et al.* [16] investigated on the effect of hydroxyapatite (HA) to mechanical behavior of bone cement. Their results showed significant decrease of the flexural and diametral tensile strength linear with the increased amount of HA.

It is noteworthy that the fracture surface of thermoset polymers can be characterized by the presence of three different regions including a flat featureless mirror zone surrounding the crack initiation point, a transition zone, in which the surface roughness steadily increases, and a final propagation zone with conical marks [17]. Figure 2 shows SEM micrograph taken from the fracture surface of pure PMMA after tensile loading. As seen in the figure the surface can be divided up to three regions consisting mirror, transition and final fracture regions. Hengy *et al.* [18] investigated on tensile properties of PMMA. The fracture surface of PMMA according to their research is very similar to current study. The

closed up mirror zone is shown in Figure 3. It seems this region is created during crack initiation. As mentioned in previous research, this region has no specification.

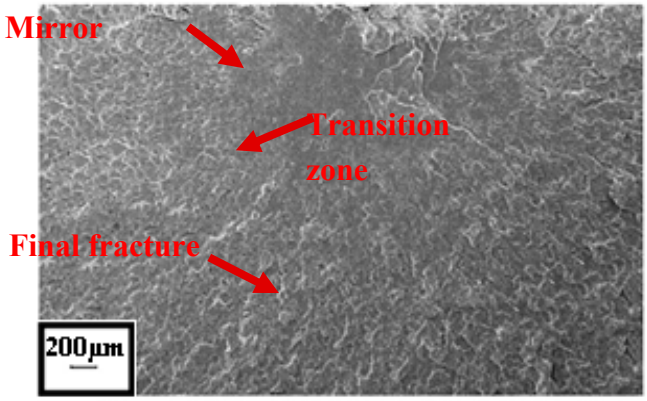

Figure 2. SEM micrograph of different zones in fracture surface of PMMA.

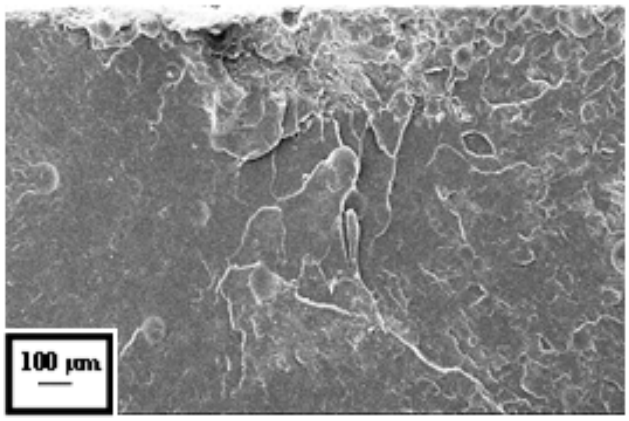

Figure 3. SEM micrograph of mirror zone in PMMA.

Figure 4 shows the close up of transit zone of fracture surface of neat polymer. The surface roughness of transition zone is much higher than that of the mirror zone. The authors believe the occurrence transit zone depends on same parameters such as embrittlement of matrix, void coalescence. This zone will be extended as the microcrack formation promoted.

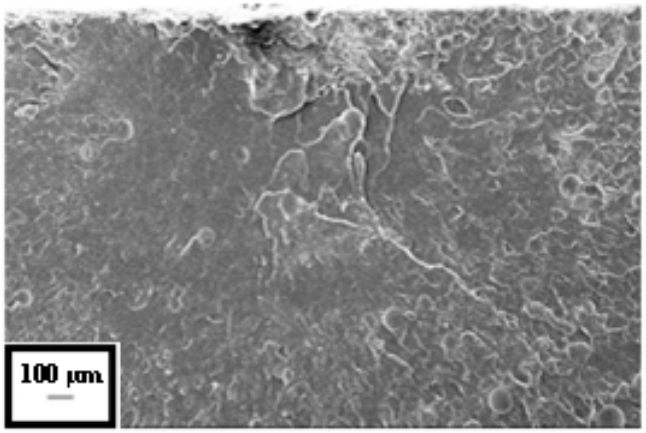

Figure 4. SEM micrograph of transition zone in PMMA.

Figure 5 shows the final fracture surface of PMMA. Increasing in the rate of creation cracks in different parts of sample due to increase of applied stress cause to change the morphology of fracture surface. The results of current research prove that addition alumina content can affect on the fracture surface (concentrate zones). It is clear that PMMA granules, voids and alumina, act like stress concentrates as well as interface of PMMA/Matrix. For example Figure 6 shows the ability of stress concentration of voids. As seen, the crack initiates near the void and propagates in the matrix.

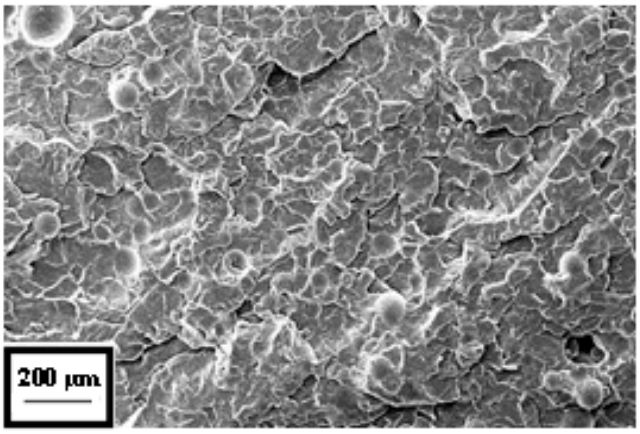

Figure 5. SEM micrograph of fracture zone in PMMA.

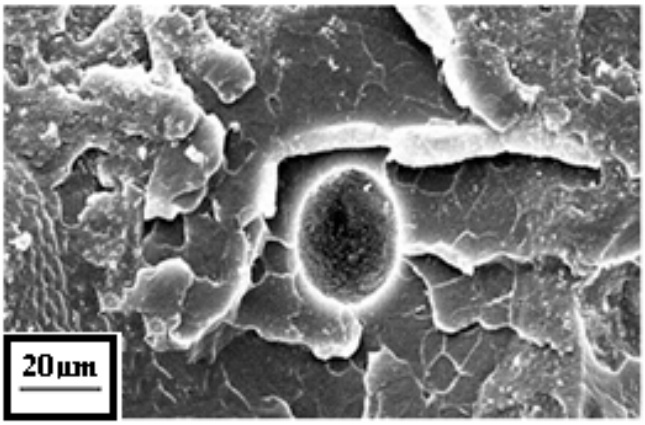

Figure 6. SEM micrograph taken from the fracture surface of PMMA containing 5 wt% Al_2O_3.

Although addition of nanoparticles causes increased viscosity of dough and a decreased amount of voids in molding step, the wettability of PMMA granules by means of the monomer decreases and creates the weakness PMMA granules/matrix interfaces. This implies that the role of weak interface in creation crack is much higher than that of strong interface. As other investigators reported, the transition of force between matrix and PMMA granules depends on adhesion quality of interface. In fact, imperfect adhesion causes pseudo voids [19]. Figure 7 is concerned with the fracture surfaces of the composite sample. This Figure indicates pseudo voids resulting from debonding of PMMA granules. Pseudo voids inside the cross-section on the fracture surfaces of samples indicate that the crack was propagated around the PMMA granules, and through them. As a result, an initiated crack can be propagated from one PMMA granule to other sites.

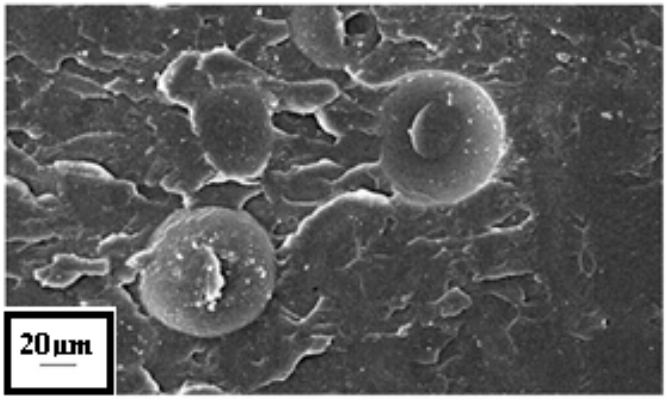

Figure 7. SEM micrograph showing crack propagation in PMMA/5 wt% Al_2O_3 nanocomposite.

The SEM images of the fracture surfaces of the PMMA/Al_2O_3 composites obtained after the tensile loading are shown in Figure 8. The fracture surface of PMMA/10wt%Al_2O_3 is shown in Figure 8a, while Figure 8b,c show the fracture surfaces of PMMA/15wt% Al_2O_3. As shown in Figure 8a,b the amount of pseudo voids depends on weight percent of nanoparticles. In fact, addition of nano alumina causes to increase pseudo voids due to creation of more debonding. Figure 8c is SEM micrograph taken at high magnification of PMMA/15wt% Al_2O_3 composite showing a poor adhesion between the PMMA granules and polymer matrix.

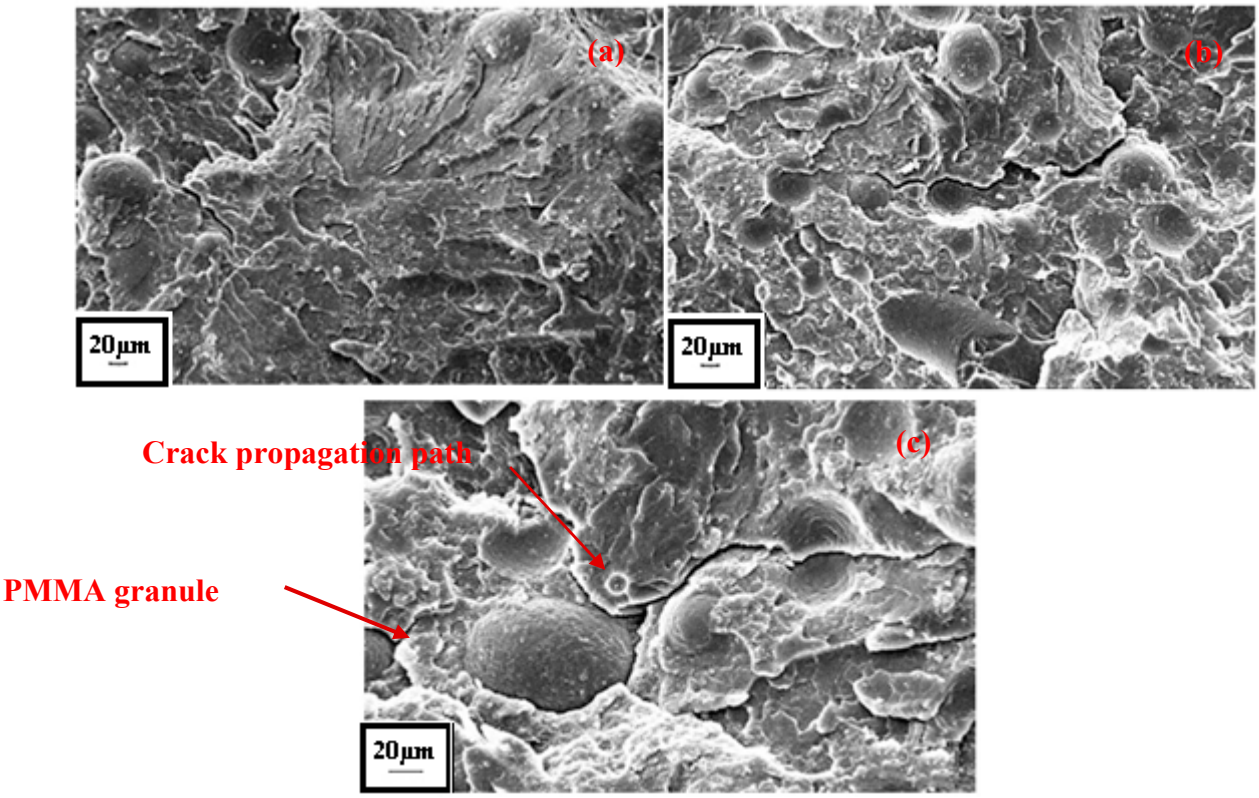

Figure 8. SEM micrographs taken from the fracture surface of (**a**) PMMA/10wt% Al_2O_3; (**b**,**c**) PMMA/15wt% Al_2O_3.

4. Conclusions

The role of Al_2O_3 content on deformation and fracture mechanism of PMMA is investigated by using a tensile test in this study. It is found that addition of nano alumina to PMMA causes an increase in modulus but not tensile strength or amount of elongation at break. Also, it is observed that the amount of debonding between the matrix and the granules has increased due to addition of nanoparticles.

Author Contributions

Seyed Mojtaba Zebarjad and Seyed Abdolkarim Sajjadi generated and supervised the research project. Arezoo Sezavar did the research. Arezoo Sezavar, Seyed Mojtaba Zebarjad and Seyed Abdolkarim Sajjadi wrote the article.

Conflicts of Interest

The authors declare no conflict of interest.

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