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The Effect of Planetary Ball Milling Technique on Physical and Mechanical Properties of Reinforced Poly (Methyl Methacrylate) Denture Base

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Abstract:
Bioceramics have great potential in biomedical applications. In the current study, hydroxyapatite (HA) was used as reinforcing filler for poly (methyl methacrylate) (PMMA) denture base material. The physical mixing of the powder components (PMMA and the filler) is strongly preferred to provide the required dispersion of the filler in the matrix. Therefore, the current study was conducted to investigate the effect of different mixing time using planetary ball milling technique (PBM) on the mechanical properties of PMMA/HA denture base composite. In this study, the powder components (PMMA and 15 wt% HA) was mixed for different times (i. e., 10, 20, 30 and 40 min) using PBM. The particles size and distribution of PMMA/HA mixtures as a function of different mixing times were studied using laser light scattering technique. The flexural and tensile tests were conducted to evaluate the mechanical performance. The scanning electron microscopy (SEM) was used to study both the powder mixtures and the fractured surface of the tested sample of PMMA/HA composite.

Keywords: Particle size, PMMA/HA, planetary ball milling technique, Denture base materials, Mixing time.

Introduction

Poly (methyl methacrylate) or PMMA is an acrylic material fabricated to be used widely as a denture base material (Ali Sabri, Satgunam, Abreeza, & N. Abed, 2021; Zafar, 2020).Its essential characteristic properties of reasonable cost, processing ease and low toxicity, together with practical performance related to biologic, physical, aesthetic, and handling characteristics, made PMMA preferred for dental applications. On the other hand, the brittleness and low impact resistance of PMMA restricted its use(J. M. Aldabib, 2021). PMMA has been used for screw fixation in bone, filler for bone cavities and skull defects, bone cements, contact and intraocular lens and vertebrae stabilization in osteoporotic patients (Frazer, Byron, Osborne, & West, 2005; Gonçalves et al., 2013). The versatility and reliability of made PMMA to remain a popular and frequently used material, although several new materials has been presented in the market (Kretlow, Young, Klouda, Wong, & Mikos, 2009; Meng & Latta, 2005; St. John, 2007). PMMA materials are vulnerable to leakage, breakage, post-processing shrinkage, and water absorption. To overcome this problem, additional materials are added as fillers and additives to PMMA, such as glass fibers, carbon fibers, aluminum oxide, zirconium oxide and barium titanate particles. (Gad, Fouda, Al-Harbi, Näpänkangas, & Raustia, 2017; Khindria, Mittal, & Sukhija, 2009). Reinforcing polymeric materials with a bioceramic fillers can possibly result in biocompatible polymer based composite material suitable for dental prosthodontics applications. A number of ceramic powders are used e.g., barium titanate, zirconium oxide, alumina and hydroxyapatite (HA)(J. Aldabib, 2020). The promise behind HA reinforcement is that HA is considered to be a biocompatible material. Moreover, HA is a preferred reinforcement because of its stiffness, density, and bioactivity (Heness & Ben-Nissan, 2004; Hing, 2005; LeGeros, 1988). Evidently, HA has been presented as filler for many polymer-based composites to reinforce the physical and mechanical properties to be used in biomedical applications (Wang, 2003; Zuo et al., 2007). When processed and manufactured, PMMA denture base material should have the sufficient mechanical requirements that are considered essential for optimum performance in the dental application. The pre-requisite mechanical requirements for a successful HA-PMMA composite to be used in the oral environment, though most applications in dentistry have a minimum mechanical property requirement, are controlled by HA loading, HA particle size, and distribution of HA(J. M. Aldabib & Ishak, 2021; Tham, Chow, & Mohd Ishak, 2010). The homogeneous distribution of filler particles in the PMMA matrix is essential in order to obtain the maximum result. Thus, the physical mixing of the powder components (PMMA and HA) is strongly recommended to

provide the required dispersion of the filler in the matrix. Several techniques have been tried such as hand mixing, stirrer mixing technique and ball milling technique. In addition, the planetary ball milling technique is found to be the most effective technique to achieve the goal. However, different variables during the milling process may affect on optimizing the mechanical properties of the output mixture. Among the milling variables (milling medium, rotation speed, ball-to-powder ratio, milling temperature, and milling time). Milling time is profoundly considered the most important controlling factor that influences the particular powder system and its workability in the composite (Suryanarayana, 2001). Unwanted effects of contamination and phase change are associated with longer than required milling time. This suggests the need to optimize the controlling factor of milling time if it is desired to enhance the biomechanic properties of PMMA/HA composite(Tham et al., 2010). The objective behind the current study is to identify the ideal time range of mixing that assure obtaining the best mechanical performance in the studied composite.

Material and methods

The material procedure adopted in this study to formulate a denture base material consisted of two components; the solid component and the liquid component. The solid component was composed of poly (methyl methacrylate) PMMA *M w ≈ 996.000* fabricated by GPC in crystalline material from USA-based manufacturer Aldrich**.** A 0.5% of benzoyl peroxide of ≤106 μm particle size was provided from Merck Chemical Company, Germany. Hydroxyapatite (HA) ceramic filler of particle size 5±1 (μm) was supplied by nanoXIMp202Fluidinova, Engenharia, S.A. Portugal. The liquid component, on the other hand, consisted of methyl methacrylate (MMA) supplied from Aldrich, USA stabilized with 0.0025% hydroquinone. Ethylene glycol dimethacrylate (EGDMA) to be used as a cross linking agent was also provided from the previous manufacturer. In the laboratory, the solid component (powder) was mixed up in zirconium oxide jar and balls with the aid of a planetary ball milling machine for 10, 20, 30 and 40 minutes, respectively. This time configuration was designed in order to allow for studying the effect of mixing time on the mechanical properties of HA filler filled PMMA matrix. The weight ratio of powder: ball (PBR) was 1:10, and the running speed of mixing was 150 RPM. The running time and pausing time were 3 and 6 minutes, respectively. The powder and liquid (P/L) was mixed according to the standard dental laboratory usage. After reaching the dough stage, the mixture was packed into a mold and was pressed under 14 MPa, at room temperature for 30 min. The final polymerization (curing process) was carried out using a water bath at 78°C for 1 1⁄2 h. The mold was then left to cool slowly at room temperature. The samples were next removed. These procedures adopted in this study was consistent to those of the prescribed standard method for preparing conventional denture base in the dental laboratory (McCabe & Walls, 2013).

Particle Size and Distribution Analysis

The particle size distribution of PMMA/HA composites after the milling for several times were determined by laser light scattering technique (Sympatec GmbH particle size analysis, Germany). The particle size of the composition was analyzed by software of HELOS particle size analysis Windox 5.

Scanning Electron Microscopy

Morphology of ground powder mixtures and composites fractured surface was studied with scanning electron microscopy (SEM), using a model Leica Cambridge S-360 microscope. All surfaces were sputter-coated with aurum/palladium alloys to enhance image resolution and avoid electrostatic charging and to obtain image resolution.

Tensile test

Tensile test was carried out according to ASTM D-638 type IV using an INSTRON 5582 10KN electromechanical tensile testing machine. The gauge length was set at 50 mm and crosshead speed at 5 mm/min. At least five samples were tested for each formulation. Tensile strength and young's modulus were recorded.

Flexural test

Three-point flexural test was performed in accordance with the ASTM D790-86 standard. The support span was set at 50 mm whilst the diameter of the loading nose and supports was 20 mm and 10 mm, respectively. The testing was conducted at a crosshead speed of 2 mm/min on the INSTRON 5582 10 KN tensile testing machine. At least five samples for each formulation was tested to determine the flexural strength and the flexural modulus magnitudes. Both flexural properties were calculated by the following equations:

$$\text{flexural modulus} = \frac{L^3 m}{4bd^3} \qquad \text{flexural strength} = \frac{3PL}{2bd^2}$$

Whereby L = span length, P = maximum load, b = specimen width, d = specimen thickness, m = tangent gradient of the initial straight line of load versus deflection curve.

Results and discussion

Particle Size Analysis for the powder mixtures

Table 1 shows the average particle size of PMMA/HA powder mixtures that subjected to planetary ball milling technique for several milling times (i. e., 10, 20, 30 and 40 min). It was observed that the PMMA/HA powder mixtures milled for 10 min has the smallest particle size (22.94 µm) and the largest surface area (0.50m²/g). However, the particle size was slightly increased to (25.01µm) when the milling time was 20 min. it is interesting to note that the particle size reduced to (23.52µm) after going to 30 min milling and increased again to (27.89µm) when the milling time was 40 min. similar observation was reported by Tham et al. (2010). This can be attributed to the fact that, during the milling the powder particles are repeatedly flattened, cold welded, fracture and re-welded. Whenever tow balls collide, some quantity of powder is trapped in between the balls. The force of the collision plastically deforms the powder particles leading to hardening and fracture. The new created surfaces make it possible the particles to weld together leading to an increase in particle size. In the early stages of milling, the particles are somewhat soft, therefore, they have high tendency to weld together and form large particle. A large range of particle sizes developed, even bigger than the starting particles in some cases. With continued deformation, the particles get work hardened and fracture resulting reduced particle size (El-Eskandarany, 2013; Suryanarayana, 2001).

Table1: Particle size of PMMA/HA composite after being subjected to planetary ball milling.

Compound	Average particle size (µm)	Specific surface area (m²/g)
PMMA+HA15% (10 min mixing)	22.94	0.5035
PMMA+HA15% (20 min mixing)	25.01	0.3892
PMMA+HA15% (30 min mixing)	23.52	0.4616
PMMA+HA15%(40 min mixing)	27.89	0.2158

Scanning Electron Microscopy (SEM)

Figure 1 illustrates the SEM micrographs at high magnification for randomly selected samples from the ground powder mixtures for different times (i. e., 10, 20, 30, 40 min). It can be clearly seen that the distribution of filler particles through the PMMA particles upwardly enhanced as a function of mixing time and reached its maxima when the mixing runs for 30 min, after which agglomeration of HA powder was recorded. According to Mohamed (2005),the particle size and particles distribution have significant effects on the mechanical properties. Filler particles of large median sizes reduced the strength and modulus of the composites. During the mixing of PMMA/HA powder to the liquid components for the curing process (polymerization), agglomeration might happen and causes a reduction of flexural strength(Tham et al., 2010).

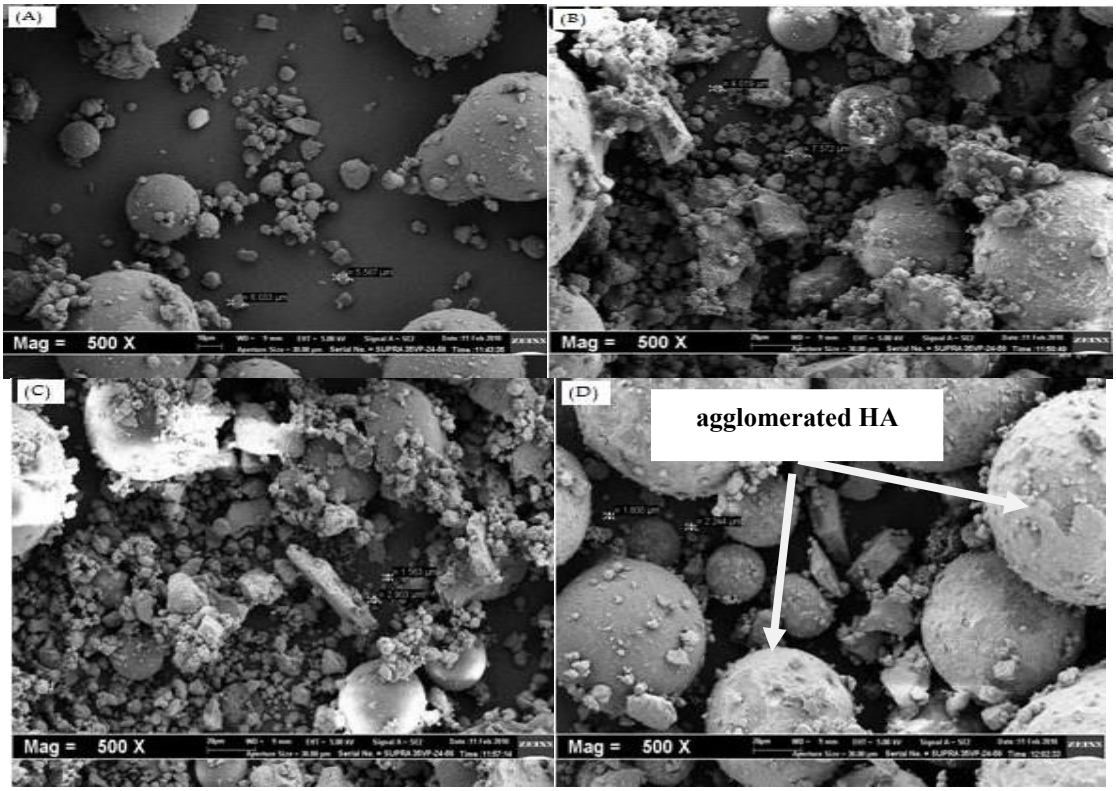

Fig 1.SEM micrographs were taken for the powder samples, (A) 10 min mixing, (B) 20 min mixing, (C) 30 min mixing and (D) 40 min mixing at the magnifications (500X).

Tensile Properties

Table 2 illustrates the output results of tensile testing of PMMA composite samples as a function of mixing time. Observations on the table show that tensile strength responses reach the maxima at 48.5 MPa, when the mixing runs for 30 minutes. Beyond this time, the mixing has a weakening effect. The increase in tensile strength can be attributed to the good dispersion of filler into the matrix. Good filler dispersion was associated with the ability to distribute stress uniformly in the samples(Mohamed, 2005). As a function of long term mixing, a reduction in tensile strength occurred due to the agglomeration of HA filler particles or simply as a result of the physical contact between adjacent agglomerates. The agglomerate is a domain that can act like a foreign body in composites and also acts as chains movement obstacles which originate failure under stress. The agglomerates act as stress concentrator and building up stresses in composites earlier than usual and caused earlier rupture (Mohamad, Muchtar, Ghazali, Mohd, & Azhari, 2008). On the other hand, the tensile modulus was not affected as a function of mixing time. This result is in agreement withMohamed (2005) who claimed that tensile is measured before any significant plastic deformation. Tensile modulus is measured during elastic deformation of the composite, whereby the movement at the filler-matrix interface is very limited.

Table 2: The effect of mixing time on the tensile properties of PMMA filled by 15 wt% of HA.

Mixing time (min)	Tensile strength (MPa)	Tensile modulus (GPa)
PMMA+HA15% (10 min mixing)	44.70 ± 1.28	2.50 ± 0.03
PMMA+HA15% (20 min mixing)	42.10 ± 0.83	2.50 ± 0.01
PMMA+HA15% (30 min mixing)	48.50 ± 1.87	2.48 ± 0.01
PMMA+HA15% (40 min mixing)	39.50 ± 2.51	2.51 0.02

Flexural Properties

Figure 2 illustrates the output results of flexural testing of PMMA/HA composite samples as a function of mixing time. Observations show that the samples' flexural strength and modulus responses reach the maxima at 78.88MPa and 2.8 GPa, respectively, when the mixing runs for 30 min. Beyond this time; the milling has a weakening effect on these two properties. The increase in both flexural strength and modulus at lower milling time is due to the homogenous dispersed filler particle, the increase of milling time led to extensive filler agglomeration. This would cause the occurrence of voids, which increase in size to form cracks. Unfortunately, agglomeration acts as stress concentration points. In such cases, the imposition of an external load will cause more stress to be concentrated on neighboring particles from the advancing crack bringing about rapid and successive propagation that finally leads to brittle failure(Tham et al., 2010). According to Tham et al. (2010) who proved that the physical mixing using PBM technique has a great influence on the dispersion and flexural strength of HA and Alumina ceramic fillers filled PMMA matrix. The uniform dispersion of the filler in PMMA matrix enhanced the brittleness and stiffness of the composite. This uniformity will impart more resistance to flexural force, which led to sustain higher stress. As the modulus of filler is high, most of stresses are received by them without deformation (John, Gangadhar, & Shah, 2001).The high filler loading in the matrix could also contribute by creating more defects weakening the material if the filler agglomerated which can reduce the mechanical properties of PMMA(J. M. Aldabib & Ishak, 2020) (Elshereksi, Mohamed, Arifin, & Mohd Ishak, 2009).

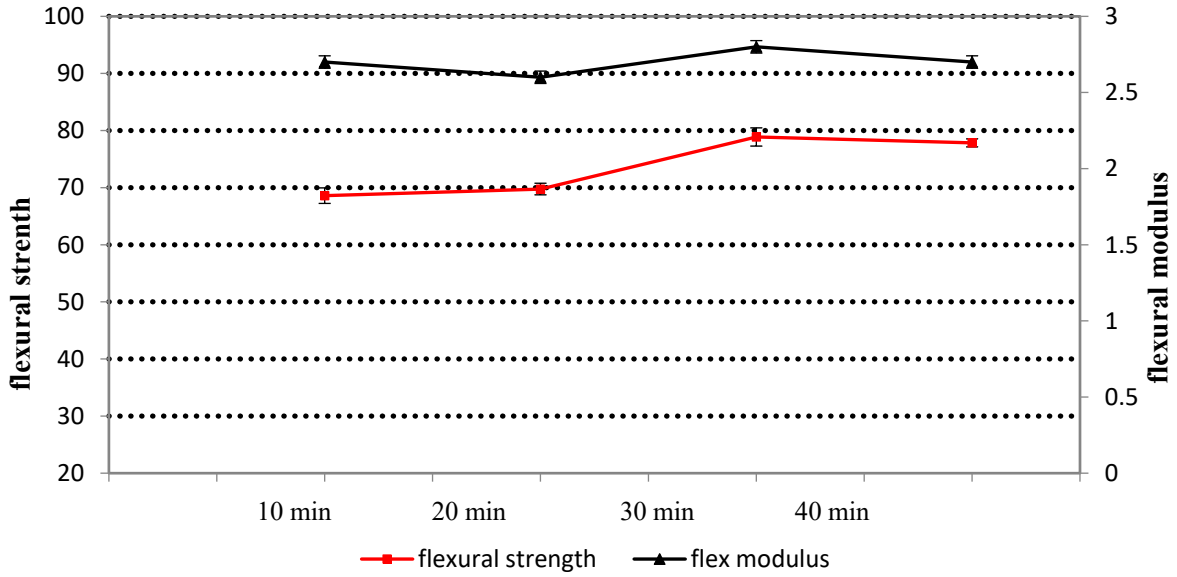

Fig 2. The effect of mixing time on the flexural properties of PMMA matrix filled by 15 wt% of HA.

Scanning Electron Microscopy

Figure 3 shows the SEM micrographs for the fractured surface of PMMA/HA composites tested samples prepared from the powder mixtures that mixed for different times (i. e., 10, 20, 30, 40 min). It can be noticeably seen that the mixing time has great influence on the existence of the voids. Fig 3 (a) shows the microporosity on fractured surface of PMMA/HA samples mixed for 10 min which is approximately (16.64%). The microporosity is a sign that can be associated with the debonding of the filler agglomerates from the PMMA matrix during the fracture process. Fig 3 (b) shows a reduction of the microporosity to 8.74% on the fractured surface of samples mixed for 20 min and to 3.32% for the samples mixed for 30 min Fig 3 (c). The considerable reduction of microporosity is probably due to the heat generated during the mixing process which reduces the moisture content in the sample(Tham et al., 2010). Fig 3 (d) shows slight increase 4.21% in microporosity on the fractured surface of the tested sample that mixed for 40 min Comparing to the samples mixed for 30 min,. This unwanted effect is most likely due to the agglomeration of filler particles as a function of long-term mixing. According to (J. M. Aldabib & Ishak, 2021; Mohamed, 2005)as a result of large particle size, stress concentrations will be raised and contributes to the formation of large cavities and voids. As discussed earlier,

agglomeration might also take place during the curing process (polymerization) causing poor mechanical properties.

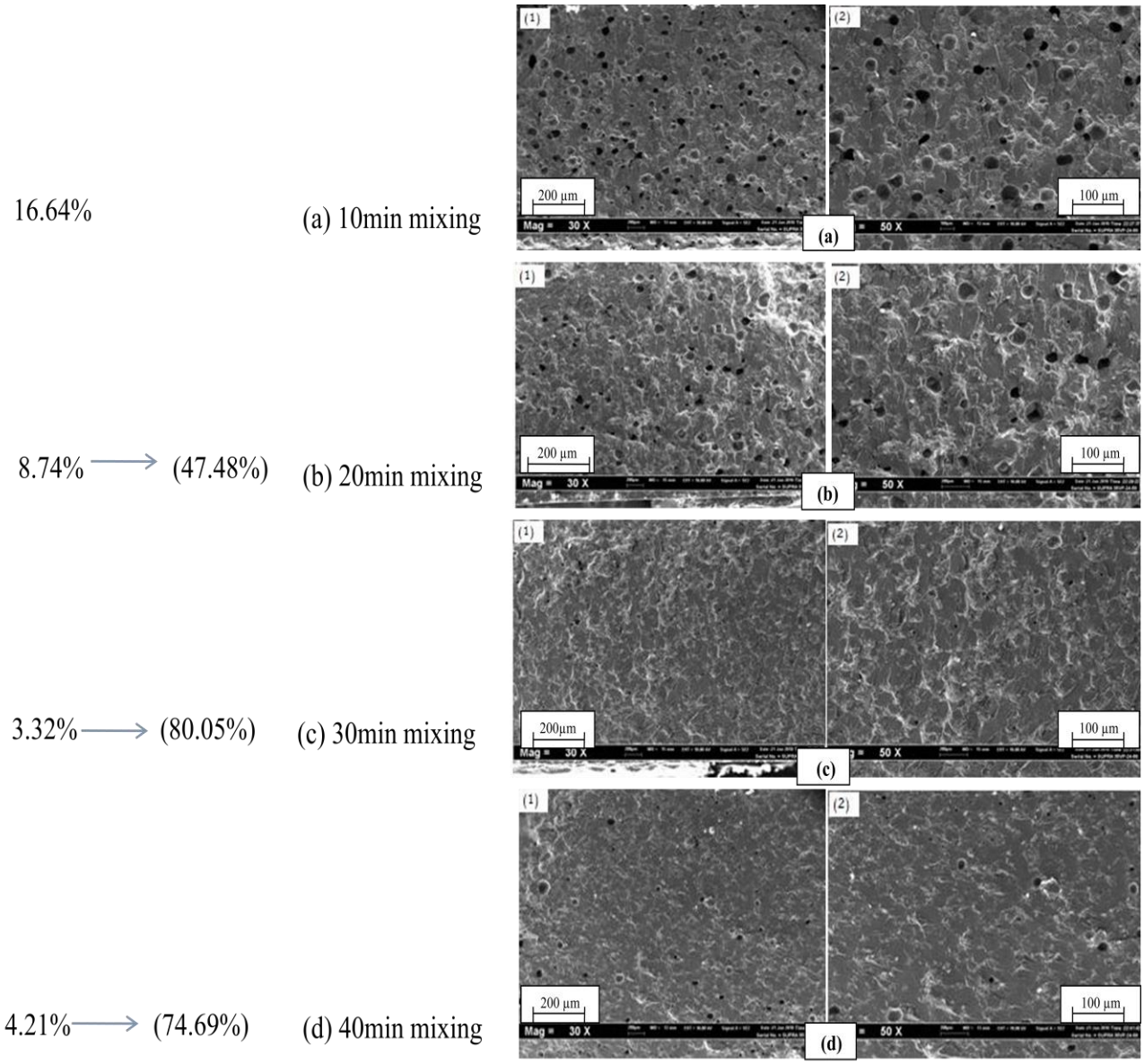

Fig 3.SEM micrographs expose the fractured surface of flexural samples, (a) 10min mixing, (b) 20min mixing, (c) 30min mixing and (d) 40min mixing at different magnifications (1) 30X / (2) 50X.

Conclusion

It was found that the particle size of PMMA/HA composite effected by using planetary ball milling technique (PBM) as a function of time. The particle size and particles distribution have significant effects on the mechanical properties, based on the mechanical testing, the mixing time of 30 minutes is considered the optimum mixing time for maintaining the highest mechanical properties in the selected composite, after which samples may lose their quality flexure and likely break as mixing proceeds. As a function of mixing time, the presence of the microporosity (voids) on the fractured surface of PMMA/HA can be controlled.

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