Research Article

Effect of hydroxyapatite filler concentration on mechanical properties of poly (methyl methacrylate) denture base

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Abstract
Poly (methyl methacrylate) or PMMA is an acrylic material has been used widely as a denture base material. The denture base is subjected to various stresses during the function, these include tensile and flexural stresses. The current study was aimed to experimentally evaluate the effect of different filler concentrations on physical and mechanical characteristics of PMMA/HA composite. PMMA reinforced with different ratios (i.e. 0, 5, 10, and 15 wt%) of silane treated HA were prepared to study the effect of HA concentration on the mechanical properties of acrylic denture base material. Tensile, flexural and fracture toughness tests were conducted to evaluate the mechanical performance. The fracture surfaces of all the composites were studied using scanning electron microscopy. The hardness of the composite was investigated using Vickers hardness. Independent t-test was also conducted to evaluate the significant difference in the values measured as a function of different filler loading. Data analyses showed a significant improvement ($P < 0.05$) in the tensile and flexural modulus of the composite 26% and 27.3% respectively, as a result of increasing the HA loading to 15 wt%. However, no significant difference ($P > 0.05$) was detected in the tensile and flexural strength as function of HA incorporation. A small increment of only 1.63% and 3% in the tensile and flexural strength respectively, was achieved at very low filler loading i.e. 5 wt%. An improvement of only 7.8% in the surface hardness was observed for PMMA loaded with 15 wt% of HA.

Keywords Polymer composites · Poly (methyl methacrylate) · Hydroxyapatite · Denture base materials · Mechanical properties

1 Introduction

A denture base material should possess adequate resilience and strength to biting, chewing, impact forces and excessive wear under mastication. It should be stable under all conditions of service. PMMA acrylic resin has been widely used in the field of dental materials. Particularly, as a denture base material [1, 2]. The physical properties adequacy of PMMA proved the its feasibility for dental applications and hence gained its popularity in dentistry. Its inherited characteristics are the ones needed for the use in oral cavity, and their performance features are related to their biologic, physical, aesthetic, and handling characteristics [3]. An increased interest and attention was paid to modify the acrylic resins due to some of their drawbacks such as polymerization shrinkage, accuracy of fit, water absorption and low mechanical properties [4, 5].

Research is currently ongoing to incorporate different materials to overcome the drawbacks and generally increase the strength of the acrylic material. Several ceramic powders are used as reinforcement for PMMA, e.g. barium titanate, zirconium oxide, alumina and hydroxyapatite (HA) [2, 6, 7]. The biodegradation, osteoconduction, osteointegration and biocompatibility of the

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HA is the promise behind the used of HA reinforcement material for biomedical application. Moreover, the stiffness, density, and bioactivity of HA made it a preferred reinforcement as a bone cement [8]. Besides the bone-bonding properties of the composites, the possibility to improve the mechanical properties of composites as well as the possibility to make the HA/polymer composite systems biodegradable by using biodegradable polymer matrices make composite systems very attractive [9].

Recently, extensive studies were conducted to investigate the effect of HA incorporation into PMMA as bone substitute material. However, there is a lack of studies about the rule of HA as reinforcement to PMMA denture base material. Therefore, the current study came to fill this gap. The denture base is subjected to various stresses during the function, these include tensile and flexural stresses. When a composite is intended to be used in a load bearing situation, the mechanical properties are primary concern. Although, it has been found that the incorporation of HA into PMMA matrix may turn an initially non-bioactive PMMA into Bioactive composite, and simultaneously improve the mechanical properties, especially the elastic modulus and hardness [10]. However, a negative effect of the HA incorporation on the strength of the PMMA has been reported.

Zebarjad et al. [11] studied the mechanical properties of nano HA-reinforced PMMA cement were by using three point bending, compressive and wear test and concluded that there was no direct proportionality between the results of bending tests and the HA content and the addition of HA to PMMA (up to 10 wt%) did not change the bending properties significantly. Similar observation was reported by Chow Wen et al. [12] who studied the flexural properties of hydroxyapatite reinforced poly(Methyl methacrylate) composites. It was found that the flexural strength and strain decreased in the presence of HA.

Several reports have dealt with the relationship between the filler concentrations in composite resins and their ultimate properties. The addition of rigid particles directly influence fracture the behavior of polymers [13]. Number of the particle's features have a significant influence on the fracture toughness such as, the chemical nature, surface nature, shape and size of the particles, interface bonding and concentration by volume. The filler concentration greatly influences the behavior of the composite material and interrelated to the other factors. Therefore, optimizing one parameter may compromise the others [14].

Although, the mechanical properties of composite materials can be improved to a certain extent by the addition of bioactive filler particles, there is still a need to improve the bonding between filler and matrix since there is clearly no other bonding force between the two phases than mechanical interlock [15]. The interface area formed as a result of the bonding between filler and matrix can resist crack growth and thus provide a reinforcing effect when the rigid particles are embedded into the polymer matrix. However, increasing the filler loading can cause agglomerations and stress concentration in the regions of high particles content, which has a weakening effect on the properties of composites [16–18]. Filler loading is profoundly considered an important factor in determining the properties of the composites [2, 6, 19]. Therefore, the objective of this study is to evaluate the effect of HA incorporation with different concentrations into PMMA as a denture base material in term of process ability, physical, and mechanical properties.

2 Materials and methods

2.1 Materials

The materials adopted in this study is powder and liquid system. The powder components consisted of PMMA (the average particle size as received is 88.4 µm) with high molecular weight (i.e. 996,000 GPC—Aldrich, USA), benzoyl peroxide BPO of particle size ≤ 106 µm (Merck Chemical Company, Germany) and Hydroxyapatite (HA) ceramic powder of particle size (as received) 5 ± 1 µm (Fluidinova, Portugal). The liquid components consisted of methyl methacrylate (MMA) (Aldrich, USA) stabilized with 0.0025% hydroquinone and ethylene glycol dimethacrylate (EGDMA) (Aldrich USA) as a cross linking agent. The silane coupling agent [3-(methacryloxy) propyl trimethoxysilane] γ-MPS (Sigma Aldrich, USA) with 98% purified contents was used for the filler treatment.

2.2 Filler treatment

HA was treated with (γ-MPS) silane coupling agent (Aldrich USA) using a 70/30 acetone–water mixed with (γ-MPS) silane coupling agent. The HA powder was added to the liquid mixture (acetone–water-silane) and mixed with a magnetic stirrer (C-MAG HS 7, IKA, Malaysia) for 4 h, subsequently the mixture was dried in oven at 110 °C for 24 h. The procedures were previously described by Kundie et al. [20]

2.3 Samples preparation

Different ratios (i.e. 0, 5, 10, and 15 wt%) of treated HA with γMPS silane coupling agent were added into the matrix (PMMA and 0.5% BPO). This filler concentration configuration was designed in order to study the effect of filler loading on the physical and mechanical

properties of the composite comparing to the conventional acrylic denture base material (Triplex, Ivoclar Vivadent technical, UK). The solid components (powders) were mixed up in zirconium oxide jar and balls with the aid of a planetary ball milling machine (Firtsch Pulverisette 5, GmbH, Duisburg, Germany) for 30 min. The mixing of powder to liquid (P/L) was done according to the standard dental laboratory usage. The ratio of powder to liquid was set at 10:4. After reaching the dough stage, the mixture was packed into a stainless steel mold fabricated in accordance with ADA specification No. 12 for denture base polymers and pressed under 14 MPa of a pressure using a compression molding machine (MESTRA, Talleres Mestraitua, S.L., Spain) at room temperature for 30 min. The final polymerization (curing process) was carried out using a water bath (Memmert, Germany) at 78 °C for min 90. The mold was then left to cool slowly at room temperature. Next, the samples were stored in a humidified incubator at 37 °C till testing. The procedure adopted in this study were consistent to those of the prescribed standard method for preparing conventional denture base in the dental laboratory [21] (Fig. 1).

2.4 Density and porosity measurements

The density of the samples was determined according to the ASTM D 792-2005 water-displacement method (method A) using the following equation [22]:

$$P = \frac{W_3 3 - W_2}{W_1} \quad (1)$$

The density of HA as quoted by manufacturer is 3.00 g/cm^3.

The porosity content of the samples can also be calculated using the following equation [22]:

$$\text{Porosity content } (\%) = \frac{W_3 - W_1}{W_3 3 - W_2} \times 100 \quad (2)$$

where W_1 dry weight, the weight of sample in air, W_2 suspended weight, the weight of sample in water, W_3 saturated weight, the weight of sample hanging in air.

2.5 Mechanical properties

Three tests were conducted in this study to determine the mechanical properties of PMMA/HA composites. A total of 100 samples were prepared and divided into four groups.

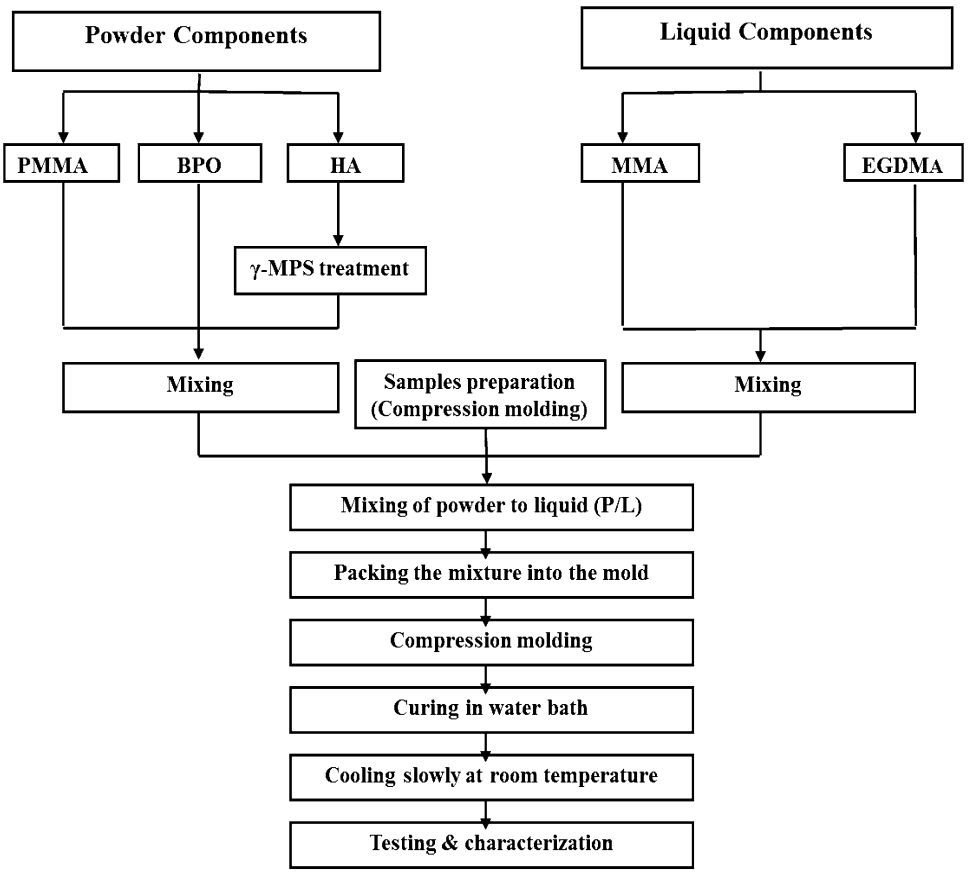

Fig. 1 Flow chart for the preparation steps of PMMA/HA composite

Each group has 25 samples for each test (At least five samples were tested for each formulation). The testing procedures are outlined in the following sub-section (Fig. 2).

2.5.1 Tensile test

Tensile test was carried out according to ASTM D-638 type IV using an INSTRON 5582 10 KN electromechanical tensile testing machine. A standard mold measuring $60 \times 12 \times 4$ mm^3 was used for samples preparation. The gauge length was set at 50 mm and crosshead speed at 5 mm/min. At least five samples were tested for each formulation.

The percentage of elongation was calculated by the following equations:

$$\varepsilon = \Delta L_0 / L_0 \tag{3}$$

The theoretical tensile strength (MPa) of the composite (σ_c) may be related to the matrix tensile strength (σ_m) using the Einstein equation:

$$\sigma_c = \sigma_m \left(1 - 1.21\, V_f^{2/3}\right) \tag{4}$$

whereby, 1.21 and 2/3 are related to stress concentration and geometry of the filler, respectively. V_f is the volume fraction of the filler. For spherical filler with no adhesion to polymer matrix, the value of first constant has been found equal to 1.21. The second constant is equal to 1 if the material fails by planar fracture and 2/3 if the failure is by random fracture [23]. Moreover, the tensile modulus (GPa) can also be theoretically calculated using Ahmed and Jones equation [18].

$$E_c = E_m \left(1 + 2.5\, V_f\right) \tag{5}$$

whereby, E_c and E_m is the elastic modulus of the composite and the matrix, respectively. V_f is the volume fraction of the filler. For the purpose of calculation, the filler particles are assumed to be spherical and the composite failed by random fracture (Fig. 3).

2.5.2 Flexural test

Three-point flexural test was performed in accordance with the ASTM D790-86 standard. A standard mold measuring $65 \times 10 \times 3$ mm^3 was used for samples preparation. 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. The flexural strength (MPa) and modulus

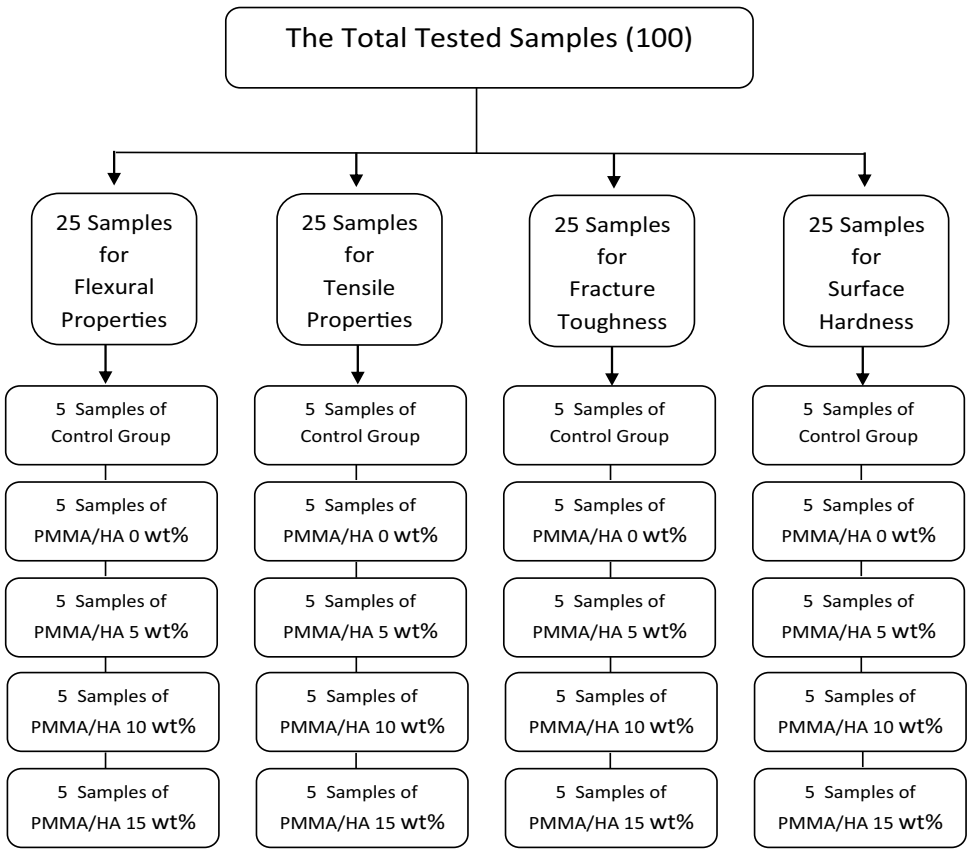

Fig. 2 Illustrates the total tested samples and the number of samples for each test

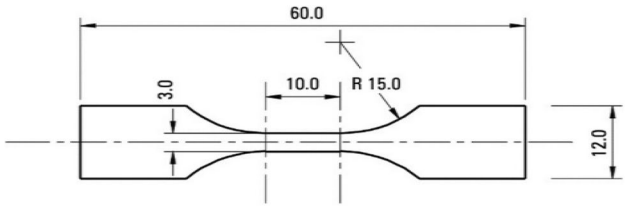

Fig. 3 Representation of tensile test sample: whereby sample length = 60 mm, sample thickness = 4 mm and sample width = 12 mm

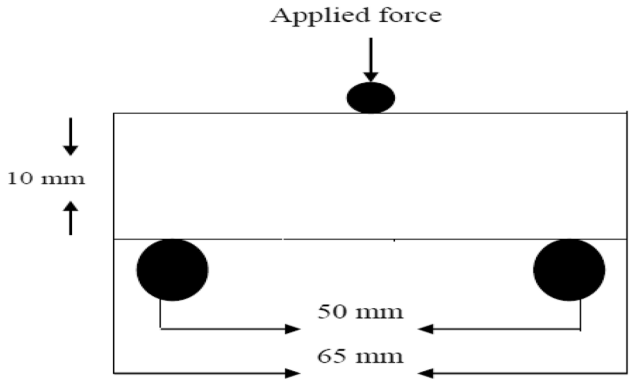

Fig. 4 Representation of flexural test sample: whereby sample length = 65 mm, span length = 50 mm and sample width = 10 mm

(GPa) were calculated by the following equations [20, 24, 25]:

$$\text{flexural modulus} = \frac{L^3 m}{4bd^3} \tag{6}$$

$$\text{flexural strength} = \frac{3PL}{2bd^2} \tag{7}$$

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 (Fig. 4).

2.5.3 Fracture toughness

Fracture toughness was determined using the single edge notch bending test (SEN-B) according to ISO 13586:2000. The sample thickness, t = 4 mm, width w = 20 mm, span length S = 64 mm, overall length = 80 mm, notch length a = 4 mm. A natural crack was generated by tapping the sample on a new razor blade placed in the notch. The SEN-B samples were tested at a crosshead speed of 1.00 mm/min. the values of K_{IC} (MPa mm½) were calculated using the following equation [20, 25]:

$$KIC = \frac{3PSa^{1/2}Y}{2tw^2} \tag{8}$$

$$Y = 1.93 - 3.07\left(\frac{a}{W}\right) + 14.53\left(\frac{a}{W}\right)^2 - 25.1\left(\frac{a}{W}\right)^3 + 25.8\left(\frac{a}{W}\right)^4 \tag{9}$$

where *P* load at peak (N), *a* notch length (mm), *S* span length (mm), *t* sample thickness (mm), *w* sample width (mm), *Y* geometrical correction factor (Fig. 5).

2.5.4 Scanning electron microscopy

The 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.

2.5.5 Surface hardness test

The hardness test was applied according to the ASTM E 384-99 standard. A calibrated Vickers tester FV (Futuretech) was used to force a diamond indenter of 0.3 kg into the polished surface of the sample and optically measure the diagonal length. The hardness test was done for all the formulations and the average of 5 readings were taken for each formulation of the all composites samples.

2.6 Statistical analysis

Descriptive statistics were carried out using (Statistical Package for the Social Sciences (SPSS) version 23, IBM, New York, NY, USA). Significant differences were evaluated by using Independent t-test to assess if the means significantly differed from those of the control group. Data were analyzed at a significance level of 0.05.

3 Results and discussion

3.1 The effect of γ-MPS silane coupling agent treatment

Figure 6 illustrates the FTIR spectra of HA particles before and after the treatment with γ-MPS silane coupling agent. The presence of bands for the carboxyl group (~ 1720 cm^{-1}) and SiO group (~ 1300–1200 cm^{-1}) indicate the availability of the coupling agent on the surface of the hydroxyapatite. This observation is in agreement with the one made by Michelot et al. [26]. Silane coupling agents work a little bit like soap; they have a

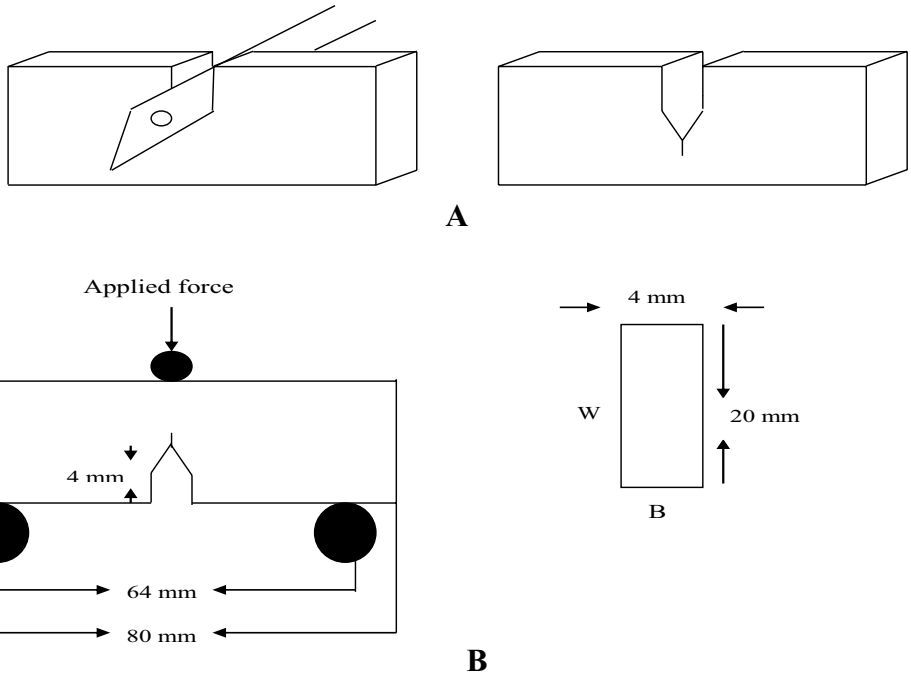

Fig. 5 Representation of SEN-B sample, **a** (right) tapping on a razor blade in the notch of a mold; (left) the sample after initiation of a pre-crack; **b** cross-section showing the dimensions of the crack

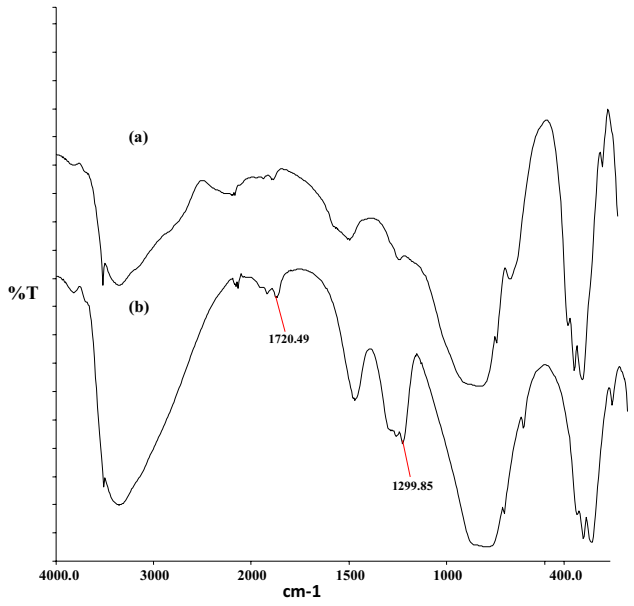

Fig. 6 FTIR spectra of hydroxyapatite particles **a** before γ-MPS treatment **b** after γ-MPS treatment

different chemical group at each end of the molecule. Silane coupling agents are long molecules that react with the polymer matrix at one end while the other end reacts with the ceramic filler. As illustrated in Fig. 7, the end that reacts with the polymer matrix has a C=C that participates in addition polymerization reaction. On the other end, there is a silane group which has silicon and oxygen atoms that react with the silicon or the oxygen on the other surface of the ceramic filler particle [27].

3.2 Scanning Electron Microscopy (SEM)

Figure 8 illustrates the SEM micrographs at high magnification for randomly selected samples from the ground powder mixtures of PMMA loaded with three different ratios (i.e. 5, 10, and 15 wt%) of HA ceramic powder. It can be clearly seen that a good distribution of filler particles through the PMMA particles was achieved at very low filler loading (i.e. 5 wt%), after which agglomeration of HA powder was recorded as result of increasing of HA loading above 5 wt%. According to Zebarjad [28], the particle size and particles distribution have significant effects on the mechanical properties. Filler particles of large median sizes reduce the strength 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 [29].

3.3 Density of the composite

Normally, denture base materials should have low value of specific gravity in order to be as light as possible. This reduces the gravitational displacing forces which may occur especially on the upper denture. Table 1 shows the density of PMMA/HA composite as a function of different filler loading. The density of PMMA/HA composites increased with increasing the filler loading and reached a maximum value of 1.25 g/cm^3 at a filler loading of 15 wt%.

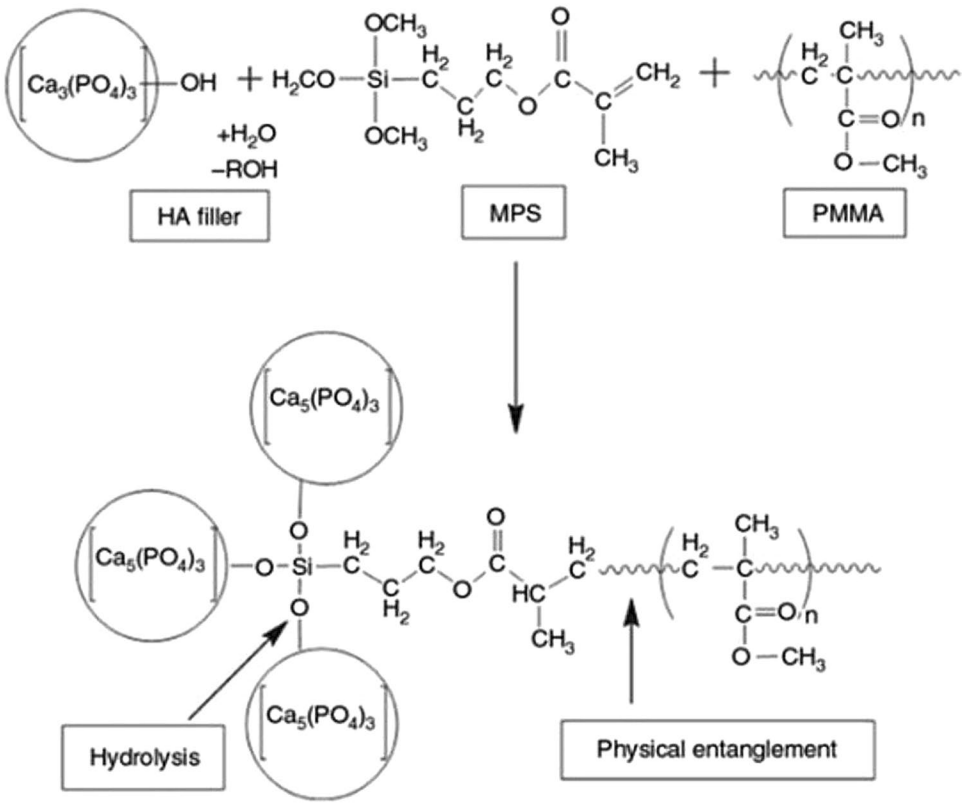

Fig. 7 Possible interaction of γ-MPS, HA and PMMA [27]

The increased density of the composite is due to the presence of dense and rigid HA in the composite. The density of HA is 3.156 g/cm^3 which is higher than that of PMMA i.e. 1.19 g/cm^3. Thus, the increase in the density of PMMA as a result of HA incorporation is expected. It can also be noticed that the experimental density of the PMMA and the composite filled with 5 wt% is considerably close to the theoretical density. However, the difference between experimental and theoretical densities increased as the HA loading increased to 10 and 15 wt%. This can be attributed to the increase of porosity content with the presence of the agglomeration at higher filler content [30]. Due to the increase in porosity content, the incorporation of synthetic bioactive particles, such as the HA ceramic powder into PMMA matrix is limited to concentrations up to 15% of HA [31, 32].

3.4 Tensile properties

Table 2 shows the effect of HA loading on the tensile properties of PMMA/HA composites. The tensile modulus increased with increasing of HA loading and reached a maximum value of 2.9 GPa at filler loading of 15 wt%. The significant improvement ($P < 0.05$) in tensile modulus of PMMA/HA can be attributed to the ability of HA to resist the stress and limit the movement of molecular chain in PMMA system when a load applied on the composite. The increase of modulus can be attributed to the sufficient stress transfer across the polymer-HA interface [33]. On the other hand, insignificant effect of HA incorporation on the tensile strength of the acrylic denture base material was observed ($P > 0.05$). An improvement of only 1.63% in the tensile strength was achieved with the incorporation of 5 wt% HA. As the HA loading increased beyond 5 wt %, a decrease was observed in the tensile strength. The increment of the tensile strength at lower HA loading can be attributed to the fact that the well-dispersed particles make the crack propagation path longer, absorb a portion of energy and enhance the plastic deformation. Consequently, the surface fracture energy and the strength of composite increased. However, with increasing filler loading, the size of voids that formed when the polymer matrix detached from the filler particles became considerably large and initiated the main crack. Additionally, the inevitably increased agglomeration of dispersed filler particles resulted in decreased strength due to the lower strength of the agglomerates themselves [22].

Based on the statistical analysis, a significant improvement in the tensile modulus was achieved as a result of the incorporation of HA into PMMA denture base material ($P < 0.05$). it can be seen that the tensile modulus of the composite continued to increase as a function of increasing HA loading in the composite. However, no significant difference was recorded in the tensile strength as

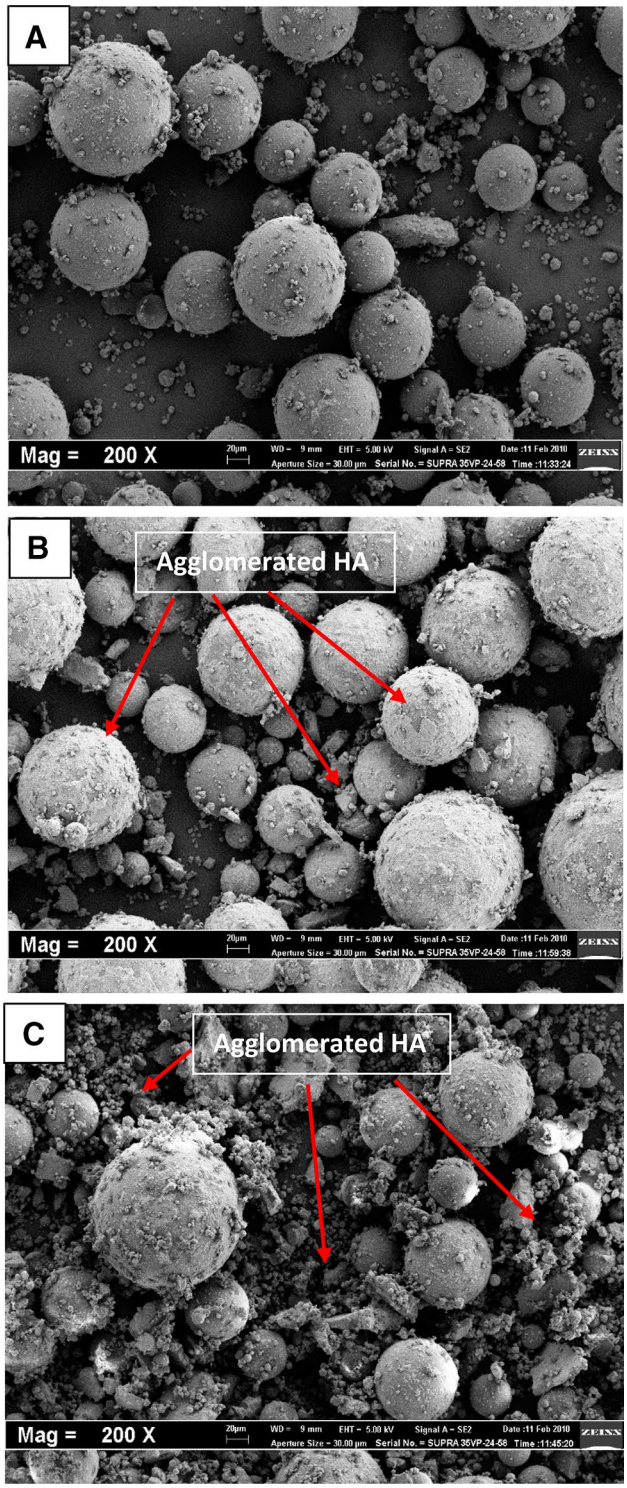

Fig. 8 SEM micrographs were taken for the p---owder samples, **a** PMMA/ HA 5 wt%, **b** PMMA/HA 10wt%, and **c** PMMA/ HA 15 wt% at high magnification (200X)

a function the HA incorporation into PMMA denture base material ($P > 0.05$). Similar observation was reported by Hamedi Rad et al. [3]. This can be attributed to the fact that the HA particles can reduce the mobility of the matrix, which might even develop a stress reinforcement around the filler of a stiffer polymer. This has been widely experienced with small particle and one of the main drawback of these fillers [34, 35] (Table 3).

The theoretical tensile strength value of PMMA composites decreases slightly as function of filler loading. In case of tensile modulus, the theoretical values of tensile are slightly higher compared with the experimental values. It also can be observed that the experimental values of tensile strength are higher compared with the theoretical values. This can be attributed to the fact that spherical filler with no adhesion to polymer matrix is theoretically assumed. On the other hand, it has been proved that both good mechanical interfacing and chemical bonding between the HA and PMMA can be achieved by the physical mixing of the powder components and the silane treatment of the HA particles [29, 33].

Strong bonding between the HA particles and the PMMA was achieved by both chemical adhesion (Silane coupling treatment) and tight mechanical interfacing (Using planetary ball milling technique PBM for the physical mixing of the powder components). In case of tensile modulus, the theoretical values are slightly higher than that of the experimental values. This can be attributed to the fact that a perfect composite is theoretically assumed which is difficult to be completely achieved. Since the non-bonded particles restrain the matrix from collapsing, they do not act completely as cracks [36]. Therefore, the modulus of the composite should increase with increasing filler loading, which is the general behavior expected. The change of the matrix-filler adhesion does not have that significant effect on modulus. As long as the frictional forces between the phases are not expected by the applied stress, the level of bonding is not an important factor [37].

3.5 Flexural properties

Figure 9 shows the effect of HA loading on the flexural properties of PMMA/HA composites. In comparison to the conventional material and neat PMMA, it can be noticed that the flexural strength of PMMA increased with the presence of HA filler and reached a maximum value of 99.25 MPa at a filler loading of 5 wt%. Beyond this loading; the filler has a weakening effect on the flexural strength. The slight increase in the flexural strength of the composite at lower filler loading can be attributed to the homogenous distribution of filler particles in the composite. A significant enhancement of the mechanical properties can be achieved at very low filler loading, somewhere in the range of 1–5 wt% if the filler particles are well dispersed in the surrounding polymer matrix [38, 39]. Additionally, if the

Table 1 The effect of filler loading on the density of PMMA/HA composites compared to that of conventional material and neat PMMA

Compound	Theoretical density (g/cm^3)	Experimental density (g/cm^3)	Porosity content (%)	Increase of porosity content (%)
Conventional	–	1.18 ± 0.01	1.21	–
PMMA	1.19	1.19 ± 0.01	1.09	0
PMMA/HA 5%	1.28	1.20 ± 0.00	1.23	11.38
PMMA/HA 10%	1.38	1.22 ± 0.00	2.98	63.42
PMMA/HA 15%	1.48	1.25 ± 0.01	3.32	67.16

Table 2 Effect of filler loading on the tensile properties of PMMA/HA composite compared to the conventional material and neat PMMA

Compound	Experimental tensile strength (MPa)	Theoretical tensile strength (MPa)	Experimental tensile modulus (GPa)	Theoretical tensile modulus (GPa)	Elongation at break (%)
Conventional	56.5 ± 1.68	–	2.2 ± 0.05	–	4.06
PMMA matrix	58.85 ± 1.5	58.85	2.3 ± 0.06	2.3	4.26
PMMA/HA 5%	59.81 ± 0.8	49.07	2.5 ± 0.05	2.58	4.68
PMMA/HA10%	55.75 ± 0.97	43.40	2.78 ± 0.02	2.87	3.3
PMMA/HA15%	54.78 ± 1.5	38.65	2.9 ± 0.07	3.1	3.16

Table 3 Statistical summary for tensile strength FS (MPa) and modulus FM (GPa) of PMMA/HA composite as a function of different HA loading

Descriptive statistics						
Group	N	Minimum	Maximum	Mean	SD	*P* value
Conventional						
FS	5	52	60	56.55	3.337	0.327
FM	5	1.90	2.51	2.2260	0.22075	0.04
PMMA/ HA 0 wt%						
FS	5	57	60	58.85	1.364	0.328
FM	5	2.13	2.31	2.2260	0.08325	0.04
PMMA/ HA 5 wt%						
FS	5	59	61	59.81	0.611	0.128
FM	5	2.29	2.80	2.5200	0.19506	0.003
PMMA/ HA 10 wt%						
FS	5	50	59	55.72	3.376	0.712
FM	5	2.71	2.84	2.7820	0.04764	0.001
PMMA/ HA 15 wt%						
FS	5	50	57	54.78	2.770	0.467
FM	5	2.81	3.10	2.9240	0.10761	0.001

interfacing between filler and matrix is well-built, the yield strength of the composite can be improved. With increasing filler loading, the flexural strength of microparticle filled composites is known to be reduced. At higher filler loading, embrittling effects occur where more agglomerates are likely to be found. Agglomerates are more related to the dispersion state of the filler particles which play a significant role in determining the flexural properties [40]. Increasing of filler loading leads to extensive filler agglomeration which remains in the matrix. Hence, a propagating crack possibly will occur as result of stress concentration and then easily leads to brittle failure [41, 42]. It can be stated that the flexural modulus of PMMA/HA composite is affected as function of filler loading. As the filler loading continued to increase from 5 to 15 wt%, the flexural modulus of the composite increased accordingly and reached a maximum value of 2.8 GPa at HA 15 wt%. The presence of HA powder in the matrix confines the movement of the matrix phases in the surrounding area of each particle, contributing to an overall increase in the modulus [29, 43].

Table 4 shows the summary of statistical analysis of flexural properties. The flexural modulus increased with

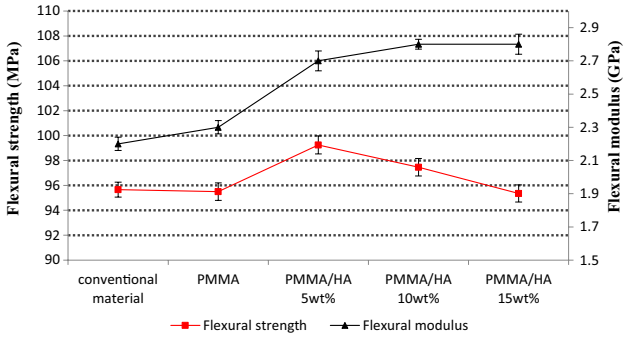

Fig. 9 Effect of filler loading on the flexural properties of PMMA/HA composite compared to the conventional material and neat PMMA

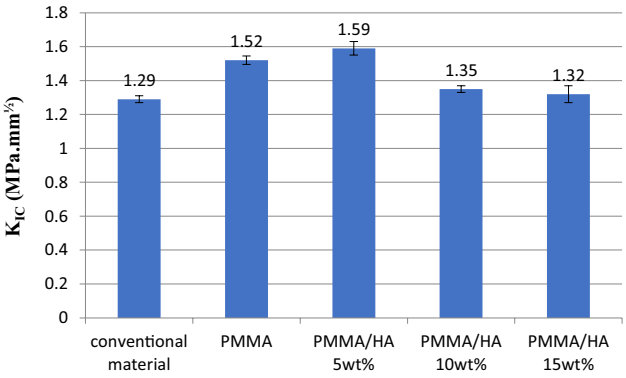

Fig. 10 Effect of filler loading on the fracture toughness of PMMA/HA composite compared to the conventional material and neat PMMA

the increasing of HA loading in the composite ($P < 0.05$). On the other hand, no significant change in the flexural strength as a function the HA incorporation into PMMA denture base material ($P > 0.05$). This is in agreement with the observation was reported by Tham et al. [29] who studied the flexural and morphological properties of PMMA/HA Composites. The HA filler could act as a stress concentration point. When an external load is applied, more stress will concentrate on the neighboring particles from the advancing crack and finally lead to brittle failure.

3.6 The fracture toughness

Figure 10 shows the effect of HA loading on fracture toughness of PMMA/HA composites. It can be observed that the conventional and neat PMMA exhibited low value of the fracture toughness. This can be attributed to the brittle fracture that usually associated with the little plastic deformation of high molecular weight of structural polymers. In this case, the propagation of a crack requires small energy which occur at low applied stress [44]. The fracture toughness of PMMA/HA composite increased with the incorporation and reached a maximum value of 1.59 MPa $m^{1/2}$ at a filler loading of 5 wt%. As result of increasing the filler loading, a decrease in fracture toughness was recorded. Increasing fracture toughness value at lower filler loading can be attributed to the enhancement of the filler distribution and concentration in the matrix, which has a strong effect on the material ability to resist the growth of a pre-existing crack. The ability to resist crack propagation can be augmented by addition of reinforcing filler [45]. The reduction in fracture toughness values as the

Table 4 Statistical summary for flexural strength FS (MPa) and modulus FM (GPa) of PMMA/HA composite as a function of different HA loading

Descriptive statistics						
Group	N	Minimum	Maximum	Mean	SD	*P* value
Conventional						
FS	5	80.70	111.30	95.6600	13.01972	0.956
FM	5	1.99	2.5	2.2076	0.09919	0.041
PMMA/ HA 0 wt%						
FS	5	89.70	99.78	95.5020	3.65992	0,956
FM	5	2.13	2.51	2.3020	0.20266	0.037
PMMA/ HA 5 wt%						
FS	5	91.10	112.40	99.2500	8.26090	0.311
FM	5	2.43	2.98	2.7040	0.20206	0.027
PMMA/ HA 10 wt%						
FS	5	86.50	113.60	98.4600	9.94223	0.387
FM	5	2.63	2.9	2.8180	0.25675	0.001
PMMA/ HA 15 wt%						
FS	5	92.36	103.60	96.6000	4.52433	0.740
FM	5	2.51	2.96	2.8020	0.11077	0.001

filler loading increased can be attributed to the agglomeration of filler particles in the matrix. The agglomerate is a domain that can act like a foreign body in the composites. Since there was a large amount of agglomerates at higher HA loading, they act as obstructions to chains movement which initiate failure under stress. It is believed that, agglomerates turn out to be as stress concentration and increase stresses in composites and initiate cracks more rapidly compared to unfilled samples [46]. The increase in filler loading does not necessarily lead to an increase in strength. This is because higher filler fractions create more defects that weaken the material. Furthermore, the resistance against local plastic deformation is increased by the orientation of the anisotropic particles in the composite causing more brittleness and weakness. As a result, crack development is going to be very quick due to the lack of the plastic deformation and failure to absorb energy [47, 48]. The filler volume fraction significantly influences the failure properties such as fracture toughness of particulate composites [49].

3.7 Scanning electron microscopy

Figure 11a, b illustrates scanning electron microscopy (SEM) micrographs were taken at high magnification for the fractured surface of the conventional material and neat PMMA samples, respectively. For the conventional material, the crack propagated from the initiation site creating a striped pattern, clearly signifying the occurrence of stable crack propagation. Additionally, the fracture surface appears smooth, indicating indiscriminate crack propagation through the conventional material which refers to brittle fracture. In the case of PMMA sample, the fracture morphology is similar to that of the conventional material which exhibits brittle fracture behavior of indiscriminate crack propagation through the PMMA matrix. This accounts for lower K_{IC} values for the conventional material and the PMMA matrix [50]. Figure 11c shows SEM micrographs were taken at high magnification for the fractured surface of the PMMA/HA 5 wt% composite samples. It can be seen that the filler particles are well-bonded to the matrix. The SEM provides evidence for the good adhesion between the HA particles and the matrix. According to Móczó, Pukánszky [51] it can be said that the presence of filler particle with good adhesion to the matrix increased the fracture resistance. Figure 11d, e shows SEM micrographs were taken at high magnification for the fractured surface of the PMMA/HA 10 and 15 wt% composites, respectively. It can be noted that an extensive agglomeration of filler particles took place as the filler loading increased to 10 and 15 wt%. The agglomerates are known to build up stresses in composites and produce unwanted stress concentration in the composite which accelerates the crack propagation [48].

3.8 Surface hardness (Vickers hardness VHN)

Sufficient surface hardness of the dental composites is essential to achieve optimum clinical performance of the dentures in stress dental bearing areas. Hardness is a surface property. However, surface hardness is a result of interaction of number of properties, among the properties influencing the hardness of a material are its strength, proportional limit, ductility and malleability. The surface hardness is known as the resistance of the material to permanent penetration or indentation. Table 5 shows the effect of filler loading on the surface hardness of PMMA/HA composite compared with the conventional material and neat PMMA. It can be observed that there is slight improvement in the Vickers hardness value with the presence of HA filler. In addition, the Vickers hardness value continued to increase as the filler loading increased and reached a maximum value of 19.24 kg/mm^2 at a filler loading of 15 wt%. It has been established that there is a positive correlation between the hardness and inorganic filler loading in the resin matrix which means that composites with higher filler loading exhibit higher surface hardness [52]. According to Kundie et al. [53], the filler loading is one of few factors that are related surface hardness of the material and affecting strongly the composite. Since synthetic HA has hardness similar to that of natural teeth, the incorporation of HA in the dental composite would improve the hardness of the composite [54].

4 Conclusion

The density of PMMA was influenced by the addition of HA. The density of PMMA gradually increased as the HA loading continued to be increased. The tensile and flexural modulus of PMMA were increased significantly by the incorporation of HA. However, the flexural, tensile strength and the fracture toughness of PMMA were slightly reduced by increasing the load of HA beyond 5 wt%. The surface hardness of PMMA was increased by the incorporation of HA. A positive correlation between the surface hardness and HA loading in the PMMA was observed. The optimum loading of HA was achieved at 5 wt% attributed to the balance of good tensile, flexural properties and fracture toughness.

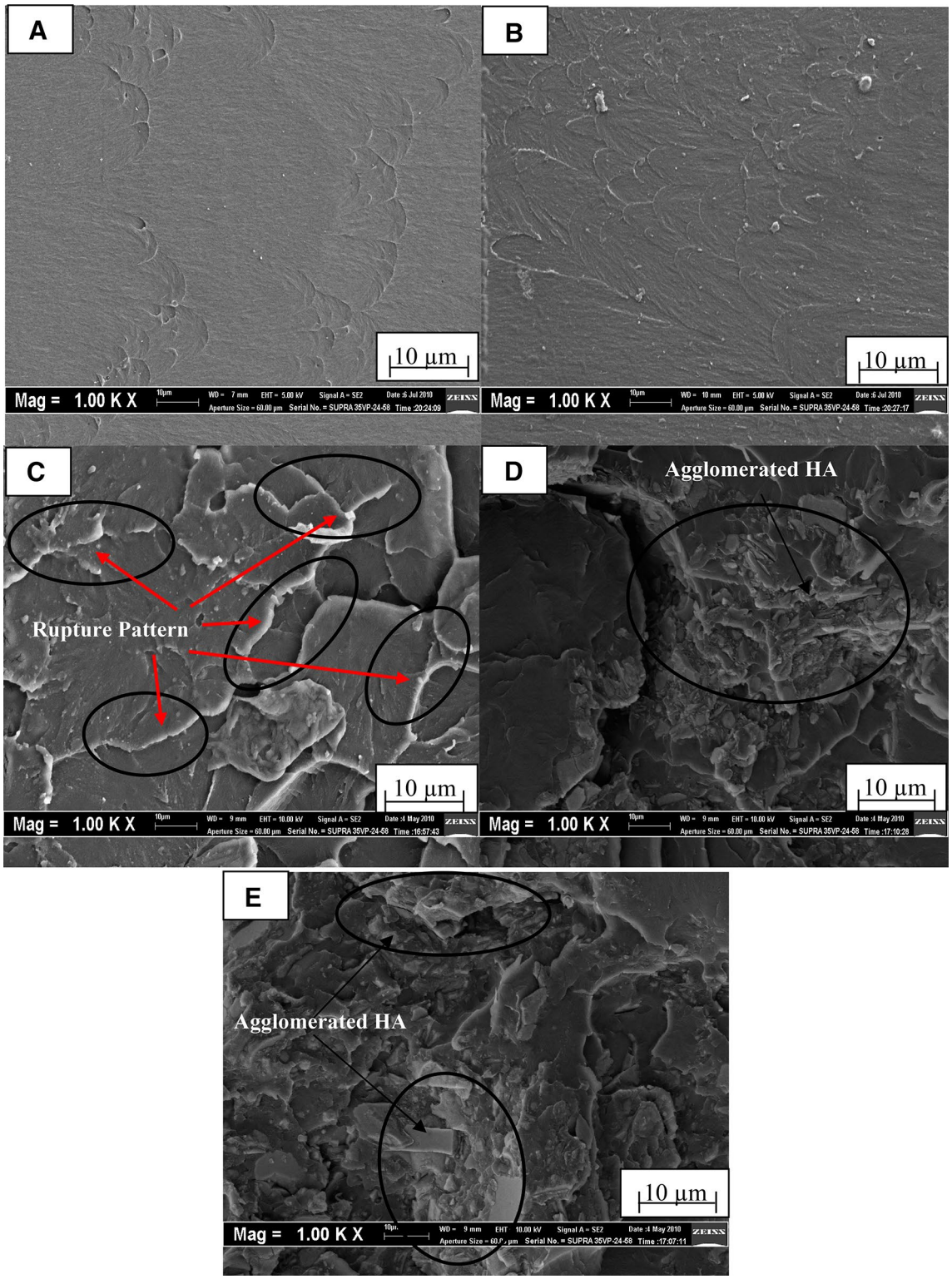

Fig. 11 SEM micrographs were taken at high magnification for the fractured surface of the flexural sample of **a** conventional material **b** neat PMMA **c** PMMA/HA 5 wt% composite **d** PMMA/HA 10 wt% composite **e** PMMA/HA 15 wt% composite

Table 5 Vickers hardness of PMMA/HA composites compared to the conventional material and neat PMMA

Compound	Vickers hardness (Kg/mm^2)	Hardness improvement (%)
Conventional material	16.25 ± 0.6	–
PMMA matrix	17.85 ± 0.5	0
PMMA/HA 5 wt%	18.58 ± 1.2	4
PMMA/HA 10 wt%	18.80 ± 0.9	5.32
PMMA/HA 15 wt%	19.24 ± 0.3	7.78

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Compliance with ethical standards

Conflict of interest We declare that all authors have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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