The Effect of 3-(Trimethoxysilyl) Propyl Methacrylate on the Mechanical, Thermal, and Morphological Properties of Poly(methyl methacrylate)/Hydroxyapatite Composites

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ABSTRACT: The poly(methyl methacrylate)/hydroxyapatite (PMMA/5HA) composites were prepared by using heat-processing polymers powder and liquid method with a ratio of 10 : 4 according to the dental laboratory practice. The hydroxyapatite (HA) was surface treated using 3-(trimethoxysilyl) propyl methacrylate (γ-MPS) with different concentrations based on HA (i.e., 2, 4, 6, and 8%). The chemical treatment of HA was examined using Fourier Transform Infrared Ray Spectroscopy (FTIR). The mechanical properties of PMMA/5HA composites were characterized using tensile, 3-point bending flexural and fracture toughness tests. The morphological properties of the PMMA/5HA composites were characterized using field emission scanning electron microscopy (FESEM). The intensities of absorption bands at 840, 873, and 1031 cm^{-1} which are corresponding to Si—O stretching were observed and became higher as the increasing concentration of γ-MPS for the HA treatment. This indicates that the HA was successfully treated by γ-MPS. It is interesting to note that the flexural modulus and strength of PMMA/5HA was increased significantly by 6% γ-MPS. The improvement of the mechanical strength could be related to the enhancement of interfacial interaction between PMMA and HA by the surface treatment of γ-MPS. In addition, the fracture toughness properties of PMMA/5HA composites were also influenced by the different concentration of γ-MPS. It is believed that the γ-MPS could act as a good silane coupling agent for the PMMA/5HA composites. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 218–228, 2010

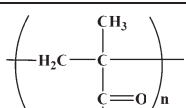**Key words:** compatibility; composites; mechanical properties; microstructure; thermal properties
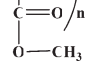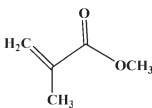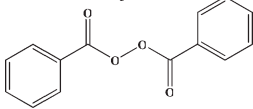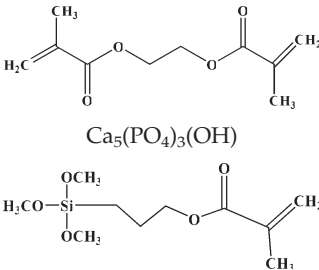
INTRODUCTION

Poly(methyl methacrylate) (PMMA), polystyrene (PS), poly (vinyl acrylic) (PVA), polyamides, and light-activated urethane dimethacrylate resins can be used for denture base application.[1] However, among these polymers, poly(methyl methacrylate) is the most commonly used material for dentures owing to their good physical and esthetic properties. Hydroxyapatite (HA) is considered as bioactive filler because of its similarity to the biological hydroxyapatite in impure calcium phosphate form found in human bone and teeth. HA has a calcium : phosphorus (Ca : P) ratio of 10 : 6 and its chemical formula is $Ca_{10}(PO_4)_6(OH)_2$.[2] Generally, HA are preferred bioceramic due to their reinforcement efficiency and bioactivity.[3] HA are always used to modify the mechanical, thermal and flow properties of PMMA. However, the drawback of the HA is their incompatibility with PMMA. This has motivated the researchers to find strategy to improve the compatibility between PMMA and HA.

3-(Trimethoxysilyl) propyl methacrylate (γ-MPS) which containing tri-alkoxy groups is widely used in the application of modern clinical dentistry. Adhesion promotion between dissimilar materials could be achieved with silane coupling agent in dentistry and also in numerous technical applications. During the treatment of mineral surfaces with silane coupling agents, the alkoxy groups (RO—) hydrolyze in an aqueous environment which producing hydroxyl groups. One or more of the hydroxyl groups may condense with hydroxyl groups which found on mineral surfaces. According to Miller and Berg,[4] tri-alkoxy silane would be expected to form the most extensive interphase which may be depressing the penetration of some of the poly (vinyl butyral) (PVB) into the interphase due to its highly cross linked structure. According to Motoyuki et al.,[5] the hydrogen bonded silanol and the hydrogen bonded water enhanced the reaction of hexyltrimethoxysilane coupling agent with silica nanoparticles. Silane coupling agents have been used to improve the mechanical properties of composites by facilitating adhesion of inorganic filler particles to the polymer matrix.[5–7] According to Vaz et al.,[7] the presence of 1% of coupling agent treated on HA was able to improve the stiffness of ethylene-vinyl alcohol copolymer

TABLE I
Chemical Structure of Materials and Their Suppliers

Materials	Chemical structure	Supplier
Poly (methyl methacrylate)		Sigma Aldrich, USA
Methyl methacrylate		Sigma Aldrich, USA
Benzoyl peroxide		Merck Chemical, Germany
Ethylene glycol dimethacrylate		Sigma Aldrich, USA
Hydroxyapatite	$Ca_5(PO_4)_3(OH)$	Sigma Aldrich, USA
3-(trimethoxysilyl) propyl methacrylate		Sigma Aldrich, USA

(SEVA-C) due to better adhesion and interaction between HA filler and SEVA-C being essential to transfer load. The modified interface surface was able to reduce debonding at the filler-matrix interface and lead to stronger and higher modulus materials.[8–10] Wang and Bonfield[8] had reported that the silane coupling agent facilitates HDPE system penetration into cavities of hydroxyapatite surface during composite processing which leads to enhancement in mechanical locking between hydroxyapatite and the HDPE matrix.

The aim of this study was to investigate the effect of different concentration of 3-(trimethoxysilyl) propyl methacrylate (γ-MPS) on the mechanical properties of hydroxyapatite (HA) reinforced poly(methylmethacrylate) (PMMA) composites. It is believed that the mechanical and thermal properties of PMMA/5HA composites were controlled by the concentration of γ-MPS. The relationship between the concentration of the γ-MPS with the mechanical and thermal properties of the composites will be established.

MATERIALS AND METHODS

Materials

The solid components consist of PMMA with typical molecular weight 996,000 GPC (Sigma Aldrich, USA) and 0.5% benzoyl peroxide (BPO) (Merck Chemical, Germany). The monomers used consists of methyl methacrylate (MMA) stabilized with 10–100 ppm monomethyl ether hydroquinone as inhibitor (Sigma Aldrich, USA) and ethylene glycol dimethacrylate (EGDMA) (Sigma Aldrich, USA). Hydroxyapatite (HA) in powder forms was supplied by Sigma Aldrich, USA with chemical formula of $Ca_5(OH)(PO_4)_3$ with an average specific surface area (BET) 50 m^2/g and average particle diameter of 18.1 μm. Silane 3-(trimethoxysilyl) propyl methacrylate was supplied from Sigma Aldrich Chemical. Table I shows the chemical structures of the materials and their suppliers.

Silanization of hydroxyapatite particles

The HA filler were silanized using 3-(trimethoxysilyl) propyl methacrylate (γ-MPS) in 90% methanol and 10% water. Methanol was used as a solvent to treat the HA filler. The γ-MPS was added into the solvent and was stirred for $\sim$ 30 min in a vessel followed by adding HA filler. The HA filler was stirred together with solvent for approximately 1 h. HA filler was then filtered and washed with methanol to drive off excess γ-MPS. HA filler was dried in oven at 80°C for 24 h to allow evaporation of residual methanol. Equation (1) shows the amount of silane (g) required to obtain minimum uniform coverage of the filler particles.[6,11]

$$X = \left(\frac{A}{w}\right)f \qquad (1)$$

In which X is the amount of silane, A is the surface area of the filler (50 m^2/g) and f is the amount of HA (g). According to Söderholm & Shang,[12] for a surface area of 175.4×10^{18} nm^2 (1.0 g) of pyrogenic colloidal silica (Cab-O-Sil), each MPS molecule

occupied at least 1.11 nm^2. Maria and Irini[11] also reported that for the Aerosil silica nanoparticles (with the specific surface area (BET) in the range of 35–65 m^2/g), the silane molecule covers 1.11 nm^2 of the filler and, thus the surface area coverage per gram of MPS is $w = 2525$ m^2/g. In this study, different concentration of γ-MPS (i.e., 2, 4, 6, and 8%) were used to treat the HA fillers.

Preparation of PMMA/5HA composites

Acrylic resins are prepared by prepolymerized PMMA powder particles which are mixed together with monomer of methyl methacrylate (MMA) and crosslinking agent such as ethylene glycol dimethacrylate (EGDMA). The powder component was prepared by mixing of PMMA, 5% HA and 0.5% BPO. The liquid component was prepared by mixing MMA monomer and EGDMA. The ratio of powder to liquid was set at 10 : 4 according to the dental laboratory practice. The powder and liquid components were mixed together. After achieving the dough stage, the mixture was packed into a mold with the pressure of 14 MPa using compressor at room temperature for 25 min. The polymerization was carried out using a water bath at 78°C for 90 min.[13,14]

Characterization of PMMA/5HA composites

Fourier transform infrared ray spectroscopy (FTIR)

FTIR spectroscopy (Perkin Elmer Spectrum One, UK) was used to characterize the functional group and silanization of the HA filler. FTIR spectra were determined from 400 cm^{-1} to 4000 cm^{-1} by using IR Spectroscopy Spectrum Version 5.0.1 software at 40 scans with a resolution of 2 cm^{-1}.

Flexural test

Three-point bending tests were performed according to ASTM D790 using an Instron 3366 machine (USA). The support span length was set at 50 mm. The testing speed was set at 2 mm/min. At least five samples for each formulation were examined. The flexural modulus and flexural strength were recorded.

Tensile test

Tensile tests were carried out on an Instron Tensile Machine model 3366 (USA) at 27°C and 50% relative humidity, according to ASTM D638. The gauge length was set at 50 mm and crosshead speed was 5 mm/min. Tensile modulus, tensile strength and elongation at break were evaluated from the stress-strain data.

Fracture toughness test

The fracture toughness test was determined by using single edge notch bending test (SEN-B) according to

ISO 13586:2000 using an Instron 3366 machine. The specimen geometry is 100 mm × 20 mm × 4 mm (length × width × thickness) with the span length (64 mm) and notch length (4 mm). The support length was set at 64 mm. A natural crack was generated by tapping on a new razor blade placed in the notch. The testing speed was set at 1 mm/min. At least five samples for each formulation were examined. The values of K_{IC} were calculated using eq. (2). The geometric factor was given in eq. (3).

$$K_c = \frac{3PS\sqrt{a}}{2BW^2} Y\left(\frac{a}{W}\right) \tag{2}$$

$$Y\left(\frac{a}{W}\right) = 1.93 - 3.09\left(\frac{a}{W}\right) + 14.53\left(\frac{a}{W}\right)^2 - 25.1\left(\frac{a}{W}\right)^3 + 25.8\left(\frac{a}{W}\right)^4 \tag{3}$$

where $Y\left(\frac{a}{W}\right)$ is the geometric factor, P is the load at peak, B is the specimen thickness (mm), W is the specimen width (mm), a is the notch length (mm), and S is the span length (mm).

Dynamic mechanical thermal analysis (DMTA)

PMMA/5HA samples were tested with a dynamic mechanical thermal analyzer (DMA861^e Mettler Toledo, Switzerland). Specimens were placed in the DMTA instrument and oscillated to 10 μm amplitude at frequency of 1 Hz in a three-point-bending mode. The specimens were heated from 20°C to 180°C at a heating rate of 10°C/min in nitrogen atmosphere.

Differential scanning calorimetric (DSC)

Thermal behaviour of PMMA composites was studied by differential scanning calorimetry (DSC), using Perkin Elmer DSC 7 (USA) instrument equipped with gas nitrogen. Thermal analysis was performed on composites to determine the glass transition temperatue (T_g). The samples were initially heated from 30°C to 190°C at a heating rate of 10°C/min and held at 190°C for 1 min. Then, the sample was cooled down to 30°C with a cooling rate of 10°C/min. A second heating similar to the first heating was then performed in order to erase the thermal history.

Thermogravimetric analysis (TGA)

The thermal stability of the PMMA/5HA composites was determined by thermogravimetric analysis (TGA) using a Mettler Toledo TGA machine, (SDTA851^e, Switzerland) with a heating rate of 10°C/min in nitrogen from 30°C to 600°C.

Field emission scanning electron microscopy (FESEM)

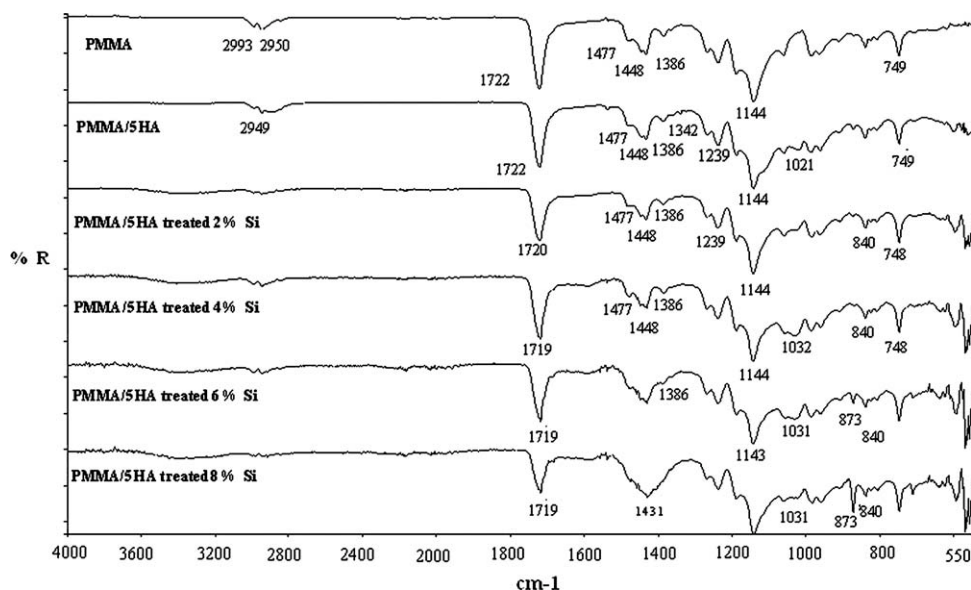The morphological studies of fractured toughness samples were carried out on FESEM Zeiss Supra

Figure 1 FTIR spectra of PMMA, PMMA/5HA, and PMMA/γ-MPS treated 5HA composites.

35VP LEO machine (Gemini). The accelerated voltage used was 5 kV. The specimen surface was coated by Aurum/Palladium alloy in order to prevent electrostatic discharge.

RESULTS AND DISCUSSION

Fourier transform infrared ray spectroscopy

Figure 1 shows the FTIR spectra of PMMA, PMMA/5HA and PMMA/γ-MPS treated-5HA composites. It can be seen that new peaks at 1021 cm^{-1} and 1342 cm^{-1} were detected. These peaks were corresponded to inorganic compound as P—O stretching and O—H stretching with the presence of HA filler. FTIR results revealed that the peaks at 1386, 1448, and 1477 cm^{-1} were disappeared by the treatment of γ-MPS on HA at 8% concentration. According to Liu,[6] γ-MPS can be adsorbed onto surface of silica from solvent in three possible form, (1) through the hydrogen bonding between silanol groups of γ-MPS and silica, (2) through hydrogen bonding of C=O and O—H group from the filler and (3) forming multilayer in between MPS molecule through hydrogen bonding. It is believed that the peak at 1386 cm^{-1} was attributed by O—H bending which derived from methanol and water. The infrared absorption frequency at 1448 and 1477 cm^{-1} were corresponding to C=O stretching. The disappearance of these peaks could be associated to the bonding between the O—H group and C=O group from γ-MPS with the O—H group from HA filler. When the concentration of γ-MPS increases, multilayer formation was occurring in between γ-MPS molecule through C=O and O—H groups. Therefore, the present of the peak

at 1430 cm^{-1} for the 8% γ-MPS treated HA due to multilayer was formed by γ-MPS itself. The 1430 cm^{-1} peak was attributed to O—H bending of carboxylic acids (—COOH). In addition, the absorption bands at 840, 873 and 1031 cm^{-1} which are corresponding to Si—O stretching were observed after the silanazation of HA. According to Matinlinna et al.,[15] a symmetric C—H stretch of the Si—O—CH$_3$ group disappeared at 2900–2990 cm^{-1}. The infrared absorption frequency at 890 cm^{-1} can be assigned to the Si—OH stretching when the concentration of silane was increased in the γ-MPS treated HA filler. The hydrogen bonded OH-group band at 3400–3200 cm^{-1} was overlapped by a broad band. Besides, siloxane, Si—O—Si was appeared at 1070–1040 cm^{-1} and Si—OH stretching mode had increased at 910–830 cm^{-1}.[5] When the silanes were activated in the alcohol-water medium, hydrolysis and condensation reactions take place. Activated silanes turn to silanols (Si—OH) that deposit onto the inorganic substrate and after curing they form a siloxane film.[6,16]

Mechanical properties

Table II shows the effect of different concentration of γ-MPS treated HA on the tensile and flexural properties of PMMA/5HA composites. In the requirement for a denture base polymer, the flexural modulus of denture base material should be 2 GPa followed in ISO specification 1567–2000. The flexural modulus of PMMA consisting of 5% HA recorded the value of 2.5 GPa. Similar observation was reported by Chow et al.[13] From Table II, it shows the effect of different concentration of γ-MPS on the flexural modulus of PMMA/5HA composites.

TABLE II
Effect of Different Concentration of γ-MPS on the Flexural and Tensile Properties of PMMA/5HA Composites

| Material designation | Mechanical properties | | | | |
| | Flexural properties | | Tensile properties | | |
	Flexural modulus (GPa)	Flexural strength (MPa)	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PMMA	2.3 ± 0.04	77.7 ± 1.95	1.96 ± 0.03	50.9 ± 0.99	4.6 ± 0.37
PMMA/5HA	2.5 ± 0.07	50.5 ± 1.43	2.24 ± 0.05	34.8 ± 0.51	2.0 ± 0.06
PMMA/5HA treated 2% Si	2.7 ± 0.02	55.3 ± 1.10	2.11 ± 0.05	41.5 ± 0.49	2.8 ± 0.32
PMMA/5HA treated 4% Si	2.8 ± 0.08	56.5 ± 2.02	2.06 ± 0.04	41.6 ± 1.07	2.9 ± 0.46
PMMA/5HA treated 6% Si	2.9 ± 0.02	61.4 ± 2.18	2.09 ± 0.07	38.0 ± 1.08	2.4 ± 0.14
PMMA/5HA treated 8% Si	2.8 ± 0.05	52.4 ± 1.68	2.02 ± 0.05	43.3 ± 1.10	3.0 ± 0.63

Incorporation of HA filler particles into PMMA matrix significantly improves their mechanical properties. The flexural modulus of PMMA was increased from 2.3 GPa to 2.5 GPa by the addition of the HA filler. Hence, it is believed that the HA could act as a reinforcing filler in the PMMA system. The HA filler restrict the movement of the matrix phase in the vicinity of each particles which consequently contribute the enhancement in modulus and stiffness.[13] According to Wang and Bonfield[8] the modulus of high density polyethylene (HDPE) was enhanced by the addition of HA. The better filler-matrix bonding can be achieved by treatment of the filler particles with a silane coupling agent. It was assumed that bonding to the silica filler surface occurs by the reaction between silanol groups of the filler surface and hydrolyzed silane molecules. During the silanization process, multiple layers of silane molecules form a film around the filler particles, which is either chemically or physically attached to the filler particles.[6,17] By the treatment of silane on the HA filler, PMMA composites had an enhancing effect on the flexural modulus. There was 8, 12, and 12% increment of PMMA composites with 2, 4, and 8% γ-MPS treated HA. However, ∼ 16% increment in flexural modulus was achieved for PMMA/5HA composites treated with 6% γ-MPS. The increment of flexural modulus for the γ-MPS treated PMMA/5HA composites is owing to the fact that the silane coupling agent is able to provide better interaction bonding between HA filler and PMMA matrix. Silane provides a crucial link between the matrix and the filler. This link has been reported to reduce the degradation process in which protects the filler against fracture. Besides, it also improves distribution and stress transformation from flexible matrix to stiffer inorganic filler particles.[11] The silane treated filler should be able to disperse more favorably in the polymer matrix and to have better adhesion to the matrix.[9]

Table II shows that the flexural strength of PMMA was decreased by the addition of HA. This is attributed to the weak interfacial interaction between PMMA and HA. Sousa et al.[18] reported that the efficiency of HA particles as reinforcement agents for HDPE is reduced due to its inherent low aspect ratio and low degree of chemical reaction with the HDPE phase. There was only mechanical interlocking mechanism to hold the filler in PMMA system developed upon the shrinkage of the polymer during cooling.[18] Besides, the agglomeration of the HA filler could acts as stress concentration points. Under the load bearing application, the agglomeration of HA filler will restrict the movement of molecule deformation. Formation of stress concentration point in the composites, more stress will concentrate on the neighbor particles and finally advancing crack in the samples. The crack carried out rapid and successive propagation that ultimately leads to brittle failure.[9,13] Table II shows that the flexural strength of the PMMA/silane-treated HA composites were increased compare to that of PMMA/untreated-HA composites. There was about 9.5%, 12%, and 3.8% increment on the flexural strength for PMMA/5HA composites treated by 2, 4, and 8% γ-MPS. However, the flexural strength of PMMA/5HA composites treated 6% Si was increased ∼ 21.6%. The improvement of strength in the presence of silane coupling agent may due to better HA filler dispersion and better interfacial interaction. Silanes are recognized as adequate coupling agents for a variety of polymer composites.[9,18,19] According to Sousa et al.[18] the increase in strength of material by treated silane was attributed to enhance interfacial adhesion between silane and filler. However, there was only small increment for 8% γ-MPS treated on HA. According to Pongdhron et al.,[20] the mixing energy reduces due to increasing of silane loading. The alkoxy groups in silane coupling agent could react chemically with silanol groups on silica surface, arising to the reduction of filler-filler interaction. However, plasticizing effect of silane coupling agent could be dominant if the concentration of γ-MPS is excessive.

Table II shows that by the addition of HA in PMMA, the tensile modulus of PMMA was increased to 2.24 MPa as compare to pure PMMA (1.96 MPa). The significant increased mechanical

properties at 5% HA loading may be due to the high stiffness of HA. The increasing of tensile modulus due to the addition of HA was sufficient to attribute stress transfer across the polymer-HA interface. Therefore, HA restrains the movement of the matrix phase in the vicinity of each particles contributing to an overall increase in elastic modulus.[3] It can be seen that the tensile modulus of PMMA/5HA composites slightly decreased by the addition of γ-MPS treated HA. There was ∼ 10% reduction in tensile modulus for 8% γ-MPS treated PMMA/5HA composites. This may again due to the plasticizing effect of the silane coupling agent. The PMMA/γ-MPS treated 5HA composite exhibited slightly lower tensile modulus compare to that of PMMA/5HA composites. The reduction of modulus at high loadings of silane is attributed to the plasticizing effect of excessive silane.[20,21] Bose et al.[22] suggested that these variations of tensile strength may due to a flexible interface layer in the composite have formed after treated with silane.

The addition of HA to PMMA resulted in decreased tensile strength and elongation at break, due to poor compatibility between filler and matrix. The decrease in tensile strength is because the interfacial interaction between the PMMA and the HA phase is restricted to the mechanical interlocking of the HA particles by the matrix. Monomers MMA which have a poor dissolving capability could exhibit low bond strength.[23] According to Ana et al.,[24] residual monomer contents may adversely affect the mechanical properties of acrylic denture base resins by a plasticizing effect which reduces the interchain forces so that deformation occurs more easily under load. According to Santos et al.,[17] the reduction of strength properties could be due to reduced wetting capacity of the resin matrix on HA filler.

Nevertheless, after silanation process on HA, the tensile strength of PMMA/5HA composites was slightly increased. Table II shows that the tensile strength of PMMA/5HA composites was increased by the incorporation of γ-MPS treated HA. The increments of tensile strength for PMMA/5HA composite was ∼ 22% by the HA treated with 8% γ-MPS. This was believed that the γ-MPS could provide sufficient wetting capacity to HA and thus have better adhesion and interaction with PMMA. The γ-MPS contribute a "bridge like" between HA filler and PMMA matrix. The increasing of tensile strength after silanation HA indicates that the silane treatment may improve the wettability of the filler and induce the interfacial interaction between HA filler and PMMA. It is believed that γ-MPS not only provide good interfacial bonding between filler and matrix, it is also favor the slippage of the molecular chain without deforms easily when load applied on the specimens. The fillers treated with silane coupling agent could be able to disperse more favorably in the polymer matrix and to have better adhesion with the matrix.[8] The formation of hydrogen bonding could originated from the C=O of γ-MPS and O—H group from the HA filler. Bonding resin composites to silanized surface is generally through interdiffusion of the oligomeric siloxanes at the interface with possible crosslinking to the interpenetrating polymer network in the interphase region.[25] According to Monticelli et al.,[26] silane enhances post resin bond strength by promoting the wetting of the etched post surface and facilitating the diffusion of the fluid composite resin into the retentive spaces among the exposed fibers. Further reactions between silane molecules and the organic surface will enhance condensation and induce a more tightly packed configuration of the coupler molecules on the post surface.

It can be seen that the elongation at break for PMMA composite was decreased rapidly by the addition of particulate fillers which indicates interference by the filler to the mobility or deformability of the matrix. Normally, the addition of HA fillers to PMMA matrix restricts molecular motions in the matrix, which in turns, reduced the elongation at break of PMMA/5HA composites. From Table II, it was found that the elongation at break of the PMMA/5HA composite increased with the presence of γ-MPS as a result of the improved compatibility between the PMMA matrix and HA filler. The slightly improvement in the elongation at break of the PMMA/γ-MPS treated HA composites could be attributed to the enhanced interfacial interaction and/or internal plasticization. Coupling agent induces lubricating/plasticizing action which has diffused into the polymer matrix to serve as an internal plasticizer.[27,28] Plasticizing effect might have reduced the intermolecular forces in the matrix and consequently increased the flexibility of the composites.[29] Incorporation of γ-MPS resulted an increase in elongation at break for PMMA/5HA composites. There was ∼ 50% increment in elongation at break for PMMA/5HA composites after the silanazation of 8% concentration of γ-MPS on HA.

Fracture toughness is defined as the resistance of a material to crack extension. Figure 2 shows the effect of different concentration of γ-MPS on the fracture toughness of PMMA/5HA composites. The fracture toughness of PMMA matrix is ∼ 1.41 MPa.m$^{1/2}$. By the 5% loading of HA filler in PMMA matrix, the fracture toughness was increased ∼ 26% (1.79 MPa.m$^{1/2}$). It is interesting to note that the fracture toughness of specimens were increased by the silanation of HA filler, regardless the concentration of γ-MPS. The fracture toughness of PMMA/5HA composites treated with 8% γ-MPS was increased for about 11% compare to PMMA/5HA composites. The
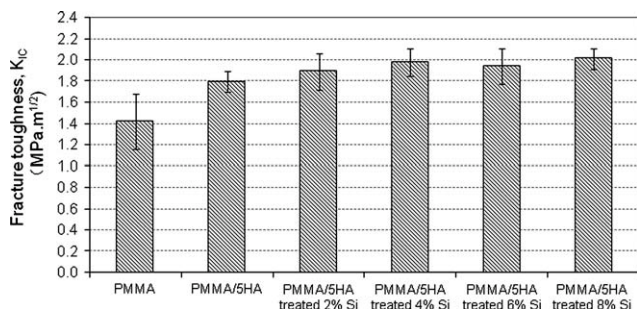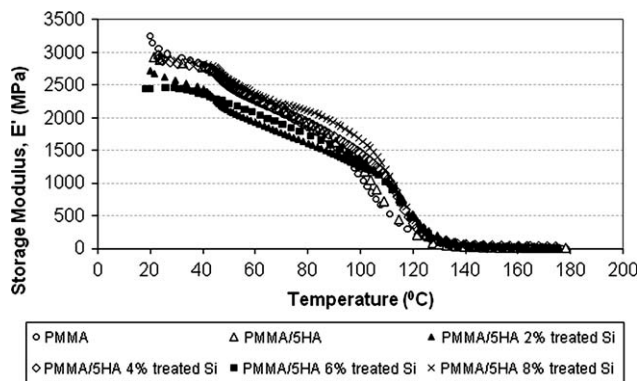
Figure 2 Effect of different concentration of γ-MPS on the fracture toughness of PMMA/5HA composites.

Figure 3 Effect of different concentration of γ-MPS on the storage modulus of PMMA/5HA composites.

fracture mechanism approach is considered a reliable indicator of the performance of brittle mechanism. Fracture toughness of PMMA/5HA composites specimens were increased after surface treatment on the HA filler due to a better interaction adhesion between filler and matrix. When the external load applied on the specimens, transferring load from matrix to filler gives rise to the overall deformation toughness of composites system. This is due to better adhesion of HA filler and PMMA matrix after silanazation. According to Wang and Bonfield,[8] the plasticizing effect of silane coupling agent could lower the Young's modulus and tensile strength. The introduction of silane coupled HA and acrylic acid grafting, forming a strong bond (chemical and mechanical) between the filler and the matrix which delayed the initial de-wetting and cavitations process.[8] Harper et al.[19] had reported that the plasticizing effect of silane coupling agent was allowing the chains slip over each other more easily, thus increase the ability of the cement to extend prior to failure.

Thermal properties

Figure 3 shows the effect of different concentration of γ-MPS on the storage modulus (E') of PMMA/5HA composites. The modulus of PMMA/5HA composites decreases with the increasing of temperature. The reduction of storage modulus is attributed

to the increase of polymer chain mobility when the temperature arises.[30,31] This phenomenon reflects that the polymer chains are more mobile at high temperature which is responsible for the reduction of the low interfacial interactions between the HA filler and PMMA matrix of the composites material and hence resistance to deformation is reduced. According to Richeton et al.,[32] the breakage of secondary bonds (e.g., Van der Waals, polar attraction) will cause transition in the polymer. This is because the termination of the attractive interaction between specific atoms involved in the molecular motion corresponding to specific relaxation, i.e. rotation of a side group and reptation of the main chains. The storage modulus of PMMA (E'_{100}) increased with the addition of HA filler (c.f. Table III). It is widely recognized that the incorporation of disperse fillers into polymers induces substantial changes in their mechanical and thermal properties. These changes are due to several factors, i.e. variations in the mobility of the macromolecules in the boundary layers, the orienting influence of the filler surface, or the different types of filler-polymer interactions.[31] From Table III, it can be seen that the storage modulus (E') at 30°C of PMMA/5HA composites did not influence much by the silanazation of HA. However, it is worthy to mention that the storage modulus (E') of

TABLE III
Dynamic Mechanical Thermal Properties of PMMA, PMMA/5HA, and PMMA/γ-MPS Treated 5HA Composites

Material designation	Tan δ peak temperature (°C)	Storage modulus, E' (MPa)		Loss modulus, E'' (MPa)	
		At 30°C	At 100°C	At 30°C	At 100°C
PMMA	132	2919	1046	352	193
PMMA/5HA	132	2842	1182	295	185
PMMA/5HA treated 2% Si	139	2574	1250	299	151
PMMA/5HA treated 4% Si	136	2834	1451	357	192
PMMA/5HA treated 6% Si	137	2456	1290	311	164
PMMA/5HA treated 8% Si	141	2878	1636	329	207
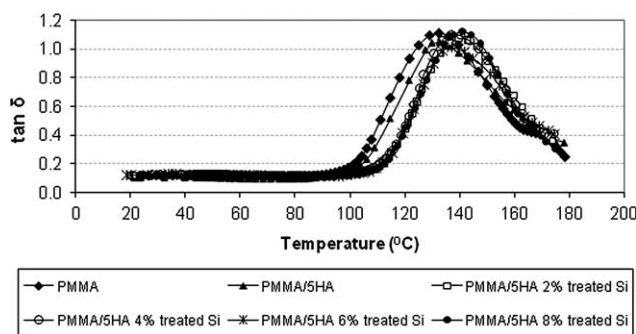
Figure 4 Effect of different concentration of γ-MPS on the tan δ of PMMA/5HA composites.

PMMA/5HA composites was increased by the γ-MPS treated HA at 100°C. The increment of 5.8%, 23%, 9%, and 38.4% were observed for PMMA/γ-MPS treated HA composite with concentration of γ-MPS 2–8%, respectively. This is probably due to the formation of chemical bond of γ-MPS which can provide better adhesion between HA filler and PMMA. Accordingly, the PMMA/γ-MPS treated HA composites could still function well in term of mechanical properties even at temperature of 100°C.

Table III also shows the loss modulus at 30°C and 100°C of PMMA, PMMA/5HA composites and PMMA/5HA composites treated with γ-MPS. It was found that the loss modulus at 30°C of PMMA/5HA composites is lower than that of PMMA. This phenomenon may be produced by a mobility restriction of the polymer molecules as a result of the presence of the filler which decreasing the possibility of energy storage of the filled polymer.[31] However, PMMA/γ-MPS treated HA composites show that the increasing of loss modulus compared to PMMA/untreated HA composites. This is due to the internal plasticization of γ-MPS, attributed to the ductile interface layer formed between the filler and polymer matrix. Therefore, the higher the loss modulus of PMMA composites, the higher of dissipated energy was. The silanazation of PMMA/5HA composites is more effective to improve interfacial adhesion and hence load transfer easily between HA filler and PMMA matrix because of its chains mobility. The loss modulus at 100°C for PMMA/γ-MPS treated HA composites are almost comparable. This is believed that the breakage of secondary bonds as Van der Waals and polar attraction on macromolecule chains at higher temperature. Therefore, the increasing mobility of the polymer molecules is responsible for the reduction of the low interfacial interaction between the two components of the composites material.[31]

Figure 4 shows the effect of different concentration of γ-MPS on the tan δ of PMMA and PMMA/5HA composites. As for tan δ, it was observed that the peak temperature shifted to higher temperature with the increasing concentration of γ-MPS on the surface

treatment of HA. The tan δ peak temperature was shifted from 132°C (PMMA and PMMA/5HA composites) to 140°C PMMA/5HA treated with 8% γ-MPS as shown in Table III. The PMMA/5HA composites treated with 8% γ-MPS possesses the highest mechanical performance at 100°C, probably motivated by the strong interaction between γ-MPS and the HA filler. These improvements of thermal properties were originated by the formation of chemical bonds of silane coupling agent and compatibility between organic and inorganic interfaces. Hideki et al.[33] reported that the peak temperature shifted to higher temperature with increasing in SiO$_2$ content. These results indicate that the mobility of the polymer network was reduced by hybridization. This improvement of thermal properties seems to originate from the formation of chemical bonds and high compatibility between organic and inorganic interfaces. The tan δ (ratio of E″/E′) depends on the filler and matrix adhesion level. According to Martinez-Hernandez et al.,[34] a weak filler/matrix bonding will reflect in higher values for tan δ. In Figure 4, we can observe that the silanazation of composites have smaller energy dissipation coefficients and shifting from 90°C to 110°C. This may indicates a good interface between the HA filler and the PMMA matrix by the γ-MPS. The damping in composites has decreased considerably due to polymeric chains attached in the HA filler diminish their mobility, which further decreasing the friction among them.

Table IV shows that the glass transition temperature (T_g) of PMMA, PMMA/5HA composites and PMMA/γ-MPS treated HA composites. The T_g values are found to increase with the increasing contents of γ-MPS in PMMA/5HA composites. However, there was no change in T_g for PMMA and PMMA/5HA composite. With the silanazation to the PMMA/5HA composites, the resulting T_g increased to 118°C for PMMA/5HA composites treated with 8% γ-MPS. This indicates that the thermal stability for the PMMA composites was enhanced by the surface treatment of γ-MPS. There are two possible reasons lead to the increment in T_g when γ-MPS participated in the reaction: (1) hydrogen bonding between the hydroxyl groups of HA and silanol groups from

TABLE IV
Thermal Properties of PMMA, PMMA/5HA, and PMMA/γ-MPS Treated 5HA Composites

Material designation	T_g (°C)	T_{10} (°C)	T_{50} (°C)
PMMA	108.4	246	354
PMMA/5HA	109.7	260	354
PMMA/5HA treated 2% Si	112.0	246	334
PMMA/5HA treated 4% Si	112.0	260	354
PMMA/5HA treated 6% Si	112.0	267	354
PMMA/5HA treated 8% Si	118.0	270	354
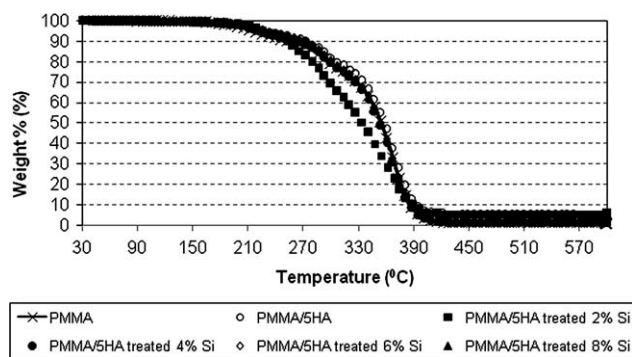
Figure 5 TGA curves of PMMA, PMMA/5HA, and PMMA/γ-MPS treated 5HA composites.

γ-MPS, and (2) organofunctional group of γ-MPS links to methyl group of PMMA. The crucial link between PMMA matrix and HA filler led to a higher energy barrier that inhibited the movement of chain segments of macromolecules. According to Chen and Kusy[35] the hydrogen bonding between the hydroxyl groups of MAA (methacrylic acid) monomer and the carbonyl groups of PMMA resulting increase in T_g due to the restriction of the macromolecules chain segments' movement. The glass transition temperature can increase and broaden due to polymer chain confinement that results from intermolecular interactions, in particular hydrogen bonding.[36]

Figure 5 shows the TGA curves of PMMA and its composites. It can be seen that the PMMA was fully decomposed at 550°C. However, for PMMA/5HA composites, there is $\sim$ 5% of remained content at 550°C. Hydroxyapatite decompose temperature is about 800–1200°C because the presence of Calcium (Ca) and Phosphorus (P) elements which have higher decomposition temperature. Therefore, $\sim$ 5% of HA still remain as char residual at 550°C due to their high decomposition temperature. There are three thermal decomposition stages for the PMMA and it composites. This can be observed from TGA curves (Fig. 5) and its respective DTG curves (Fig. 6). The first two decompositions steps are approximately between 170–250°C and 270–335°C. The third step of the thermal decomposition curve is in the range of 350°C to 430°C. The first two decomposition steps correspond to the cleavage of head-to-head linkages and end-initiated vinyl-terminated PMMA. The maximum thermal decomposition temperature of the composite materials in these two steps are similar to that of the PMMA. The third step of the thermal decomposition curve, corresponding to the random scission of PMMA main chains which obtained by free radical polymerization.[37,38] It can be observed that the T_g of PMMA and PMMA/5HA composites was comparable. It was believed that the decomposition of material is

majority on PMMA with the presence of C, O and H which have lower thermal stability.

Table IV shows the thermal degradation data of PMMA and PMMA/5HA composites. T_{10} refer to the onset temperature of the degradation at which 10% weight loss occurred. T_{50} refer to the midpoint temperature at which 50% weight loss took place. An enhanced thermal stability of the composite with functionalized HA fillers was observed compare to the non-functionalized filler. As shown in Table IV, the T_{10} of PMMA matrix recorded at 246°C, while the addition of HA filler into PMMA matrix increased the T_{10} of PMMA to 260°C. Recall that the HA contains Ca and P which can increase the thermal stability for the PMMA. As the γ-MPS concentration was increased from 2% to 8% for the HA treatment, the T_{10} were achieved in the range of 246 to 270°C. This may due to improvement of interfacial bonding between the functionalized filler and polymer matrix, which enhanced the barrier effect to the evaporation of small molecules generated during the thermal decomposition of the PMMA matrix.[39] Besides, the increase of γ-MPS concentration in PMMA/5HA composites, the increase of Si contents in PMMA/5HA composites. Si is a tetravalent metalloid. It is less reactive and exhibit high thermal stability. Therefore, it was believed that the enhancement of T_{10} could be due to the presence of Si element for the γ-MPS treated PMMA/5HA composites. Note that the T_{50} of all the PMMA/5HA composites were recorded at 354°C. This thermal decomposition is corresponding to the random scission of PMMA main chains (as discussed earlier).

Morphological properties

The FESEM micrographs of PMMA/5HA composites and PMMA/γ-MPS treated 5HA composites were shown in Figure 7. Figure 7 shows the randomly propagated smooth fractured surface which indicates the brittle behavior induced by the PMMA
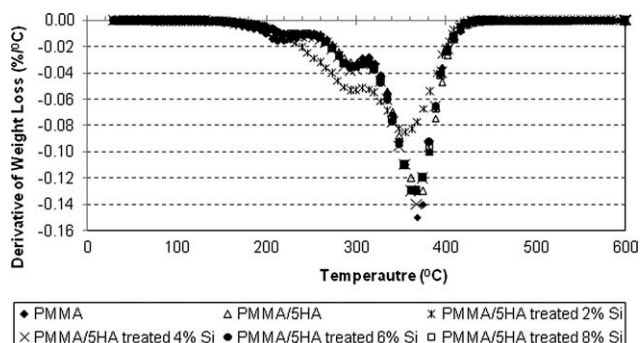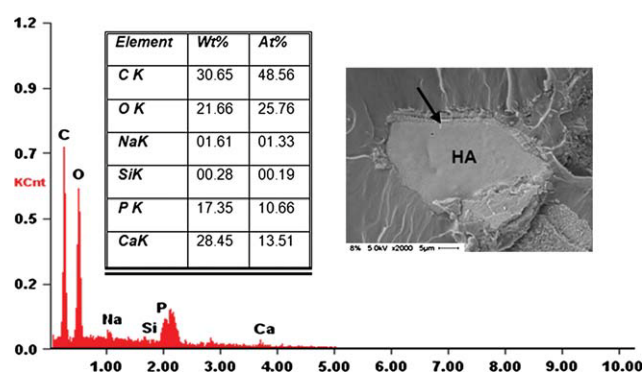

Figure 6 DTG curves of PMMA, PMMA/5HA, and PMMA/γ-MPS treated HA composites.
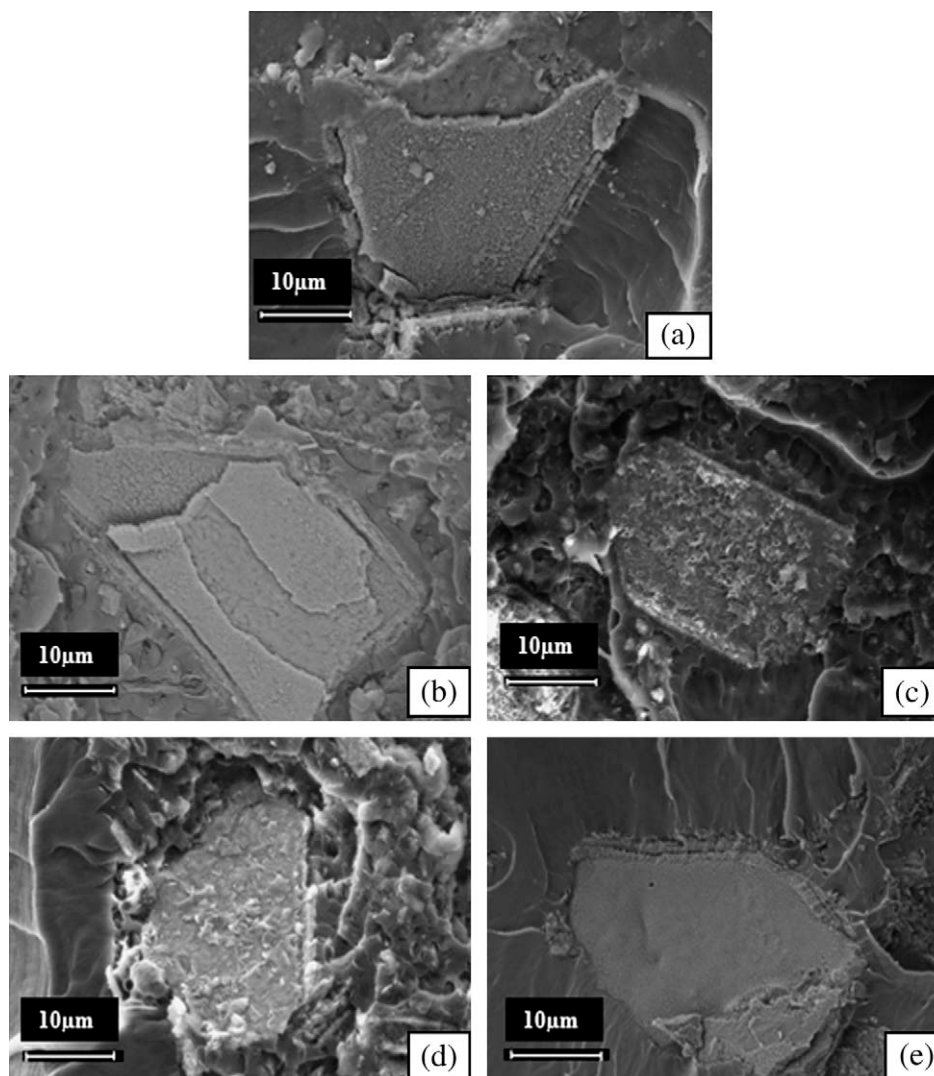
Figure 7 FESEM micrograph of (a) PMMA/5HA composites, (b) PMMA/5HA composites treated with γ-MPS 2% Si, (c) PMMA/5HA composites treated with γ-MPS 4% Si, (d) PMMA/5HA composites treated with γ-MPS 6% Si and (e) PMMA/5HA composites treated with γ-MPS 8% Si.

matrix. In Figure 7(a), it was found that the fracture proceeds along the interface of PMMA and HA. The HA particle embedded in the polymers with gaps between fillers and matrix. It is rather clear that the untreated HA fillers unable to bond to the PMMA matrix well which reveals that the filler-matrix interface are weak and thus adhesive failures prevail. However, the composites treated with γ-MPS [Fig. 7(b-e)] shows that the HA fillers embedded in PMMA matrix without noticeable gap between filler and matrix. It can also be observed from Figure 7(b–e) that the silane treatment did improve the wettability of the filler. More irregular boundaries fractured surface was observed which was indicated the improvement adhesion between the phases. Interestingly to note that, it was observed that the γ-MPS treated HA was surrounded by "ring-like" interface structure. It is believed that the γ-MPS can be adsorbed onto the surface of HA and further forma-

tion of multilayer through hydrogen bonding. Figure 8 shows the EDX spectra of PMMA/γ-MPS treated 5HA composites containing Si element. Recall that

Element	Wt%	At%
C K	30.65	48.56
O K	21.66	25.76
NaK	01.61	01.33
SiK	00.28	00.19
P K	17.35	10.66
CaK	28.45	13.51

Figure 8 EDX spectra taken from PMMA/5HA composites treated with 8% γ-MPS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the HA used for this study containing O, Na, P and Ca. It can be seen that carbon (C) and silicone (Si) was detected in the "ring like" structure. This may prove that the interface multilayer is associated to γ-MPS. In Figure 7(b–e), the "ring-like" interface surrounded HA filler could be related to the interaction between silanol groups of γ-MPS and hydroxyl groups of the HA filler surface, which have the capability of forming a Si—O linkage. These morphological observations indicate the improved adhesion between HA filler and PMMA matrix due to silanazation of HA. This is in line with the enhancement of mechanism properties, as discussed in the earlier section. The coupling agent does favor a better polymer-filler interaction due to the replacement of hydration water of the inorganic surface of the filler, with organo-functional coupling agent rendering inorganic polymer interface compatible with matrix and thereby eliminating air voids in the systems.[27,28]

CONCLUSION

The FTIR absorption bands at 840, 873, and 1031 cm^{-1} which are corresponding to Si—O stretching were observed after the silanazation of HA. This prove that the silane treatment of HA was performed successfully. The introduction of 3-(trimethoxysilyl) propyl methacrylate (γ-MPS) treated on HA filler has resulted improvement of flexural properties for PMMA/5HA composites. Improved bonding between the HA particles and the PMMA which is achieved by both chemical adhesion (evidenced by FESEM) and mechanical coupling leads to improved mechanical properties of PMMA/5HA composites. Besides, the present of flexible interface layers between HA filler and PMMA matrix after treated with silane coupling agent was able to increase the tensile strength and fracture toughness of PMMA/5HA composites treated with 8% concentration of γ-MPS. The T_g was increased from 108°C to 118°C due to the improvement of interaction bonding between silanazation of HA filler and PMMA. TGA results indicate that the thermal stability of PMMA is improved by the silanazation of HA using γ-MPS.

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