MECHANICAL AND THERMAL PROPERTIES OF HYDROXYAPATITE FILLED POLY(METHYL METHACRYLATE) COMPOSITES

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Poly(methyl methacrylate) (PMMA) filled with hydroxyapatite (HA) filler has been widely used in biomaterial application. Acrylic denture base material was prepared from PMMA filled with HA. This research work attempted to investigate the effects of hydroxyapatite (HA) on the flexural properties, fracture toughness, and thermal properties of poly(methyl methacrylate). PMMA powder was mixed with monomer of methyl methacrylate (MMA) stabilized with hydroquinone. Benzoyl peroxide (BPO) and ethylene glycol dimethacrylate (EGDMA) were used as initiator and crosslinking agent, respectively. The HA loading was ranged from 5- 20%. The PMMA/HA composites were prepared by using heat-processing polymer powder and liquid method. The polymerization of PMMA/HA were carried using water bath. The thermal properties of the PMMA/HA composites were characterized using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The flexural modulus of PMMA was increased by the addition of HA. This is attributed to the reinforcement effects of HA. Experimental data of flexural modulus for PMMA/HA composites was compared with several theoretical models and equations. In addition, it was found that the storage modulus (E'), glass transition temperature (T_g), and fracture toughness properties of PMMA were influenced by the HA loading.

Introduction

A lot of polymeric materials have been used as dental base materials such as vulcanized rubber, plastic molding materials, and phenol formaldehyde resin. Most of these materials have poor aesthetics, tasted bad and became foul smelly [1]. Recently, polymer-hydroxyapatite composites have attracted great attention due to their ability to substitute the bone tissue and dentistry implant. The polymer system can be used are high density polyethylene (HDPE), polymethyl methacrylate (PMMA), polylactic acid (PLA) and ultra-high molecular weight polyethylene (UHMWPE). PMMA is used almost universally for denture base construction [2-3]. Hydroxyapatite (HA) has been extensively used as a substitute material for damaged teeth or bone over the past three decades, and its compatibility with surrounding tissues has been experimentally proven. An ideal bone tissue engineering approach would incorporate osteoconductivity and osteoinductivity into the design of the supporting biomaterial, as well as biocompatibility, degradability, mechanical integrity, and the ability to support cell transplantation. Hydroxyapatite is an important bioceramic with tremendous potential for biomedical applications depending on stoichiometry, crystallinity and particle size. Its unique bioactivity promotes rapid bone growth on a strong interfacial fixation that has particular benefit to orthopaedic and dental applications. In this research work, the objective is to study the effect of HA on the flexural properties, fracture toughness and thermal behaviors for PMMA. In addition, the experimental data will be compared with several theoretical models and equations in order to understand the flexural behavior of the PMMA/HA composites.

Materials and Experimental

Materials

Solid components consist of PMMA (Sigma Aldrich, USA) and 0.5% benzoyl peroxide (BPO) (Merck Chemical, Germany). The liquid components consist of methyl methacrylate (MMA) (Fluka, UK) stabilized with 0.025% hydroquinone and ethylene glycol dimethacrylate (EGDMA) (Sigma Aldrich, USA). Hydroxyapatite (HA) powders were supplied by Sigma Aldrich, USA.

Experimental- Preparation of PMMA/HA composites

The powder component was prepared by mixing PMMA, HA and BPO using ball milling. The liquid component was prepared by mixing MMA and EGDMA. The mixing of powder to liquid was carried out according to dental laboratory practice. The ratio of powder to liquid was set at 2.5: 1. After reaching dough stage, the mixture was packed into a mold followed by pressing under a pressure of 14MPa at room temperature for 30 min. The final polymerization was carried out using a water bath at 78^{o}C for 90 min.

Experimental – Sample characterization

Three point bending tests were performed according to ASTM D790 using an Instron 3366 machine. The support span length was set at 50mm. The testing speed was set at 5mm/min. The flexural modulus, strength and displacement were recorded.

The fracture toughness of specimens was determined by using single edge notch bending test (SEN-B) according to ISO 13586:2000. A natural crack was generated by tapping on a new razor blade placed in

the notch formed by band saw cutter. The SEN-B specimens were tested at a crosshead speed of 1.00 mm/min. The value for K_{IC} was calculated by using the following equation:

$$K_{IC} = \frac{P_c \frac{S}{4}}{B\frac{W^2}{6}}[1.93 - 3.07\left(\frac{a}{w}\right) + 14.53\left(\frac{a}{w}\right)^2 - 25.1\left(\frac{a}{w}\right)^3 + 25.8\left(\frac{a}{w}\right)^4]a^{1/2}$$

P_c = load at break (N)
B = specimen thickness (mm)
W = specimen width (mm)
a = notch length (mm)
S = span length (mm)

The determination of the glass transition temperature (T_g) of the PMMA and PMMA/HA composites were characterized by using a Perkin Elmer Differential Scanning Calorimeter (DSC 6). The DSC tests were carried out at a heating rate of 10°C/min in nitrogen atmosphere. The storage modulus (*E'*), loss modulus (*E''*), and tan delta as a function of temperature (*T*), were assessed by dynamic mechanical analyzer (DMA) using a Mettler Toledo DMA machine. DMA spectra were taken in three point bending mode at 1 Hz frequency in a temperature range of 30-150°C. The heating rate was set at 10°C/min.

Results and Discussion

From Figure 1, it can be seen that the flexural modulus of PMMA was increased significantly by the addition of HA. The HA could act as a good reinforcing filler in PMMA. Figure 2 shows the flexural modulus of PMMA/HA composites obtained from experiment and calculated by several theoretical models. The theoretical model and equations include Guth Model, Kerner's Equation, Ahmed & Jones Equation and Hirsch's Model. Hirsch's model gives the most accurate prediction value among all the theories.

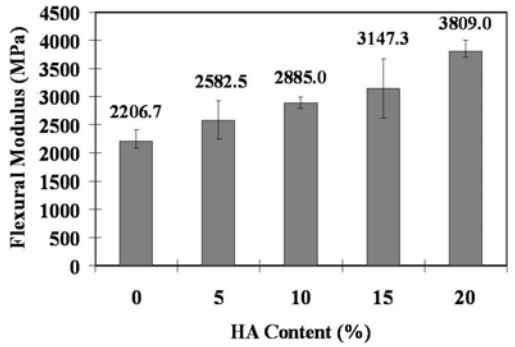

Figure 1: Effects of HA loading on the flexural modulus of PMMA.

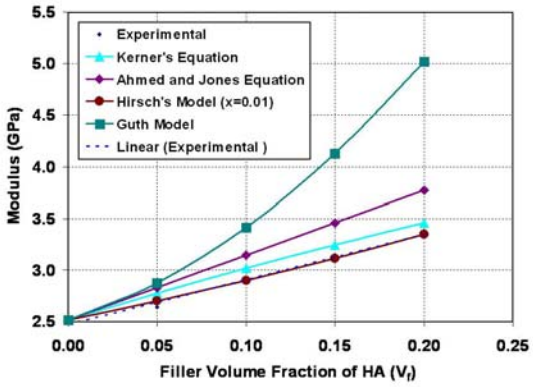

Figure 2: Comparison between experimental and several equations calculated flexural modulus values as a function of filler volume fraction.

Figure 3 shows the effects of HA loading on the flexural strength of PMMA. It can be found that the flexural strength of PMMA was decreased by the incorporation of HA. This is maybe due to the agglomeration of HA particles in PMMA matrix. In addition, the reduction of strength could be related to the incompatibility between PMMA and HA, as well as the presence of matrix-particle interfacial defects.

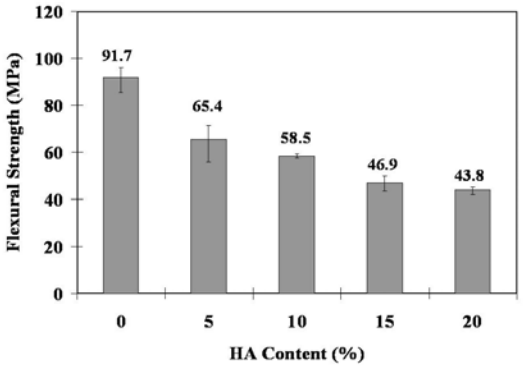

Figure 3: Effects of HA loading on the flexural strength of PMMA.

Figure 4 shows the storage modulus as a function of temperature for PMMA and PMMA/HA composites. Note that the storage modulus of PMMA was increased significantly by the addition of HA.

From Table 1, it can be seen that the T_g of PMMA was slightly increased by the addition of HA.

Table 1: Glass transition temperature (T_g) of PMMA and PMMA/HA composites recorded from DSC.

Materials	T_g (°C)
PMMA	103.8
PMMA/5HA	107.4
PMMA/10HA	110.1
PMMA/15HA	108.4
PMMA/20HA	111.3

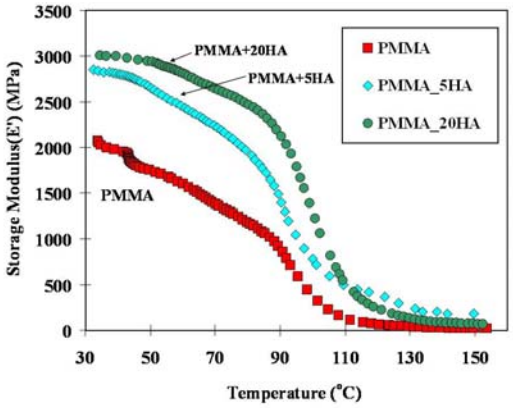

Figure 4: Storage modulus vs temperature traces for PMMA and PMMA/HA composites.

Figure 5 shows the effects of HA loading on the fracture toughness of PMMA. It can be observed that the K_{IC} of PMMA increased until an optimum loading of HA is attained at 5 wt%. Further incorporation of HA reduced the K_{IC} gradually.

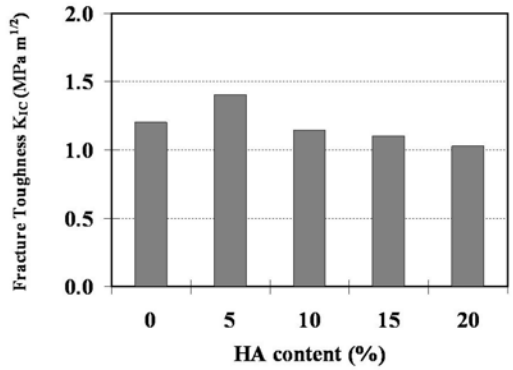

Figure 5: Effects of HA loading on the K_{IC} of PMMA.

Conclusions

The flexural modulus and storage modulus of PMMA was increased significantly by the addition of HA. However, the flexural strength of PMMA was reduced by the incorporation of HA. The fracture toughness of PMMA was influenced by the addition of HA. Hirsch's model gives the reasonable close prediction value to the experimental results of flexural modulus. From the DSC analysis, it was found that the T_g of PMMA was slightly increased in the presence of HA. The optimum loading of HA was achieved at 5 wt% attributed to the balance of good flexural properties and fracture toughness.

Acknowledgements

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