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Preparation of hydroxyapatite/poly(methyl methacrylate) and calcium silicate/poly(methyl methacrylate) interpenetrating hybrid composites

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Abstract Hydroxyapatite/poly(methyl methacrylate) (HAp/PMMA) and calcium silicate/poly(methyl methacrylate) (CS/PMMA) composites were prepared by interpenetrating bulk polymerization of methyl methacrylate (MMA) monomer in porous structures of HAp and CS. The porous HAp and CS templates were prepared by mixing their calcined powders with poly(vinyl alcohol) (PVA) solution, shaping by uniaxial pressing and then firing at 1,100 °C for HAp and 900 °C for CS. The templates were soaked in the solution mixture of MMA monomer and 0.1 mol% of benzoyl peroxide (BPO) for 24 h. The pre-composites were then bulk polymerized at 85 °C for 24 h under nitrogen atmosphere. The microstructures of the composites showed the interpenetrating of PMMA into the porous HAp and CS structures. Thermogravimetric analysis indicated that the PMMA content in the HAp/PMMA and CS/PMMA composites were 13 and 26 wt%, respectively. Weight average molecular weights ($\overline{M}_w$) of PMMA were about 491,000 for HAp/PMMA composites and about 348,000 for CS/PMMA composites. Compressive strengths of these composites were about 90–131 MPa in which they were significantly higher than their starting porous templates.

Introduction

Bioactive materials such as glasses [1, 2], glass-ceramics [3, 4], hydroxyapatite [5–7], composite materials [8, 9] etc. have been synthesized and developed for medical applications since the early of 1970s. One of the most attractive candidates is hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), HAp) [5–7] due to its biocompatibility and being the same chemical compositions as bone mineral. There are, however, some disadvantages of HAp, i.e., difficulty to shape and relatively low mechanical properties. Alternatively, calcium silicate ($CaSiO_3$, CS) plays an important role as bioactive materials since it can induce the fast formation of an HAp layer after soaking in simulated body fluid (SBF), indicating the high ability to bond with living bone [10–12]. However, the CS has the same problem with the HAp as low mechanical properties.

From the above reason, many researches have enrolled with composites dealing with the combination of ceramics and polymers in order to improve some properties, especially mechanical properties [13, 14]. Therefore, our research studied on the preparation of hydroxyapatite/poly(methyl methacrylate) (HAp/PMMA) and calcium silicate/poly(methyl methacrylate) (CS/PMMA) composites by interpenetrating polymerization of methyl methacrylate (MMA) monomer in the porous HAp and CS templates. The PMMA was selected because it was one of the medical materials, which commonly used as bone cement, thus it was considered to be a biocompatible material. Compressive strengths of the as-prepared composites were measured in comparison with the starting porous ceramics.

Experimental procedures

Preparation of HAp and CS powders

HAp was prepared by co-precipitation of calcium hydroxide ($Ca(OH)_2$) and phosphoric acid (H_3PO_4). First,

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0.5 mol of $Ca(OH)_2$ was suspended in 50 mL of water. The suspension was vigorously stirred and kept at 10 °C. Concentrated H_3PO_4 was diluted to 0.3 mol/L, then 250 mL of the diluted H_3PO_4 and 250 mL of ammonium hydroxide (NH_4OH) were simultaneously added into the suspension at a rate of about 1 mL/min using peristaltic pump. After all the H_3PO_4 solution was added, the precipitate was filtered, dried overnight at 100 °C and calcined at 500 °C for 2 h.

CS was prepared by co-precipitation of calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) and tetraethyl orthosilicate ($Si(OC_2H_5)_4$), TEOS) using sodium hydroxide (NaOH) as precipitant. The starting substances were dissolved in 300 mL of ethanol with stirring for 2 h, and the concentration of solution was adjusted to 0.1 mol/L. The desired product was precipitated by adding 300 mL of 0.33 mol/L NaOH. The precipitate was filtered and washed twice by 150 mL of distilled water. The precipitate was then dried overnight at 100 °C and calcined at 500 °C for 2 h.

Chemical compositions of the synthesized HAp and CS powders were analyzed by X-ray fluorescence spectrometer (XRF; Bruker AG, SRS3400).

Preparation of porous HAp and $CaSiO_3$ templates

A polymeric binder was prepared by dissolution of 20 g of poly(vinyl alcohol) (PVA) in 100 mL of distilled water. The calcined powders (HAp or CS) were dispersed in the PVA solution and then dried overnight at 100 °C. The mixed powders were uniaxially pressed into cylindrical shape with the dimension of 1 cm in diameter and 0.5 cm in height. The HAp and CS green bodies were calcined at 1,100 °C for 5 h and 900 °C for 2 h, respectively. The porous HAp and CS templates were obtained due to the burning out of PVA binder at high temperature.

Preparation of HAp/PMMA and CS/PMMA composites

Commercially available MMA monomer was extracted twice with an aqueous solution of 10 mol% NaOH in order to remove the inhibitor. The extracted MMA was washed with distilled water several times to eliminate the base residue and then added an anhydrous sodium sulfate (Na_2SO_4) to absorb the moisture content.

The porous HAp and CS templates were soaked in the solution mixture of MMA monomer and 0.1 mol% benzoyl peroxide (BPO) for 24 h in order to obtain the pre-composites saturated with the monomer and catalyst. The pre-composites were polymerized at 85 °C for 24 h under nitrogen atmosphere.

Characterization of HAp/PMMA and CS/PMMA composites

Specific densities of pure ceramic templates and composites were measured by water replacement method. Crystalline phase and microstructure of the composites were characterized by X-ray diffractometer (XRD; D8 Advance, Bruker AG) and scanning electron microscopy (SEM; LEO1455VP, LEO), respectively. Weight % of the PMMA in the composites was determined by thermogravimetric analyzer (TGA; Pyris 1 TGA, Perkin elmer), in which the composites were heated from 50 to 900 °C at a heating rate of 10°C/min under air. The PMMA product was extracted from the composites by immersing in chloroform for 24 h. The extracted PMMA was characterized by Fourier transform infrared spectrometer (FTIR; IFS28, Bruker AG) using KBr disc. Weight average molecular weight ($\overline{M}_w$), number average molecular weight ($\overline{M}_n$) and molecular weight distribution (MWD) of the extracted PMMA were determined by gel permeation chromatography (GPC; WATER150-cv, Millipore) using tetrahydrofuran (THF) as the mobile phase at a flow rate of 1 mL/min. The GPC measurement was carried out at 30 °C and commercial polystyrene standards were employed for calibration to calculate the molecular weights of polymer.

Compressive strengths of HAp/PMMA and CS/PMMA composites

Compressive strengths of the HAp/PMMA and CS/PMMA composites were measured by universal mechanical testing machine (LR30K, Lloyd Instrument) with 30 kN load cell and a cross-head speed of 2.5 ± 2 mm/min.

Results and discussion

Characteristics of HAp/PMMA and CS/PMMA composites

Chemical composition of the synthesized HAp powder measured by XRF was 55.0–56.5 wt% CaO and 43.0–44.5 wt% P_2O_5. The Ca/P molar ratios of the HAp precursors were in the range of 1.56–1.67, which were close to the theoretical value of hydroxyapatite. The synthesized CS powder was composed of 48.1–48.4 wt% CaO and 51.6–51.8 wt% SiO_2. The Ca/Si molar ratio of the CS precursor is 1.00, which was equal to the theoretical value of wollastonite.

Figure 1 shows the XRD patterns of the HAp/PMMA and CS/PMMA composites. The main crystalline peaks of the HAp/PMMA composite were observed at $2\theta = 25.8°$, 31.8°, 32.2°, 33.0°, 39.8°, 46.8°, and 50.6°, corresponding

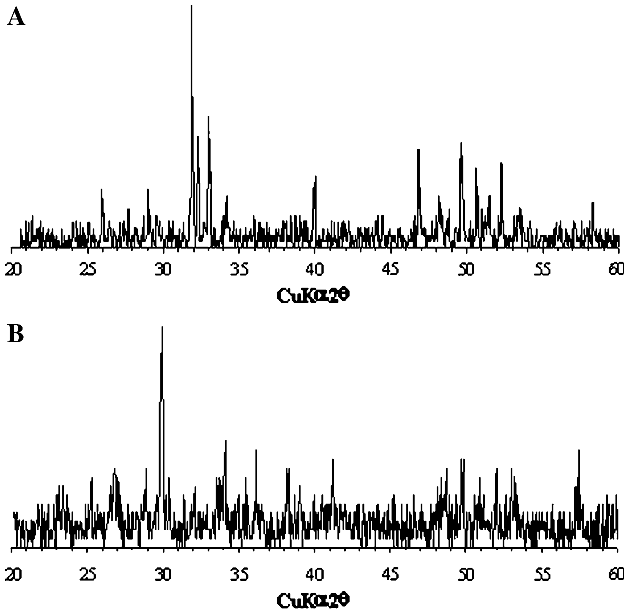

Fig. 1 XRD patterns of hydroxyapatite/poly(methyl methacrylate) (HAp/PMMA) (**A**) and calcium silicate/poly(methyl methacrylate) (CS/PMMA) (**B**) composites

to those of HAp (Fig. 1A). In Fig. 1B, the crystalline peaks of β-wollastonite were observed in the CS/PMMA composite at $2\theta = 23.2°$, 25.3°, 26.8°, 28.8°, 29.9°, 36.2°, and 49.8°. The PMMA peak was not observed in the XRD patterns of both composites because PMMA is mostly amorphous phase. However, the existence of PMMA in the composites could be proved by FTIR spectra as shown in Fig. 2A and B. The FTIR spectra of the extracted products from both HAp/PMMA and CS/PMMA composites showed the typical bands assigned to PMMA polymer: 1,731 cm^{-1} stretching vibration of the carbonyl group, 2,950–3,000 cm^{-1} stretching vibration of CH_2 and CH_3, 1,400–1,450 cm^{-1} bending vibration of CH_2 and CH_3, and 1,242 and 1,149 cm^{-1} stretching vibration of C–O.

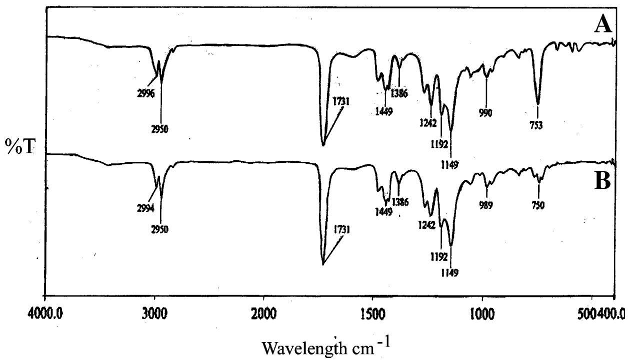

Fig. 2 FTIR spectra of extracted PMMA from hydroxyapatite/poly(methyl methacrylate) (HAp/PMMA) (**A**) and calcium silicate/poly(methyl methacrylate) (CS/PMMA) (**B**) composites

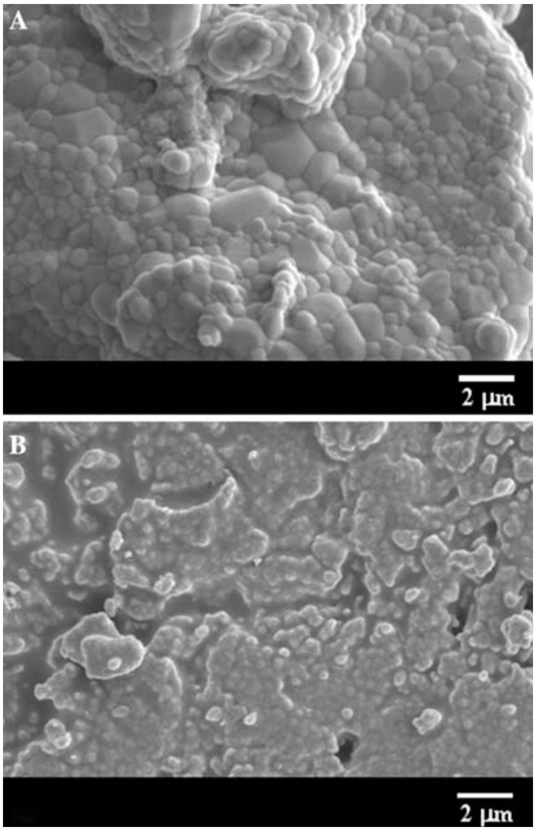

Fig. 3 Microstructures of the fracture surfaces of pure hydroxyapatite (HAp) (**A**) and hydroxyapatite/poly(methyl methacrylate) (HAp/PMMA) composite (**B**)

Figure 3 shows the microstructures of the fracture surfaces of pure HAp template and HAp/PMMA composite. The HAp template was observed as agglomeration of almost round shape grains with sharp grain boundaries as shown in Fig. 3A. Pores of various sizes generated from the decomposition of PVA were also observed in the SEM micrograph. In Fig. 3B, the polymerized PMMA was observed as a thin film continuously covering on the HAp grains, causing the HAp grain boundaries was not clearly observed in the SEM micrograph of HAp/PMMA composite. Figure 4A shows the microstructure of the pure CS template as a rough surface due to the clusters of small $CaSiO_3$ grains. The microstructure of the polymerized PMMA in the CS/PMMA composite was similarly found as the thin film coating on the $CaSiO_3$ grains as shown in Fig. 4B. The existence of the PMMA films in the fracture surfaces of both composites indicated that the MMA monomer could interpenetrate and polymerize properly in the porous HAp and CS templates.

The content of PMMA in the composites was determined from the TGA results as shown in Table 1. It was found that the weight loss occurred at the range of temperature between 200–650 °C, corresponding to decomposition of

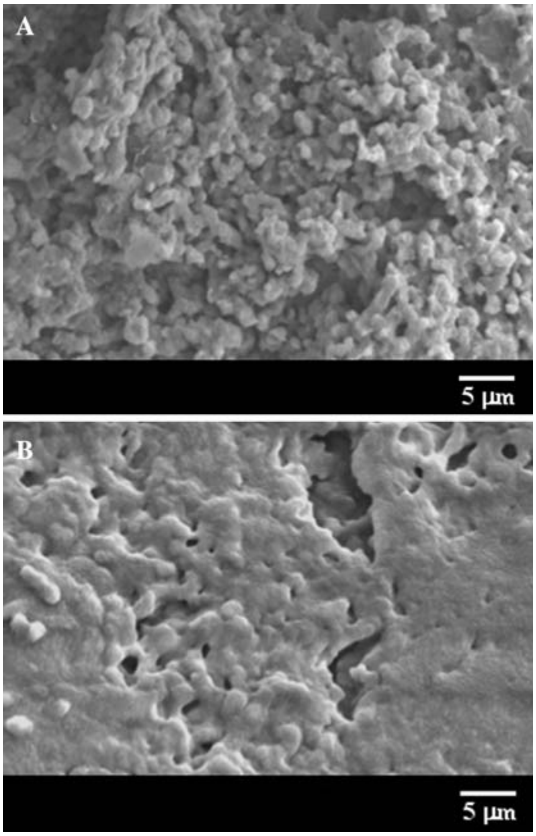

Fig. 4 Microstructures of the fracture surfaces of pure CS (**A**) and calcium silicate/poly(methyl methacrylate) (CS/PMMA) composite (**B**)

PMMA phase, was about 13 and 26 wt% in the HAp/PMMA and CS/PMMA composites, respectively. Difference in PMMA content of both composites depended directly on porosity of the starting porous templates, corroborated with their specific densities as shown in Table 1. The specific density of CS template was lower than that of HAp template, indicating the higher porosity of CS template. Consequently, the amount of MMA monomer diffused into the porous CS template was higher than that in the HAp template. The polymerization of MMA monomer in the porous templates caused the increase of the specific densities of both HAp/PMMA and CS/PMMA composites.

Table 1 Specific density, PMMA content, and compressive strength of ceramic templates and their composites

Sample	Specific density[a]		PMMA content (wt%)[b]	Compressive strength (MPa)[a]	
	Mean	SD		Mean	SD
HAp	1.61	0.02	–	13.27	0.35
HAp/PMMA	2.03	0.03	13	130.87	7.04
CS	1.04	0.02	–	3.09	0.22
CS/PMMA	1.71	0.05	26	90.29	8.36

[a] Mean values and standard deviation (SD) of five samples

[b] Calculated from TGA results

Table 2 Molecular weights and molecular weight distributions of the extracted PMMA from the composites

Samples	MW and MWD of extracted PMMA[a]		
	$\overline{M}_n$	$\overline{M}_w$	MWD
HAp/PMMA	153,000	491,000	3.21
CS/PMMA	155,000	348,000	2.25

[a] By GPC relative to polystyrene standards

The polymerized PMMA was extracted from the composites and analyzed by GPC. Their molecular weights and molecular weight distributions were summarized in Table 2. The PMMA with $\overline{M}_w$ = 491,000 g/mol and MWD = 3.21 was obtained in the HAp/PMMA composites. While the PMMA with $\overline{M}_w$ = 348,000 g/mol and MWD = 2.25 was obtained in the CS/PMMA composites. Those molecular weights were slightly different, suggested that the different types and structures of ceramic templates had no significantly effect on molecular weights of the polymerized PMMA.

Compressive strengths of HAp/PMMA and CS/PMMA composites

Compressive strengths of the HAp/PMMA and CS/PMMA composites are shown in Table 1. It was found that the average compressive strength of the HAp/PMMA composites was about 131 MPa, increasing 10 times from that of the porous HAp templates. Similarly, the average compressive strength of the CS/PMMA composites significantly increased about 30 times from that of the porous CS templates to about 90 MPa. The drastic increase of the compressive strength was attributed to the partial replacement of PMMA in the porous structure of ceramic templates. The PMMA film was considered to function as binder and load absorber among the HAp and CS grains. Therefore, the fracture behavior of brittle ceramic templates was changed since the relatively flexible PMMA film could transfer the external load from the templates, resulting in the decrease of severe crack initiation and propagation in the ceramic templates. The compressive strength of the CS/PMMA composites obviously increased with higher ratio than that of the HAp/PMMA composites. This result was considered to be the effect of PMMA content in the composites, i.e., the higher amount of PMMA in the composites, the higher increasing ratio of compressive strength was obtained.

In comparison to human bones, the compressive strengths of HAp/PMMA and CS/PMMA composites are in the range of cortical bones [15]. These results suggested that the HAp/PMMA and CS/PMMA composites are possible for use as implant materials.

Conclusions

The HAp/PMMA and CS/PMMA composites were able to prepare by bulk polymerization of MMA monomer within the HAp and CS porous templates at 85 °C for 24 h under nitrogen. The polymerized PMMA was observed as a thin film covering on the ceramic grains in the porous HAp and CS templates. The compressive strengths of HAp/PMMA composites with 13-wt% of PMMA content was 131 MPa, while that of the CS/PMMA composites with 26-wt% of PMMA content was 90 MPa. The compressive strengths of both composites were in the range of cortical bones.

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