Preparation and Properties of Carbon Fiber/Hydroxyapatite-Poly(methyl methacrylate) Biocomposites

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ABSTRACT: An *in situ* polymerization with a later solution co-mixing approach was used in the preparation of polymethyl methacrylate (PMMA) matrix composites using hydroxyapatite (HA) nanoparticles and short carbon fibers($C_{(f)}$) as reinforcing materials. The microstructures and fracture surface morphologies of the prepared $C_{(f)}$/HA-PMMA composite were characterized using XRD, FTIR, SEM, EDS, and FESEM analyses. The mechanical properties of the composites were tested by a universal testing machine. Results show that the surface of nitric acid-oxidized carbon fibers and lecithin-treated HA contain new functional groups. Uniform dispersion of short fibers and HA nanoparticles in PMMA matrix is successfully achieved and the mechanical properties of the composites are obviously improved. The flexural strength, flexural modulus, and Young's modulus of the composites reach the maximum value 128.12 MPa, 1.150 GPa, and 4.572 GPa when carbon fiber and HA mass fraction arrive to 4% and 8%, respectively. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1782–1787, 2010

Key words: composites; fibers; PMMA; mechanical properties; microstructures

INTRODUCTION

Since Polymethyl methacrylate (PMMA) was introduced as the bone cements in the early 1960s by Charnley and Smith, the potential applications of PMMA or its derivatives in medical field have been well investigated.[1,2] Many researches were carried out to improve the mechanical, biological, and thermal properties of PMMA bone cements. Some studies included the addition of small quantity of reinforcing materials such as carbon fiber,[3] bone particles,[4–6] titanium,[7] tricalci-umphosphate (TCP)[8–10] or hydroxyapatite (HA)[11–13] into the PMMA bone cements. Among these additives, HA was proved to be a biocompatible and osteoconductive material. However, the mechanical properties of HA-reinforced PMMA composites could not meet the application requirements. Therefore, fiber reinforced polymer composites were developed.[14] To achieve optimum mechanical strength and bioactivity whilst retaining the workability of PMMA resin, it is valuable to reinforce PMMA with short fiber and HA powder together. However, up to now, little work on the preparation of short fiber reinforced HA-PMMA composites has been reported.

In the present work, short carbon fiber($C_{(f)}$) reinforced HA-PMMA composites were successfully prepared by an *in situ* polymerization with a later solution co-mixing process. The morphologies and mechanical properties of the composites were primarily investigated.

EXPERIMENTAL

Materials

Methyl methacrylate monomer (MMA) was obtained from Jinyu Chemical Co. Inc. (Tianjin, China). Benzoyl peroxide (BPO) was purchased from K.L. Chemical Reagent Co. Inc. (Chengdu, China). Lecithin was obtained from Tianjin Chemical Co. Inc. (Tianjin, China). Poly acrylonitrile (PAN) precursor carbon fibers with an average diameter of 7 μm and an average length of 3mm were supplied by Jilin Carbon Co. Inc. (Jilin, China). The fiber properties are listed in Table I. The nano-HA powders were prepared by a sonochemical process reported in the previous publication.[15]

TABLE I
Properties of Carbon Fibers

Average diameter	7 μm
Tensile strength	2–4 GPa
Young's modulus	30–50 GPa
Electrical resistivity	$3–7 \times 10^{-3} \Omega \cdot cm$
Density	1.6–1.8 g cm^{-3}
Carbon content	98 wt %

Surface modification of carbon fibers

First, carbon fibers were oxidized in concentrated HNO$_3$ solution at 333 K for 6 h. Then fibers were separated from solution and washed with distilled water. The filtrates were dried in a drying cabinet with air-blasting at 373 K for 2 h. Next, the dried fibers were soaped in pure dimethyl sulfoxide (DMSO) solution for 12 h. Finally, the fibers were filtered and dried at 363 K for 8 h.

Preparation of C$_{(f)}$/HA-PMMA composites

A typical preparation process of C$_{(f)}$/HA-PMMA composites was shown in Figure 1. First, the 0–0.6 g as-modified carbon fibers were dispersed in distilled water (30 mL) with the aid of ultrasonic irradiation for 2 h. Second, the solution with 10 mL MMA and 1.6 g BPO was added into the above solution. Then, the mixed solution was heated by a water bath at 353 K and continuously agitated during the reaction process. After 50 min reaction, the carbon fiber reinforced PMMA polymer was separated from the solution and removed into a beaker. Meanwhile, 0.7–1.6 g nano-HA and 0.075 g lecithin, which was used as coupling agent, were dispersed in 30 mL chloroform to make a HA suspension liquid. Next, the as-prepared C$_{(f)}$/PMMA composites were dissolved
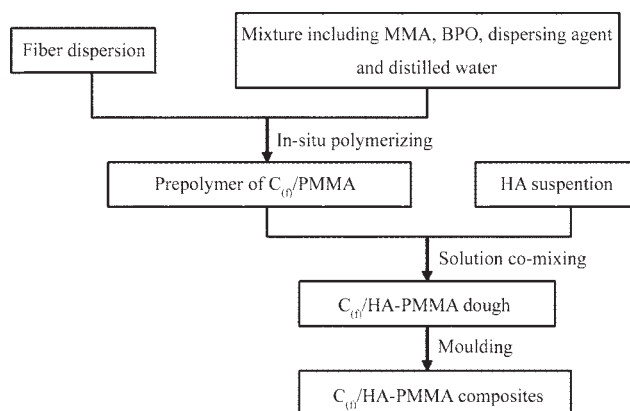
into the above HA suspension by continually stirring and simultaneously heating at 353 K until the mixture solution was changed into a composite precursor dough. After the dough was shaped in a special mould at the conditions of $P = 12$ MPa, $t = 10$ h, and $T = 298$ K, the mould was dried at 333K for 2 h to obtain the final C$_{(f)}$/HA-PMMA product.

To make clear the influence of carbon fibers and HA particles on the mechanical properties of the C$_{(f)}$/HA-PMMA composites, the C$_{(f)}$/-PMMA and HA-PMMA composites were also prepared by the above process without adding HA particles and carbon fibers respectively.

Characterization

The mechanical properties of the as-prepared C$_{(f)}$/HA-PMMA composites were measured with a universal testing machine (PT-1036 PC, Taiwan, China). Specimen dimensions and test method were performed according to the GB/T 1449–2005 of China. The mechanical properties of specimens were determined using five samples for each composition. Three-point flexural strength was measured with a crosshead speed of 5 mm per minute and a supporting span of 34 mm at room temperature. The data were acquired by a computer.

The morphologies of the flexural fracture surface of C$_{(f)}$/HA-PMMA composites were characterized by SEM (JSM-6460, Japan) with EDS and FESEM (EOS6700F, Japan). The phase composition of nano-HA was analyzed by XRD (D/max2200PC, Japan) using Cu-Kα radiation. The surface molecular functional groups of the modified HA, carbon fiber, and the composites were investigated by FTIR analysis (VECTOR-22, Germany).
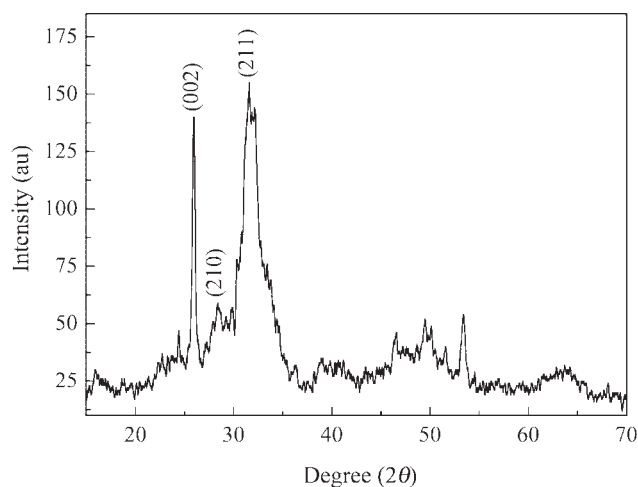

Figure 1 Preparation process of C$_{(f)}$/HA-PMMA composites.
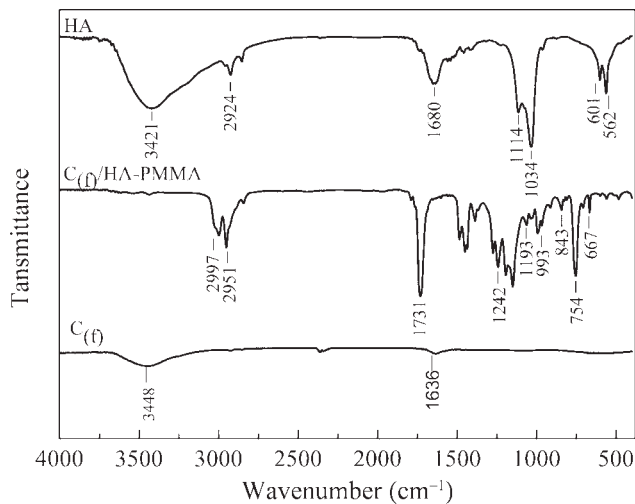

Figure 2 XRD pattern of the as-prepared HA powder.

Figure 3 The FTIR spectra of HA, $C_{(f)}$ and $C_{(f)}$/HA-PMMA composites modified with lecithin coupling agent.

Figure 4 SEM image of fracture surface of the $C_{(f)}$/HA-PMMA composites (District A means the EDS analyses area).

RESULTS AND DISCUSSION

Microstructure analyses of the composites

Figure 2 displays the XRD pattern of the as-prepared HA powder. It reveals that the sonochemical process is a suitable method to produce monophase HA powders. By calculation according to the Sherrer formula, the crystallites size along (211) direction is around 9 nm.

Figure 3 shows the FTIR spectra of lecithin coupled HA, $C_{(f)}$, and $C_{(f)}$/HA-PMMA composites. In the FTIR spectrum of lecithin-coupled HA powder, the broad peak at 3421 cm^{-1} can be attributed to the stretch vibration of O—H group. An intense PO_4^{3-} peak appears at 1034 cm^{-1}. Other phosphates group bands are found at 1034, 601, and 562 cm^{-1}. In addition, the C=O and P=O absorption bands at 1680 and 1114 cm^{-1} are visible in the lecithin-HA spectrum. In the FTIR spectrum of treaded $C_{(f)}$, the broad band at 3448 cm^{-1} is assigned to the —H bond. Peak at 1636 cm^{-1} comes from —C=N stretch vibration. It infers that the surface of treated fibers contain a lot of active functional groups. In the FTIR spectrum of the $C_{(f)}$/HA-PMMA composite, the bands at 2997 cm^{-1} and 2951 cm^{-1} are assigned to C—H stretch vibration. A very strong band appearing at 1731 cm^{-1} and 1242 cm^{-1} belongs to the carbonyl group and C—O—C group, respectively. This indicates that PMMA exists in the as-prepared composites. Two strong phosphate peaks are found at 993 and 754 cm^{-1}. The additional phosphate group bands appear at 843 cm^{-1} and 667 cm^{-1}. There is no peak appears at 1550–1650 cm^{-1}, indicating the absence of no residual —C=C functional group, which also infers that no MMA monomer is contained in the composites. The aforementioned anal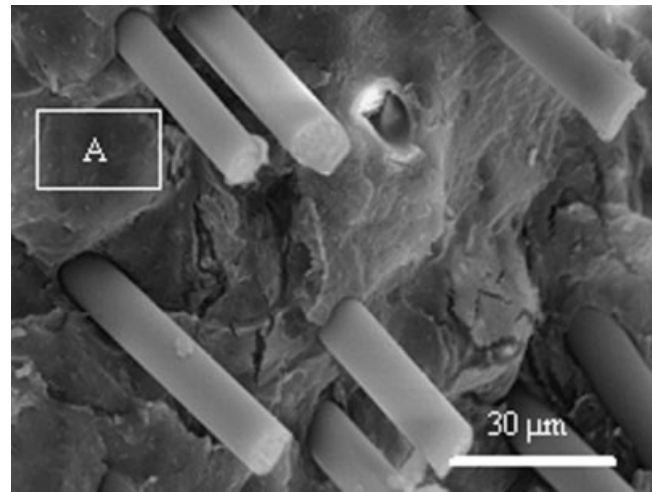yses illustrate that the as-prepared composites are composed by PMMA, HA, and carbon fiber. This deduction is also demonstrated by the SEM (Fig. 4) and EDS analyses (Fig. 5).

Figure 4 displays SEM images of fracture surface of the $C_{(f)}$/HA-PMMA composites. A uniform distribution of the fibers throughout the matrix can be clearly found from the fracture surface. There are some fibers are found to be pulled out during the loading process. Moreover, the homo-dispersion of HA particles can also be verified by the EDS analysis (Fig. 5). Figure 5 shows the EDS analyses results of the $C_{(f)}$/HA-PMMA composite. It indicates that calcium and phosphorus elements exist in the composite matrix. Combine with XRD and FTIR analyses (Figs. 2 and 3), the existence of HA powders in the composite can be concluded.
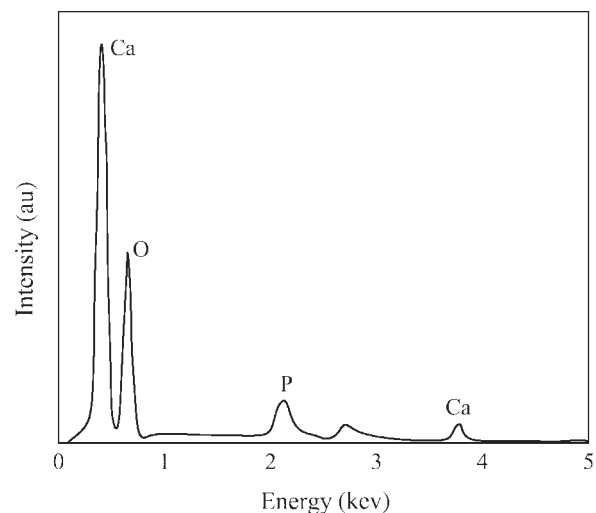

Figure 5 EDS fracture surface analyses results of the $C_{(f)}$/HA-PMMA composites.
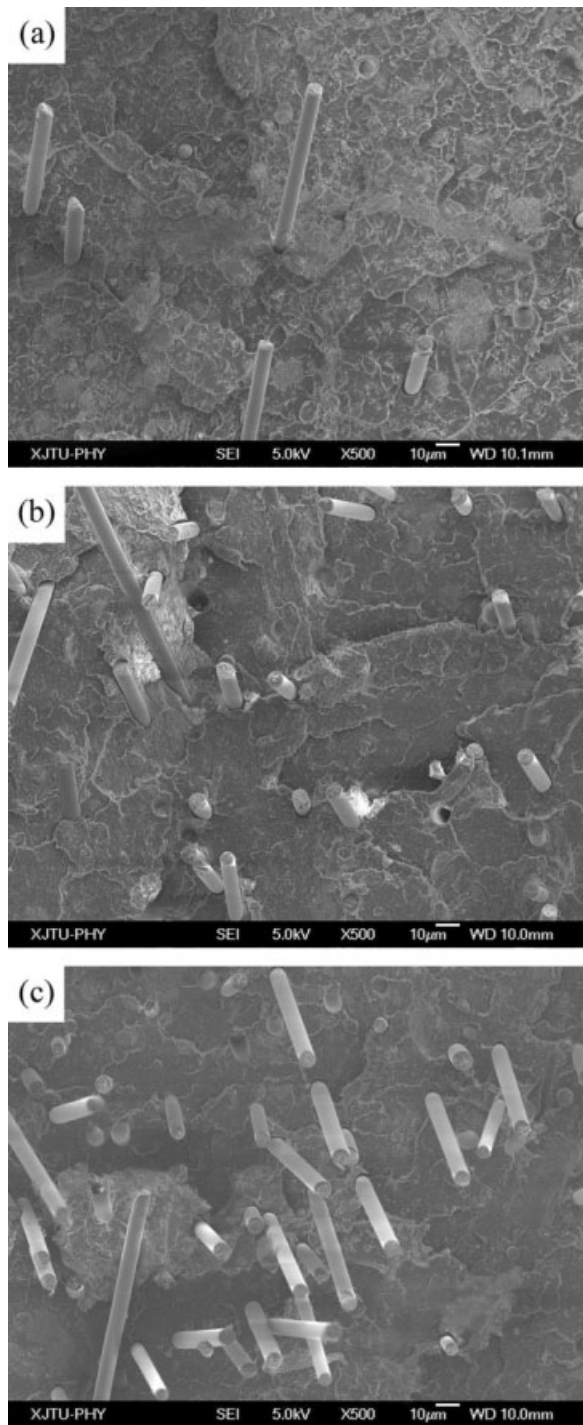
Figure 6 SEM fracture fracture images of the $C_{(f)}$/HA-PMMA composites (a) $C_{(f)}$(wt %) = 1%; (b) $C_{(f)}$(wt %) = 4%; (c) $C_{(f)}$(wt %) = 6% (HA mass fraction is 8%).

Figure 6 shows the SEM fractured surface images of $C_{(f)}$/HA-PMMA composites. The homo-dispersion of carbon fibers in the PMMA matrix is achieved when carbon fiber content is less than 4 wt %, which infers that the adopted preparation process is suitable [Fig. 6(a,b)]. When carbon fiber mass fraction reaches 6%, the nonuniform distribution of fibers in

the matrix is found [Fig. 6(c)], which will result in the decrease in mechanical performance.

Figure 7 shows FESEM fracture surface images of the $C_{(f)}$/HA-PMMA composites with different HA content. When HA mass fraction is 8%, homogeneous distribution of HA nano-particles in the PMMA matrix is achieved. In addition, some holes generated by the pulling out of slice-HA from matrix are observed [Fig. 7(a)]. With the increase of HA content to 16 wt %, the nonhomogeneous distribution and aggregation of HA particles in the matrix is observed [Fig. 7(b)], which may result in the decrease in mechanical performance of the composites.

Mechanical properties of the composites

Tables II and III show the influence of carbon fiber mass fraction on the flexural strength, flexural, and Young's modulus of the $C_{(f)}$/PMMA and $C_{(f)}$/HA-PMMA composites respectively. Clearly, the flexural strength, flexural modulus, and Young's modulus of
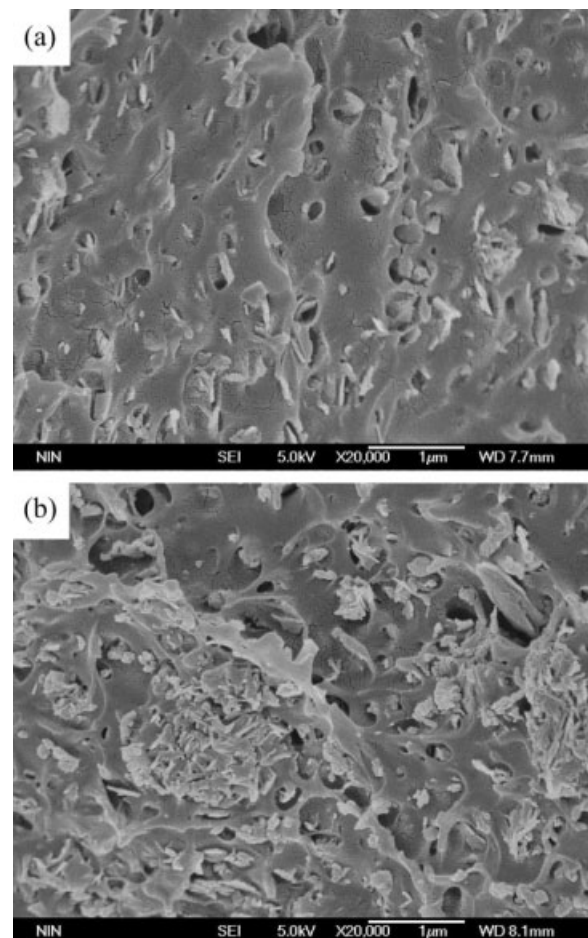

Figure 7 FESEM fracture surface images of the $C_{(f)}$/HA-PMMA composites (a) HA(wt %) = 8%, (b) HA(wt %) = 16% (carbon fiber mass fraction is 4%).

TABLE II
Influence of Carbon Fiber Mass Fraction on Flexural Strength, Flexural Modulus,
and Young's Modulus of the $C_{(f)}$/PMMA Composites

Carbon fiber mass fraction (%)	0	1	2	4	6
Flexrual strength (MPa)	129.27	117.05	127.65	134.59	105.26
Flexrual modulus (GPa)	1.151	0.859	1.018	1.198	1.020
Young's modulus (GPa)	1.135	1.862	3.935	5.071	3.965

TABLE III
Influence of Carbon Fiber Mass Fraction on Flexural Strength, Flexural Modulus,
and Young's Modulus of the $C_{(f)}$/HA-PMMA Composites (HA Mass Fraction Is 8%)

Carbon fiber mass fraction (%)	0	1	2	4	6
Flexrual strength (MPa)	115.15	112.23	124.69	128.12	102.31
Flexrual modulus (GPa)	1.102	0.841	0.959	1.150	1.015
Young's modulus (GPa)	1.124	1.453	3.531	4.572	3.951

the $C_{(f)}$/PMMA and $C_{(f)}$/HA-PMMA composites can be effectively enhanced by the introduction of carbon fibers. When carbon fiber mass fraction arrives to 4%, the flexural strength, flexural modulus, and Young's modulus of the $C_{(f)}$/PMMA and $C_{(f)}$/HA-PMMA composites will reach their maximum value together. When more fiber mass fraction is introduced (6%), the flexural strength and modulus of the two composites will decrease. It is because that the mechanical properties of the composites not only depend on the characterization of carbon fibers and matrix, but also in relation to the combination intensity between them. Too much fibers may result in the nonuniform distribution and aggregation of them in the PMMA and HA-PMMA matrix [Fig. 6(c)], which will result in the decrease in the mechanical properties of the two composites. This is also in agreement with the results of Li.[16] In addition, it can be concluded from Tables II and III that the mechanical properties of $C_{(f)}$/HA-PMMA is

slightly lower than that of $C_{(f)}$/PMMA composites, which may result from the introduction of HA particles though further research is need.

Figures 8 and 9 show the influence of HA mass fraction on the flexural strength, flexural and Young's modulus of the HA-PMMA and $C_{(f)}$/HA-PMMA composites, respectively. It is displayed that the flexural strength and modulus of the two composites both improve with the increase of HA mass fraction from 7 to 8%. When HA mass fraction arises to 8%, the flexural strength, flexural modulus, and Young's modulus of the HA-PMMA composites reaches the maximum value 115.15 Mpa, 1.102 GPa and 1.124 GPa, respectively; meanwhile, the mechanical performance value of the $C_{(f)}$/HA-PMMA composites arrives to 128.12 MPa, 1.150 GPa and 4.572 GPa, respectively. Continue to increase the HA mass fraction from 8% to 9%, the decrease in the flexural strength and modulus of the two composites is
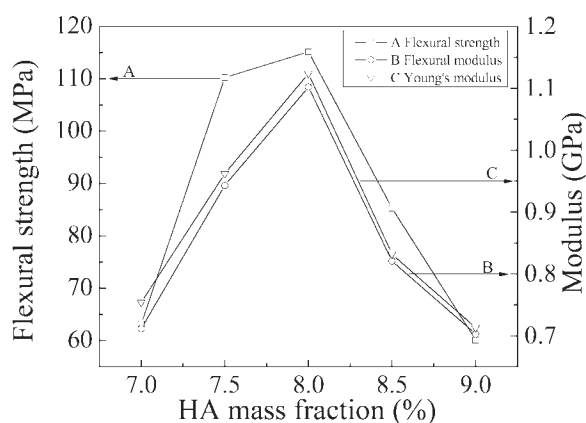

Figure 8 Influence of HA mass fraction on flexural strength, flexural modulus, and Young's modulus of the HA-PMMA composites.
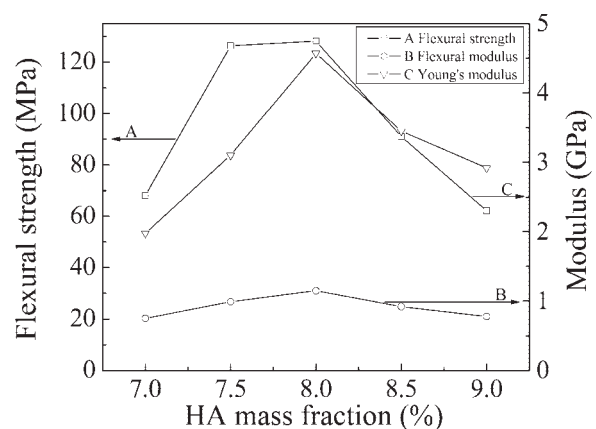

Figure 9 Influence of HA mass fraction on flexural strength, flexural modulus, and Young's modulus of the $C_{(f)}$/HA-PMMA composites (carbon fiber mass fraction is 4%).

found. This is because HA particles as load carriers will lead to good mechanical properties if they are introduced in small amounts and distributed homogeneously in the matrix [Fig. 7(a)]. Excessive introduction of HA particles will lead to nonhomogeneous distribution and aggregation in matrix [Fig. 7(b)], which will result in the decrease in flexrual strength and modulus of the composites. In addition, from Figures 7 and 8, it can be concluded that the mechanical performance of HA-PMMA composites is lower than that of the $C_{(f)}$/HA-PMMA composites, which may result from the introduction of carbon fibers into the matrix.

CONCLUSIONS

The $C_{(f)}$/HA-PMMA composites with uniform distributed short carbon fibers and HA nanoparticles have been successfully prepared by an *in situ* polymerization with a later solution comixing process. New functional groups appear on the surface of HA modified with lecithin coupling agents and preoxidized carbon fibers, which is helpful for the combination between carbon fiber, HA particles, and the PMMA matrix. The flexural strength and modulus of the prepared $C_{(f)}$/HA-PMMA composites are obviously improved with the introduction of carbon fibers and HA particles. With the increase of carbon fiber and HA mass fraction, the flexural strength and modulus of $C_{(f)}$/HA-PMMA composites first increase and then decrease. When carbon fiber mass

fraction and HA mass fraction arrives to 4 and 8%, the flexural strength, flexural modulus, and Young's modulus of the prepared composites reaches the maximum value 128.12 MPa, 1.150 GPa, and 4.572 GPa, respectively.

References

1. Seok, B. K.; Young, J. K.; Taek, L. Y. Biomaterials 2004, 25, 5715.
2. Hass, S. S.; Brauer, G. M.; Dickson, G. J Bone Joint Surgery 1975, 57, 380.
3. Pal, S.; Saha, S. Biomaterials 1982, 3, 93.
4. Heini, P. F.; Walchli, B.; Berlemann, U. Eur Spine J 2000, 9, 445.
5. Barralet, J. E.; Gaunt, T.; Wright, A. J.; Gibson, I. R.; Knowles, J. C. J Biomed Mater Res 2002, 63, 1.
6. Dai, K. R.; Liu, Y. K.; Park, J. B.; Clark, C. R.; Nishiyama, K.; Zheng, Z. K. J Biomed Mater Res 1991, 25, 141.
7. Yamaguchi, I.; Tokuchi, K.; Fukuzaki, H. Key Eng Mater 2001, 673, 192.
8. Wang, M.; Bonfield, W. Biomaterials 2001, 22, 1311.
9. Hochin, H. K. X.; Carl, G. S., Jr Biomaterials 2005, 26, 1337.
10. Bohecr, M. Biomaterials 2004, 4, 741.
11. Dalby, M. J.; Silvio, L. D.; Harper, E. J.; Bonfield, W. Biomaterials 2002, 23, 569.
12. Vallo, C. I.; Montemartini, P. E.; Fanovich, M. A. J Biomed Mater Res 1999, 48, 150.
13. Wan, T.; Yan, Y. H.; Chen, X. M.; Li, J. H.; Li, S. P. Chin J Biomed Eng 2002, 22, 935.
14. Fu, S. Y.; Mai, Y. W.; Bernd, L. Composites 2000, 31, 1117.
15. Cao, L. Y.; Zhang, C. B.; Huang, J. F. Ceramics Int 2005, 31, 1041.
16. Li, Z. M.; Yang, M. B.; Xie, B. H.; Feng, J. M.; Huang, R. Polym Eng Sci 2003, 43, 615.