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Preparation and mechanical properties of carbon fiber reinforced hydroxyapatite/polylactide biocomposites

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Abstract A novel biocomposite of carbon fiber (CF) reinforced hydroxyapatite (HA)/polylactide (PLA) was prepared by hot pressing a prepreg which consisting of PLA, HA and CF. The prepreg was manufactured by solvent impregnation process. Polymer resin PLA dissolved with chloroform was mixed with HA. After reinforcement CF bundle was impregnated in the mixture, the solvent was dried completely and subsequently hot-pressed uniaxially under a pressure of 40 MPa at 170°C for 20 min. A study was carried out to investigate change in mechanical properties of CF/HA/PLA composites before and after degradation in vitro. The composites have excellent mechanical properties. A peak showed in flexural strength, flexural modulus and shear strength aspects, reaching up 430 MPa, 22 GPa, 212 MPa, respectively, as the HA content increased. Degraded in vitro for 3 months, the flexural strength and flexural modulus of the CF/HA/PLA fell 13.2% and 5.4%, respectively, while the shear strength of the CF/HA/PLA composites remains at the 190 MPa level. The SEM photos showed that there were gaps between the PLA matrix and CF after degradation. Water uptake increased to 5%, but the mass loss rate was only 1.6%. The pH values of the PBS dropped less than 0.1. That's because the alkaline of HA neutralize the acid degrades from PLA, which can prevent the body from the acidity harm.

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1 Introduction

The traditional ways for recovering bone defect are autotransplantation or allotransplantation, due to the scarcity of the possible tissues, the man-made biological material has been receiving a great deal of interest. At first, metals such as stainless steel and titanium alloy are taken for the internal fixation of bone fracture. Comparing with the natural bone tissue, these materials characterize high modulus of elasticity. However, numerous studies have shown that these rigid metal plates interfere with normal bone physiology by stress shielding of the bone beneath the plates [1–5]. Also metals can't degrade in vivo. People would suffer the extra pain during the surgery to fetch the fixation material.

Hydroxyapatite (HA) is the main inorganic component of bone with great bioactivity and bone bonding ability [6–8]. Polylactide (PLA) is widely used in the bone fixation material and surgical suture because of its good degradation [9–11]. However, the low mechanical strength of the pure PLA can't meet the requirement of the repairing of weight bearing bones which limits the application.

Nowadays, inorganic/polymer biomaterials have been the subjects of intense study in surgical reconstruction and bone tissue engineering [12–15]. HA/PLA composite becomes an important representative of these materials since they combine the osteoconductivity and bone bonding ability of HA with the absorbability and the easy processing property of the polymer matrix PLA [16–19]. Nevertheless, the mechanical strength still fails to meet the demands of the fixture of weight bearing bones. Carbon fiber (CF) was widely chosen as a reinforced material in the bone implant for its great biocompatibility and high strength. Though the long-term effect of carbon fiber in the living tissues is still an opening question, many researches

indicated that the bone grew on the exposed carbon fibers and cause no inflammation [20–22]. Furthermore, Czajkowska and Bhiewicz reported that, by oxidizing treatment of carbon fibers with nitric acid as mentioned in our paper, the powders of carbon fiber can be phagocytized [23]. CF reinforced HA/PLA composite not only improves the mechanical properties, but also keeps the advantages of HA/PLA composite material. The flexural and shear strength along the fiber direction is believed to be still poor. However, most of the time fibers are perpendicular to the direction of the applied load when the implanted material located in the tensile area of the construction. It is hopefully to be the internal fixation material with its good bioactivity, absorbability, degradation and high mechanical strength.

2 Materials and methods

2.1 Surface treatment of CF

CF (T300, Toray Industries, Inc. Japan) and HNO_3 were introduced into a flask. The mixture was heated up to 70°C, refluxing and oxidation for 5 h. After the treatment, CF was washed with vast amount of deionized water, the resulting CF was dried for 24 h before use. The surface areas of CF before and after the oxidation were determined by a gas sorption analyzer (AUTOSORB-1-C, QUANTACHROME Apparatus company, USA).

2.2 Preparation of CF/PLA/HA composites

Weighed HA (Sinopharm Chemical Reagent Co. Ltd, China), PLA ($M_n = 172{,}000$, $M_w = 214{,}000$, Zhejiang Hisun Biomaterials Co. Ltd, China) in the mass ratio of HA to PLA 2.5/97.5,5/95,10/90,15/85,20/80,25/75, 30/70. First, solved PLA with chloroform, after the ultrasonic dispersion of HA in a little chloroform for 15 min, put the dispersed HA into the PLA solution, and then stirred for 4 h. Second, weighed 20% CF in volume fraction, and then dip the CF into the mixture solution made in the first step to form the pre-impregnating belt. Solvent was volatilized later. In order to decrease the alveoli in the specimens, we took the following steps: cold pressing in room temperature for 10 min, then hot pressing at 170°C, 40 MPa for 20 min, transfer the specimens to the cold press machine for cooling to the room temperature. The sample we obtained indicated that the carbon fiber paralleled along the length and mechanical properties tests were carried out perpendicularly from the fiber direction. The flexural strength and modulus of the intact CF/HA/PLA composites and after in vitro exposure were measured by the three-point bending method, using a universal material testing machine (SANS-CMT 4204,SANS,China) at room temperature. The distance between supports was 30 mm. The testing speed was 1 mm/min. Samples for three-point bend tests had dimensions of approximately 2 mm × 3 mm × 40 mm.

The shear strength of the intact CF/HA/PLA composites and after in vitro exposure, was measured by means of a tool, which was constructed by modifying the standard BS 2782, Method 340B [24]. The tool consisted of two parts, which were joined together by the implant (Fig. 1). During the test, the parts were pulled apart using a universal material testing machine operating at a crosshead speed of 10 mm/min. Thus the implant, resting in a drill hole, was cut into three pieces perpendicular to the long axis of the rod. The size of the drill hole was chosen such that it was easy to push the test sample through the holes in the tool (approximate diameter of the drill hole 0.1 mm larger than the test sample). The shear strength was calculated using

$$\tau_s = \frac{2F_{\max}}{\pi d^2} \quad (1)$$

where τ_s is the shear strength (MPa), $F_{\max}$ the maximum force recorded (N) and the d the diameter of the rod (mm). Samples for shear tests were cylindrical with an approximate diameter of 3 mm and height of 30 mm.

2.3 Degradation in vitro of CF/PLA/HA

Several specimens of CF/HA/PLA composites (mass ratio of HA to PLA 15/85) were chosen. Phosphate buffer

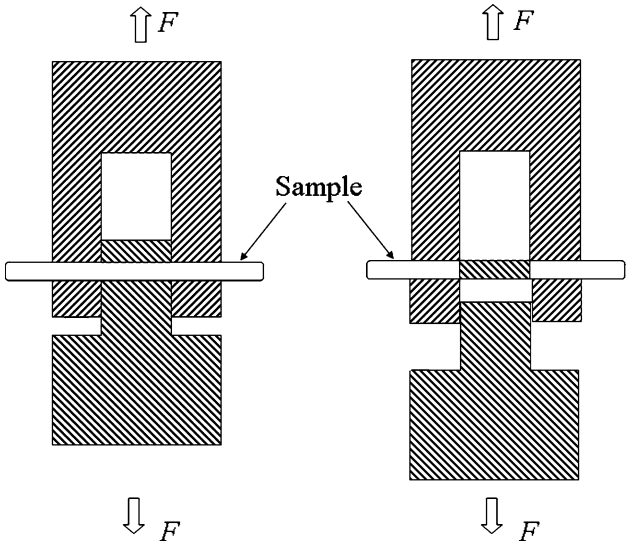

Fig. 1 A schematic cross-sectional drawing of the shear strength test. During the test, the two parts of the hardened stainless steel test tool were pulled apart such that the test sample resting in a drill hole, and initially joining the parts of the tool together (**a**), was cut into three pieces perpendicular to the long axis of the rod (**b**)

solution (PBS) with the initial pH value of 7.40 was prepared. Put the specimens into the PBS (10 ml PBS for each specimen). After that, specimens were storied in the 37°C incubator, replaced PBS once a week. Five specimens have been chosen every few weeks, to determine the mechanical properties of CF/HA/PLA by a universal material testing machine in the whole 3 months. Meanwhile, the variation of pH values, water uptake and mass loss of CF/HA/PLA composites were studied by the general ways as below: number 10 specimens and weigh each specimen with electronic balance, soak them in 100 ml PBS, change PBS once a week. Measure the pH value of PBS with pH meter and weigh the wet weight of specimens regularly. After that, vacuum dry the specimens at 50°C until constant weight is attained. Record the constant weight. Then calculate the water uptake and mass loss of the 10 specimens and average them. The formula for calculating the water uptake W_A and mass loss W_L are shown as follows:

$$W_A\% = 100\ (W_s - W_r)/W_r \quad (2)$$

$$W_L\% = 100\ (W_0 - W_r)/W_0 \quad (3)$$

where, W_s is the wet weight, W_r the constant weight, W_o the initial weight.

2.4 Scanning electron microscopy (SEM)

SIRION FE-SEM (FEI, Netherlands) was used to characterize the surface morphology of the CF before and after oxidized by HNO_3 and the microstructures of the intact CF/HA/PLA composites and after in vitro exposure.

3 Results and discussion

3.1 Surface treatment of CF

SEM photos of CF before and after oxidized by HNO_3 show that it increases the surface roughness of CF, as presented in Fig. 2. Its smooth surface has been shift to be grooved one after the oxidation. According to the analysis of specific surface area, the specific surface area of oxidized CF is 1.172 m^2/g nearly 5 times than the previous one untreated (0.289 m^2/g). Thus increase the contact area and mechanical interlocking effect between CF and matrix.

3.2 Flexural properties and degradation in vitro of CF/HA/PLA

Figure 3 shows the dependence of flexural strength (a) and flexural modulus (b) on HA mass fraction of CF/HA/PLA composites. Figure 3a suggests that when HA mass fraction is low, flexural strength increases as HA mass fraction

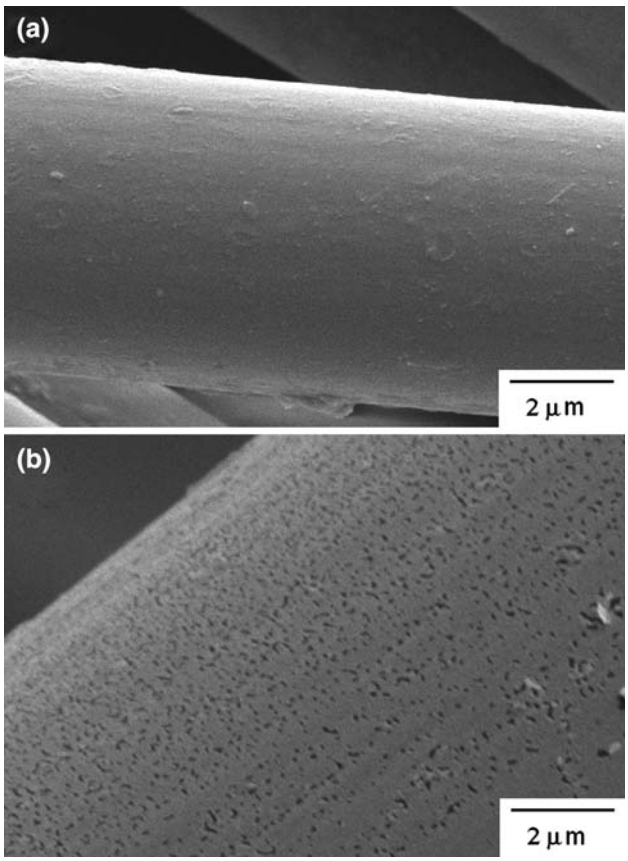

Fig. 2 SEM photos of CF before (**a**) and after (**b**) oxidized by HNO_3

rises, it reaches the maximum when HA mass fraction is 15%, after reaching the peak, flexural strength decreases as HA mass fraction rises. In the Fig. 3b, it illustrates that the flexural modulus performed the similar trend to Fig. 3a. The trend is nearly the same as the literatures reported, but the flexural strength is almost 4–6 times that of the HA/PLA composite [14]. The reason why the strength of this kind of composite is higher than HA/PLA is that CF plays the role of strengthening material. HA could increase the flexural modulus because of its rigidity, on the other hand, with the joining in of HA particles, the interfacial bonding between CF and matrix weakens, and it increases the opportunity to form defects in the composite. When the added HA mass fraction reaches a certain amount, the dispersal of HA particles reduces, which causes the stress concentration, and finally the flexural strength to decrease. The mutual competition of the two mechanisms leads to the trend that the flexural strength and flexural modulus increase in the beginning and decrease after the peak.

The in vitro degradation behavior of the ternary composite is mainly investigated in following aspects: the strength of the material, the attenuation of the modulus, mass loss, water absorption and the change of the pH value

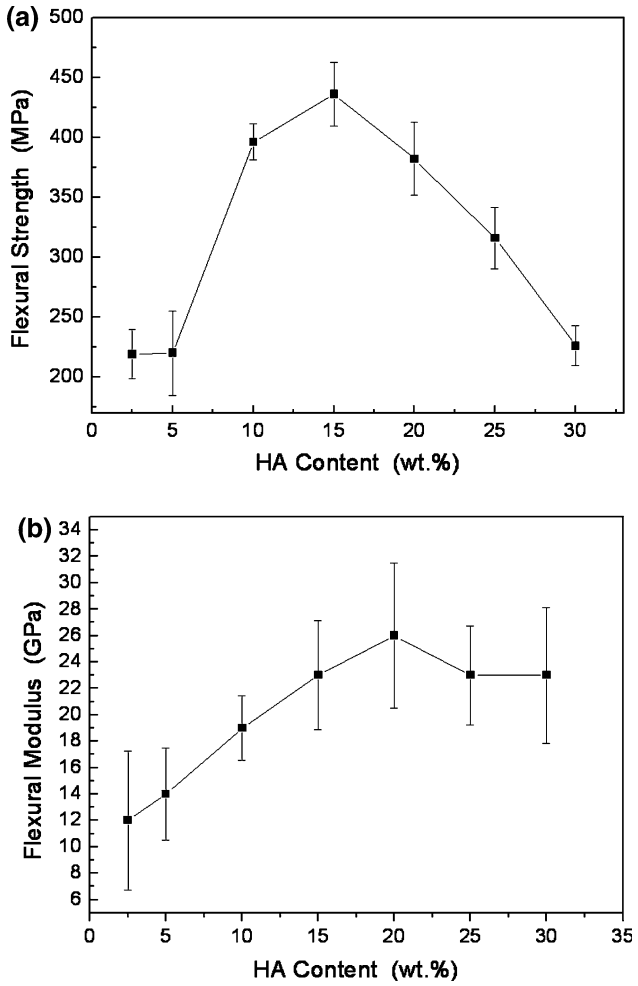

Fig. 3 The dependence of flexural strength (**a**) and flexural modulus (**b**) on HA mass fraction of CF/HA/PLA composites (CF volume fraction 20%)

during soaking in certain solution. Figure 4 shows the changes in flexural strength and flexural modulus of CF/HA/PLA during the degradation in phosphate buffer solution (PBS) at 37°C, it can be observed that as the degradation goes, the flexural strength and flexural modulus decrease continuously. With the 12-week degradation, the flexural strength decrease 10% from 430 MPa to 388 MPa, the flexural modulus decrease 13%, from 22 GPa to 19 GPa. The CF/HA/PLA composite can Maintain the excellent mechanical properties for several months, which is conducive to the regeneration of bone tissue in an early stage. Figure 5 indicates the changes in water uptake and mass loss during the degradation in PBS at 37°C. It represents that with the extension of degradation, water uptake and mass loss both increase, after degradation for 12 weeks, water uptake is 5% while mass loss is only 1.6%. Figure 6 shows SEM photos of the CF/HA/PLA composites degraded in PBS for 1 week (a) and 12 weeks (b). It shows that CF and matrix combine closely in the first week, but then there're gaps between CF and matrix after soaking 12 weeks. Interfacial degradation is the most important factor of the strength falling. SEM photos would prove it. As the interfacial bonding strength declines, the strength of the material declines. Between CF and matrix, there exists interface where the water uptake effects take place. Water diffuses to the inner of the composite easily through the interfaces because of capillarity. These account for the continuously increasing water uptake. Figure 7 states the changes in pH values of PBS during the degradation. The pH value of PBS during the whole degradation drops less than 0.1, shows that the alkaline of HA neutralize the acid degrades from PLA.

3.3 Shear strength and degradation in vitro of CF/HA/PLA

We can see in the Fig. 8 that the dependence of shear strength on HA content of CF/HA/PLA composites is

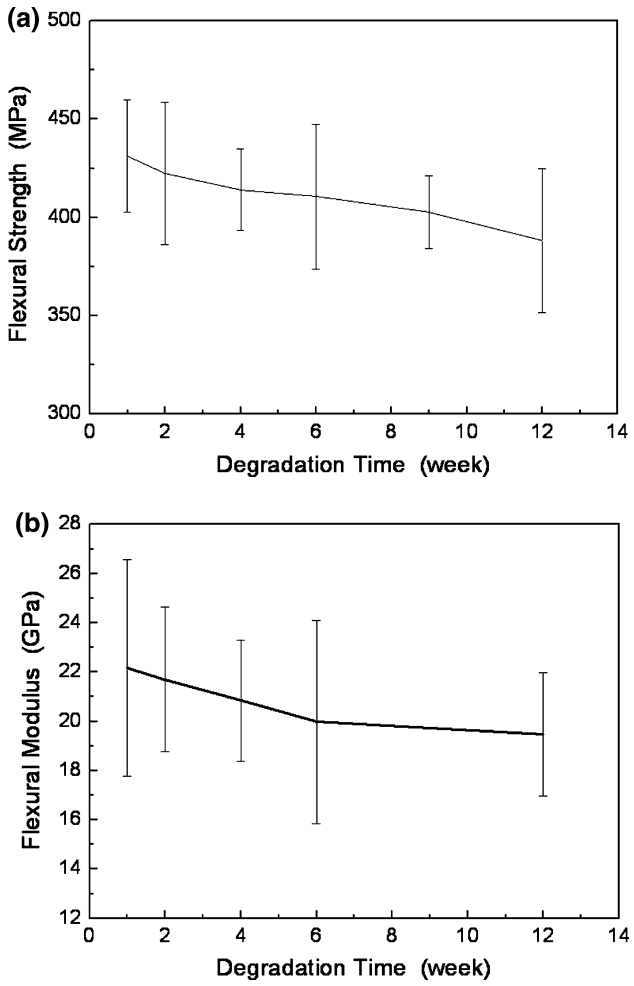

Fig. 4 Changes in flexural strength and flexural modulus of CF/HA/PLA during the degradation in phosphate buffer solution (PBS) at 37°C (CF volume fraction 20%, HA/PLA mass ratio 15/85)

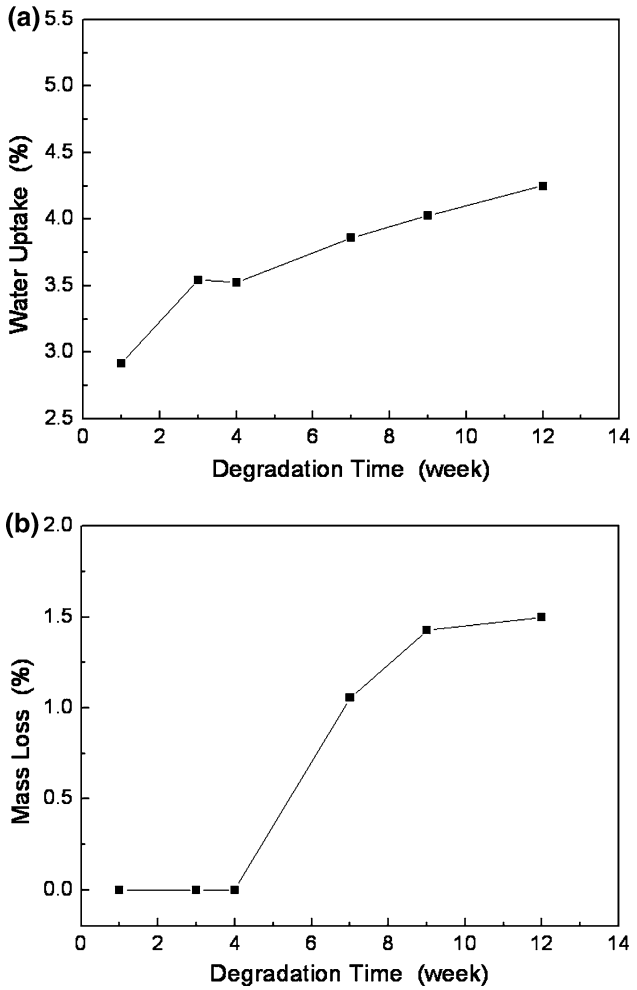

Fig. 5 Changes in water uptake (**a**) and mass loss (**b**) during the degradation in PBS at 37°C (CF volume fraction 20%, HA/PLA mass ratio 15/85)

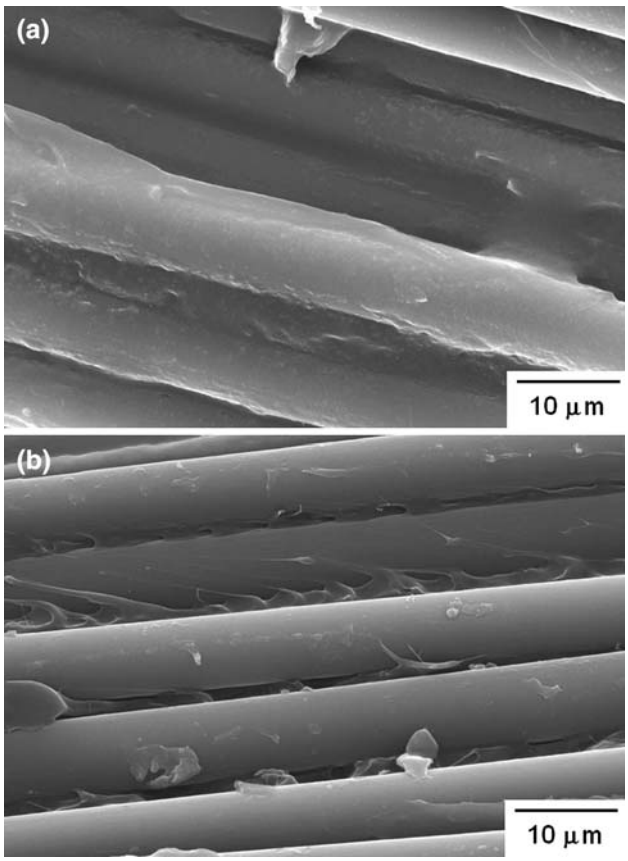

Fig. 6 Longitudinal profile (fiber direction) SEM photos of the CF/HA/PLA composites degraded in PBS for 1 week (**a**) and 12 weeks (**b**) (CF volume fraction 20%, HA/PLA mass ratio 15/85)

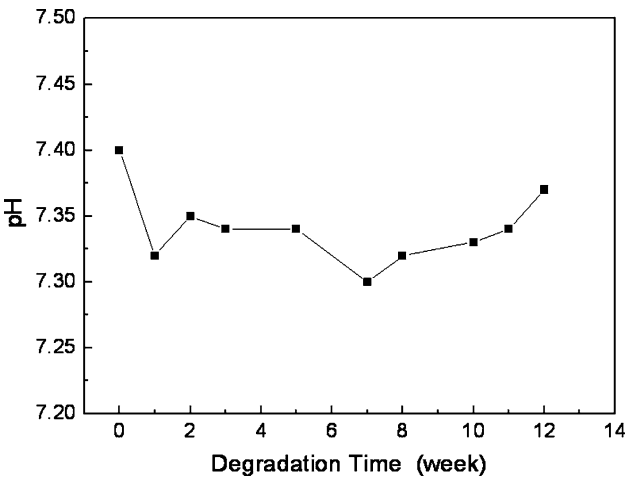

Fig. 7 Changes in pH values of PBS during the degradation (CF volume fraction 20%, HA/PLA mass ratio 15/85)

similar to the dependence of flexural strength on HA content of CF/HA/PLA composites. When HA mass fraction is low, shear strength increases as HA mass fraction rises, it reaches the maximum when HA mass fraction is 20%, after that, shear strength decreases as HA mass fraction rises.

Figure 9 shows the changes in shear strength during the degradation in PBS at 37°C of the CF/HA/PLA composites. It indicates that after degradation for a week, it is saturated in water uptake, the shear strength drops by 10 MPa, while the degradation goes, there is no obvious change in the shear strength, keeping it at the level of 190 MPa. Figure 10 shows SEM photos of fracture faces of the CF/HA/PLA composites degraded in PBS for 1 week (a) and 12 weeks (b). We can see that the PLA matrix has not been degraded after soaking in PBS for 1 week. However the PBS immersing takes place in the interface and leads to the strength decline. After immersing for 12 weeks, as degradation of a few PLA matrix, we can observe that there are gaps between CF and PLA, as shown

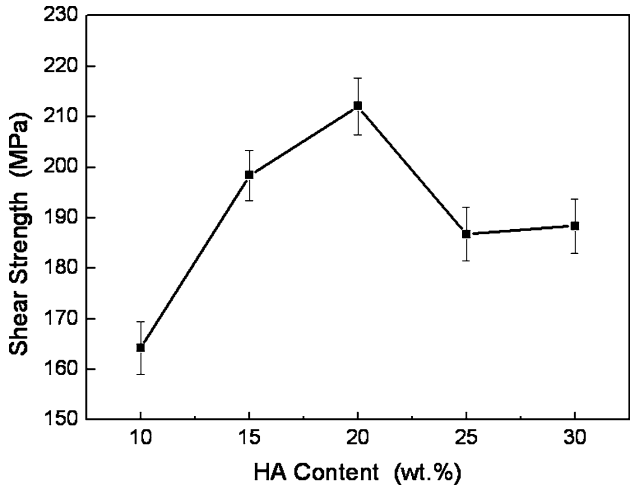

Fig. 8 The dependence of shear strength on HA mass fraction of CF/HA/PLA composites (CF volume fraction 20%)

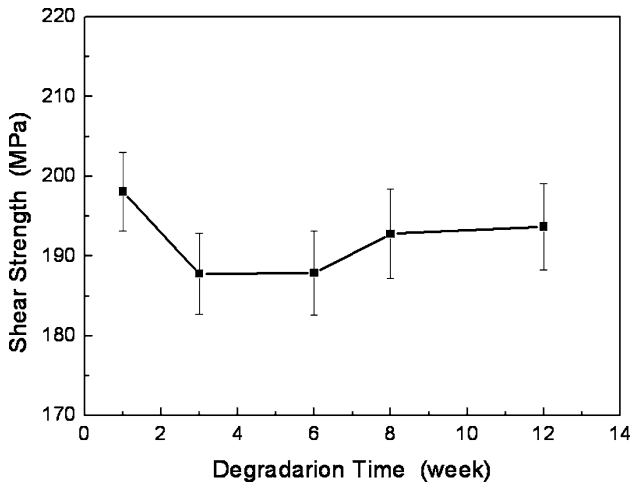

Fig. 9 Changes in shear strength during the degradation in PBS at 37°C of the CF/HA/PLA composites (CF volume fraction 20%, HA/PLA mass ratio 15/85)

in Fig. 10b. Because there are no changes on CF, the shear strength of the composite levels off in the later degradation.

4 Conclusion

CF reinforced HA/PLA degradable biomaterial is prepared by hot pressing a prepreg which consisting of PLA, HA and CF. The composites have excellent mechanical properties. After 3 months degradation in vitro, the composite has great mechanical retentivity and the pH values of the PBS changed little because the alkaline of HA neutralized the acid degrades from PLA, this can do some favors to the recoveries.

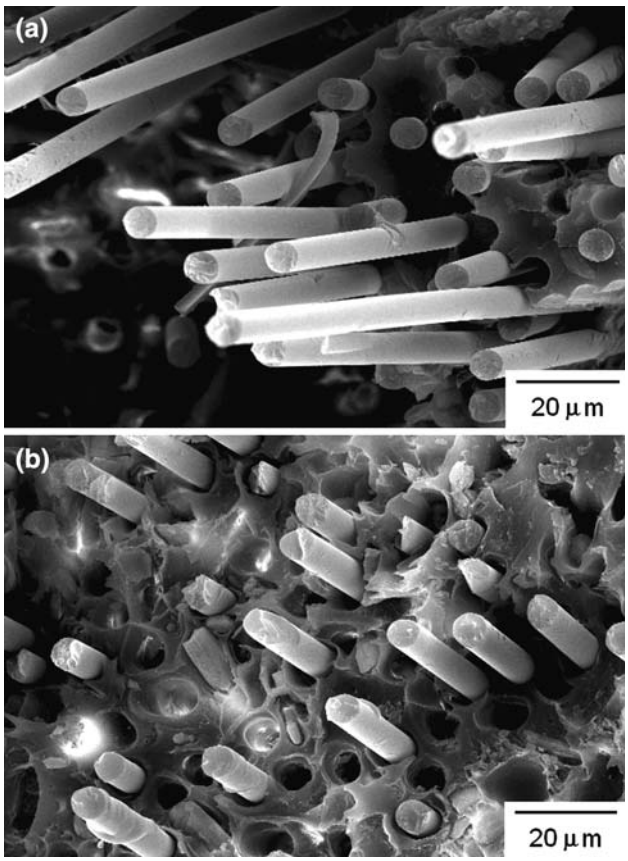

Fig. 10 SEM photos of fracture faces of the CF/PLA/HA composites degraded in PBS for 1 week (**a**) and 12 weeks (**b**)

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References

1. Anderson LD. Treatment of ununited fractures of the long bones; compression plate fixation and the effect of different types of internal fixation on fracture healing. J Bone Joint Surg Am A. 1965;47:191.
2. Terjesen T. Bone healing after metal plate fixation and external fixation of the osteotomized rabbit tibia. Acta Orthop Scand. 1984;55:69.
3. Terjesen T, Apalset K. The influence of different degrees of stiffness of fixation plates on experimental bone healing. J Orthop Res. 1988;6:293. doi:10.1002/jor.1100060218.
4. Uchikura C, Hirano J, Kudo F, Satomi K, Ohno T. Comparative study of nonbridging and bridging external fixators for unstable distal radius fractures. J Orthop Sci. 2004;9:560. doi:10.1007/s00776-004-0828-x.
5. Huang TL, Huang CK, Yu JK, Chiu FY, Liu HT, Liu CL, et al. Operative treatment of intra-articular distal radius fractures using the small AO external fixation device. J Chin Med Assoc. 2005;68:474.
6. Luklinska ZB, Bonfield W. Morphology and ultrastructure of the interface between hydroxyapatite-polyhydroxybutyrate composite implant and bone. J Mater Sci: Mater Med. 1997;8:379. doi:10.1023/A:1018589018205.

7. Rho JY, Kuhn-Spearing L, Zioupos P. Mechanical properties and the hierarchical structure of bone. Med Eng Phys. 1998;20:92. doi:10.1016/S1350-4533(98)00007-1.
8. Yasunaga T, Matsusue Y, Furukawa T, Shikinami Y, Okuno M, Nakamura T. Bonding behavior of ultrahigh strength unsintered hydroxyapatite particles/poly(L-lactide) composites to surface of tibial cortex in rabbits. J Biomed Mater Res. 1999;47:412. doi:10.1002/(SICI)1097-4636(19991205)47:3<412::AID-JBM17>3.0.CO;2-B.
9. Kulkarni RK, Moore EG, Hegyeli AF, Leonard F. Biodegradable poly(lactic acid) polymers. J Biomed Mater Res. 1971;5:169. doi:10.1002/jbm.820050305.
10. Vainionpää S, Rokkanen P, Törmälä P. Surgical applications of biodegradable polymers in human tissues. Prog Polym Sci. 1989;14:679. doi:10.1016/0079-6700(89)90013-0.
11. Matsusue Y, Yamamuro T, Ikada Y. Tissue reaction of bioabsorbable ultra high strength poly (L-lactide) rod. A long-term study in rabbits. Clin Orthop Relat Res. 1995;317:246.
12. Devin JE, Attawia MA, Laurencin CT. Three-dimensional degradable porous polymer-ceramic matrices for use in bone repair. J Biomater Sci Polym Ed. 1996;7:661. doi:10.1163/156856296X00435.
13. Marra KG, Szem JW, Kumta PN, DiMilla PA, Weiss LE. In vitro analysis of biodegradable polymer blend/hydroxyapatite composites for bone tissue engineering. J Biomed Mater Res. 1999;47:324. doi:10.1002/(SICI)1097-4636(19991205)47:3<324::AID-JBM6>3.0.CO;2-Y.
14. Bleach NC, Tanner KE. Effect of filler type on the mechanical properties of self-reinforced polylactide-calcium phosphate composites. J Mater Sci: Mater Med. 2001;12:911. doi:10.1023/A:1012884310027.
15. Maquet V, Boccaccini AR, Pravata L, Notingher I, Jérôme R. Porous poly(alpha-hydroxyacid)/Bioglass composite scaffolds for bone tissue engineering. I: Preparation and in vitro characterisation. Biomaterials. 2004;25:4185. doi:10.1016/j.biomaterials.2003.10.082.
16. Zhang R, Ma PX. Poly(alpha-hydroxyl acids)/hydroxyapatite porous composites for bone-tissue engineering. I. Preparation and morphology. J Biomed Mater Res. 1999;44:446. doi:10.1002/(SICI)1097-4636(19990315)44:4<446::AID-JBM11>3.0.CO;2-F.
17. Shikinami Y, Okuno M. Bioresorbable devices made of forged composites of hydroxyapatite (HA) particles and poly l-lactide (PLLA). Part II: practical properties of miniscrews and miniplates. Biomaterials. 2001;22:3197. doi:10.1016/S0142-9612(01)00072-2.
18. Kasuga T, Maeda TH, Kato K. Preparation of poly(lactic acid) composites containing calcium carbonate (vaterite). Biomaterials. 2003;24:3247. doi:10.1016/S0142-9612(03)00190-X.
19. Hong ZK, Zhang PB, He CL. Nano-composite of poly(l-lactide) and surface grafted hydroxyapatite: mechanical properties and biocompatibility. Biomaterials. 2005;26:6296. doi:10.1016/j.biomaterials.2005.04.018.
20. Chlopek J, Morawska-Chochol A, Bajor G, Adwent M, Cieslik-Bielecka A, Cieslik M, et al. The influence of carbon fibres on the resorption time and mechanical properties of the lactide-glycolide co-polymer. J Biomater Sci Polym Ed. 2007;18:1355. doi:10.1163/156856207782246858.
21. Hojo Y, Kotani Y, Ito M, Abumi K, Kadosawa T, Shikinami Y, et al. A biomechanical and histological evaluation of a bioresorbable lumbar interbody fusion cage. Biomaterials. 2005;26:2643. doi:10.1016/j.biomaterials.2004.07.020.
22. Al-Shawi AK, Smith SP, Anderson GH. The use of a carbon fiber plate for periprosthetic supracondylar femoral fractures. J Arthroplasty. 2002;17:320. doi:10.1054/arth.2002.30291.
23. Czajkowska B, Bhiewicz M. Phagocytosis of chemically modified carbon materials. Biomaterials. 1997;18:69. doi:10.1016/S0142-9612(96)00103-2.
24. BS 2782: Part 3: Methods 340A and 340B. London: British Standards Institution; 1978.