MECHANICAL PROPERTIES OF POLYLACTIC ACID COMPOSITES CONTAINING β -Ca(PO₃)₂ FIBERS

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Abstract Polylactic acid (PLA) composite biomaterials were prepared by using biocompatible β -calcium metaphosphate (β -Ca(PO₃)₂) fibers. The composites showed bending strength of ≈ 40 MPa and modulus of elasticity of 5 GPa similar to that of natural bone. The fracture of the composites proceeds step by step even beyond the maximum stress. After PLA and the composites were soaked in simulated body fluid at 37 °C for 3 months, the strength of PLA was reduced seriously to $\approx 1/5$ as large as the initial value due to hydrolysis of PLA. On the other hand, degradation in the strength of the composites (e.g., fiber content of 35 wt.%) was restricted to $\approx 1/2$ as large as the initial value. Although PLA was converted into a typical brittle material by the soaking, the composites in toughness were not degraded. The mechanical properties of PLA can be improved effectively by introducing the β -Ca(PO₃)₂ fibers.

INTRODUCTION

High-strength β -Ca(PO₃)₂ fibers with low modulus of elasticity have been developed ; they can be extracted from the crystallized products of calcium ultraphosphate glasses.¹ The inorganic fibers show good biological compatibility and safety.² New types of bioceramics have been prepared using the fibers.^{3,4}

Biomaterials with high modulus of elasticity induces a problem of stress shielding which leads to bone resorption.⁵ The materials with modulus of elasticity which is similar to that of natural bone (5 ~ 15 GPa) are requisite for some applications. Polylactic acid (PLA) is one of the polymers showing good biocompatibility and bioresorbability. The resorption rate is controllable by degree of polymerization or copolymerizing. The modulus of elasticity of PLA, however, is much lower (2 ~ 3 GPa) than that of natural bone. Some efforts have been carried out for preparation of composites consisting of PLA and calcium phosphate particles such as hydroxyapatite or β -tricalcium phosphate with osteoconductivity.^{6,7} The composites, however, have a disadvantage that they show

catastrophic fracture typically, since a large amount of the particles (70 ~ 80 wt. %) should be introduced into PLA or its copolymer as a matrix phase for meeting the requirements on the modulus.⁷ In the present work, novel artificial bones with ductility and modulus of elasticity close to that of natural bone are obtained by preparation of the composites consisting of PLA with the β -Ca(PO₃)₂ fibers, and also, changes in their mechanical properties after soaking in simulated body fluid are discussed.

EXPERIMENTAL PROCEDURE

β -Ca(PO₃)₂ fibers were prepared by following a method described in our previous papers.^{1,3,4} The obtained fibers were 2 ~ 10 μ m in diameter with aspect ratios of 20 ~ 100. Almost no bond between PLA and the fibers is formed. C=O in ester group in PLA can form weak bonds with calcium ions in the orthophosphates.⁸ We found that surface of the β -Ca(PO₃)₂ fibers can be converted successfully into the orthophosphate phase by chemical treatment⁹; the fibers were soaked in 0.2-M NaOH aqueous solution for 5 h at 70 °C.

FIGURE 1. (a) Scanning electron micrographs of β -Ca(PO₃)₂ fibers treated with 0.2-M NaOH *aq.* and (b) laser Raman spectra of the fibers before and after the chemical treatment.

Although only $\beta\text{-Ca}(\text{PO}_3)_2$ was identified as a crystalline phase in an x-ray diffraction pattern of the fibers after the treatment, new particle-shaped products of several tens nanometer in size were seen densely on their surface as shown in Fig. 1(a). Raman bands due to PO_4 group were observed in Fig. 1(b) with strong those due to PO_3 group in the spectrum of the fibers after the treatment. The modified fibers (denoted by CPF, hereafter) were used for preparation of the PLA composites.

Poly-L-lactic acid (Shimadzu Corp., LACTY #2012; mean molecular weight of $\approx 160,000$) was used as a matrix phase. The 10 g of PLA was soaked in 100 mL of methylene chloride at room temperature. After PLA was dissolved, CPF was put into the PLA-solution and then the mixture was kneaded for 30 min at 25 rpm. The resulting mixture was cast into a stainless steel die of 38-mm diameter and was dried completely for 8 h at room temperature. The product was hot-pressed in the die uniaxially for 15 min at 180 °C under a pressure of 40 MPa.

To discuss mechanical properties of the composites after implantation into living body, the specimens shaped into a rectangular prism ($3 \times 5 \times 35 \text{ mm}^3$) were soaked in simulated body fluid (SBF) at 37 °C. After soaking for 1 ~ 90 days, a three-point bending test was carried out at a loading rate of 0.375 mm/min in SBF.

RESULTS AND DISCUSSION

Figure 2 shows bending strengths and moduli of elasticity of the composites as a function of CPF content. The strengths of the composites were almost independent of the content when it was $\leq 60 \text{ wt.}\%$. The materials showed bending strengths of 30 ~ 50 MPa. It is difficult to prepare the composite containing CPF over 70 wt.%, since a large amount

FIGURE 2. Three-point bending strength and modulus of elasticity of PLA composites as a function of CPF content.

of the fibers is apt to be agglomerated in the matrix phase of PLA. The modulus of elasticity was improved by introducing CPF. The value (≈ 5 GPa) is close to that of natural bone. CPF would form a chemical bond with PLA; the bond may play an important role in improvement of the mechanical properties. It is supposed that CPF and PLA dissolved by methylene chloride are linked together during the mixing, resulting in development of the composite without the serious agglomeration of the fibers.

Figure 3 shows bending strengths of PLA and the composite containing 35 wt.% CPF after soaking in SBF. Their strengths were decreased with increasing the soaking time. After soaking for 90 days, the strength of PLA was seriously decreased to $\approx 1/5$ as large as that of an as-prepared specimen. On the other hand, degradation in the strength of the composite was restricted to $\approx 1/2$ as large as the initial value.

Figures 4(a) and 4(b) show typical patterns of stress-strain curves measured by a three-point bending test for PLA without the fibers and the composite containing 35 wt.% CPF, respectively, before and after soaking in SBF. Fracture of PLA proceeds gradually without large deformation; the behavior may be originated from high crystallinity of PLA¹⁰ in the present work. After the PLA was soaked in SBF for 90 days, the maximum stress was decreased extremely and the specimen showed typical brittle fracture similar to that of conventional ceramics. Hydrolysis of PLA induces serious degradation in the mechanical properties.

FIGURE 3. Three-point bending strengths of PLA and the composite containing 35 wt.% CPF after soaking in SBF at 37 °C. The test was carried out in SBF.

On the other hand, the composite was not broken catastrophically ; its fracture proceeds step by step even beyond the maximum stress. The maximum strain of the composite is an order of magnitude larger ($\approx 2 \times 10^{-2}$) than that of a hydroxyapatite ceramic ($\approx 1 \times 10^{-3}$). That is, the fracture surface energy of the composite in the present work is estimated to be more than 20 times higher than that of the ceramic. The composite has high toughness. The toughness is believed to be originated from mechanisms of fiber-pull-out and crack-deflection.⁹

Note that the fracture pattern is not changed drastically even after the soaking for 90 days in contrast to that of PLA, although the maximum stress is decreased. PLA as a matrix phase in the composite would be also converted into a brittle material by the soaking in SBF. However, since CPF in the composite can share an applied load successfully, the material shows non-catastrophic fracture even after the soaking. Hybridization of CPF into PLA as a matrix phase has great advantages that modulus of elasticity is improved to the value close to that of natural bone and that degradation and toughness of the material in a wet environment is relatively restricted.

The mechanical properties of the PLA composite are expected to meet the biomechanical requirements of some applications such as fracture plates or temporary internal fixation of bones broken or damaged.

FIGURE 4. Typical stress-strain curves in a three-point bending test of (a) PLA and (b) the composite containing 35 wt.% CPF before and after soaking in SBF at 37 °C for 90 days. The test was carried out in SBF.

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