Preparation and mechanical properties of polylactic acid composites containing hydroxyapatite fibers

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Abstract

Ceramic-polymer composite biomaterials were prepared by hot-pressing a mixture consisting of poly-
\textit{l}-lactic acid (PLA) and hydroxyapatite fibers (HAF) with dimensions of 40–150 \(\mu\)m length and 2–10 \(\mu\)m diameter, which were converted from \(\beta\)-Ca\(^{3+}\)(PO\(_4\))\(_2\) fibers. After PLA dissolved with methylene chloride was mixed with the fibers, the mixture was dried completely and subsequently hot-pressed uniaxially under a pressure of 40 MPa at 180 \(^\circ\)C, resulting in the fabrication of the PLA/HAF composite. The modulus of elasticity was improved effectively even by introducing a small amount of HAF; almost no degradation in the bending strength was observed and the modulus of elasticity showed high values of 5–10 GPa when the fibers of 20–60 wt\% were introduced. With increasing HAF content, the maximum strain decreases and the specimen is apt to show a brittle fracture; this result implies that HAF in the composites can share the applied load efficiently due to the formation of a bond between HAF and PLA.

Keywords: Composite; Hydroxyapatite; Fiber; Poly(lactic acid); Modulus of elasticity

1. Introduction

Polylactic acid (PLA)-based materials showing bio-resorbability are used for applications such as bone plates or temporary internal fixation of broken or damaged bones (for example [1]). The resorption rate is controllable by the degree of polymerization or copolymerization with aliphatic polyesters. The modulus of elasticity of PLA, however, is relatively low (2–7 GPa) [1,2] compared with that of natural cortical bone (3–30 GPa) [3–5]. Some effort has been made to prepare composites consisting of PLA or its copolymer and calcium phosphate particles such as hydroxyapatite (HA) or \(\beta\)-tricalcium phosphate (TCP) with osteoconductivity [6–8]. For meeting the requirements imposed on the modulus (~ 5 GPa), however, a large amount of particles of 75–80 wt\%, must be introduced into PLA or its copolymer as a matrix phase [6]. If HA with a large aspect ratio is introduced into PLA, the modulus would be improved effectively.

Many methods for the preparation of needle-like or fibrous HA have been reported [9–11]. For example, HA whiskers with lengths of 10–30 \(\mu\)m and diameters of 0.1–1 \(\mu\)m were synthesized under hydrothermal conditions using citric acid [9]. Recently, we reported a new and simple method for the preparation of polycrystalline, long HA fibers by using a solid-phase reaction [12]. The prepared fibers were 40–150 \(\mu\)m in length and 2–10 \(\mu\)m in diameter. We anticipate that novel artificial bone with a modulus of elasticity close to that of natural bone can be developed by the preparation of composites consisting of PLA and our HA fibers. In the present work, the preparation of the PLA composites and their mechanical fracture behavior are discussed.

2. Materials and methods

2.1. Preparation of hydroxyapatite fibers

Hydroxyapatite fibers (denoted by HAF) used in the present work were prepared using a conversion method.
of crystalline $\beta$-Ca(PO$_3$)$_2$ fibers which were reported in our earlier work [12]. A batch mixture with a molar ratio of CaO/P$_2$O$_5$ = 0.85 was prepared using CaCO$_3$ and H$_3$PO$_4$ (85% liquid) as starting materials. The mixture was melted in a platinum crucible at 1200°C for 1 h, and subsequently cast onto a carbon plate to obtain a block of the ultraphosphate glass. The glass was reheated at 600°C for 30 h for crystallization, resulting in the formation of fibrous $\beta$-Ca(PO$_3$)$_2$ crystals as a major phase with a crystalline Ca$_2$P$_6$O$_{17}$ phase and the matrix glasses. The crystallized block was crushed into pieces smaller than several millimeters in size. Approximately 100 g of the pieces was put into a glass beaker filled with 3 l of distilled water (DW) to dissolve the matrix phase. After the mixture was stirred at 80°C for ~ 70 h, the crystals were classified by sieving to obtain $\beta$-Ca(PO$_3$)$_2$ fibers 40–200 μm in length and 2–15 μm in diameter [13]. After 15 g of quick lime (CaO) powders was added to a suspension which was prepared by dispersing 5 g of $\beta$-Ca(PO$_3$)$_2$ fibers in 0.15 l of DW, the mixture was dried at ~ 100°C to obtain a compact. The compact was heated at 1000°C for 1 h in air and subsequently treated with 0.5N HCl aq. As shown in Fig. 1, the $\beta$-Ca(PO$_3$)$_2$ fibers in the compact were converted successfully into polycrystalline fibers by the heating, and the residual CaO phase was removed by the acid-leaching treatment. The fibers had almost the same dimensions as those of the $\beta$-Ca(PO$_3$)$_2$ fibers; they were 40–150 μm in length and 2–10 μm in diameter. It was verified by X-ray diffraction (XRD) analysis, Fourier-transmission infrared spectroscopic (FT-IR) analysis and inductively coupled plasma atomic emission spectroscopic (ICP–AES) analysis that the fibers consist of a crystalline hydroxyapatite phase with the almost stoichiometric composition.

2.2. Preparation of polylactic acid composites containing HAF

Poly-l-lactic acid produced by Shimadzu Corp. (LACTY #2012) was employed as the matrix phase. The PLA has a molecular weight (Mw) of ~ 160,000. 10 g of PLA was soaked in 100 ml of methylene chloride at room temperature. After soaking for 24 h, PLA was dissolved completely. HAF was added to the PLA solution and the mixture was stirred for 0.5 h. The ratio of PLA/HAF was 90/10–30/70 by weight. The mixture was cast into a stainless-steel die of 38 mm diameter and was dried for 8 h at room temperature. Laser Raman spectra showed that there exists no methylene chloride in the dried product; it was volatilized completely during this processing [14]. The product was heated in the die from room temperature to 180°C and maintained at the temperature for 1 h. Subsequently, it was hot-pressed uniaxially for 0.25 h at 180°C under a pressure of 40 MPa, and cooled in the die to room temperature.

2.3. Analysis and mechanical testing

Crystallinity of the PLA phase in the resulting composite was examined by differential scanning calorimetry (DSC; Rigaku DSC8230D) at a heating rate of 5°C/min using 20–25 mg of the specimen. Three-point bending strengths of the composite were measured at a loading rate of 0.375 mm/min using a span length of 12 mm and a rectangular-prism-shaped specimen (~ 3 mm × ~ 4 mm × ~ 20 mm) cut by a diamond saw in water was used. Tangent moduli of elasticity were estimated using stress–strain curves obtained from the bending tests under the guidance of ASTM [15]. The microstructure of the PLA/HAF composite was examined by scanning electron microscopy (SEM; JEOL, JSM-6301F). The density of the composite was estimated using an Archimedes method.
3. Results and discussion

Fig. 2 shows relationships between bending strength or modulus of elasticity of the PLA/HAF composites and HAF content when the tensile surface is perpendicular to the hot-pressing axis. The composites containing ≤ 60 wt% HAF showed bending strengths of 50–60 MPa on average; the strengths were almost independent of the content. The mechanical properties such as strength and elastic modulus of PLA are influenced by Mw [1]. Since Mw (≈ 160,000) of PLA used in the present work is reasonably high, its bending strength is relatively high; the values of 50–60 MPa are comparable to those in earlier reports [16]. To examine orientation effects of HAF, the bending strengths were measured when the tensile surface of the specimens was not only perpendicular to, but also parallel to, the hot-pressing axis. No significant difference between their strengths was found. HAF does not lead to the large orientation effect on the strength since the orientation is not completely planar. The relative densities of the composites containing ≤ 60 wt% HAF were ≈ 94%, while that of the composites containing 70 wt% HAF was ≈ 90% (where, theoretical true densities were estimated using the values of 1.27 g/ml for PLA [16] and 3.16 g/ml for HA crystal [17]). The strength of the composite containing 70 wt% HAF varies widely. It seems that a large amount of HAF is apt to be agglomerated in the PLA matrix phase.

On the other hand, the modulus of elasticity of the composites was improved effectively with increasing HAF content. It was reported that a large number of calcium phosphate particles of ≥ 75 wt% should be introduced into the polymerized PLA matrix phase in order to prepare the composites with a modulus of elasticity close to that of natural bone [6]. The modulus of the PLA composite can be improved even by introducing 20 wt% HAF. It has been reported by Casper et al. [18] that PLA composites containing 30–70 wt% calcium metaphosphate glass fibers have high moduli of 6.4–12.8 GPa. The moduli of PLA/HAF composites (6–11 GPa) are almost comparable to those of the composites fabricated by Casper et al. Since the composite containing 70 wt% HAF has a high modulus of elasticity of > 10 GPa, the modulus of HAF itself is suggested to be relatively high. If PLA with very high Mw (e.g., 250,000), which has a high modulus of elasticity of 7 GPa [2], could be used as the matrix of the HAF composites, materials with very high moduli would be obtained.

In DSC curves of the bulk PLA without HAF and of the composites prepared by a method in the present work, only an endothermic peak at 171°C due to melting of a crystalline phase, and no exothermic peaks, were observed. The endothermic quantities per PLA-unit gram were estimated from the curves to be almost the same as ≈ 50 J. The bulk PLA and the PLA matrix phase in the composites were found to be crystallized.

Fig. 2. (a) Bending strengths and (b) moduli of elasticity of the PLA composites as a function of HAF content. Error bar indicates standard deviation.

Fig. 3. Typical stress–strain curves of specimens in a three-point bending test. (a) PLA, (b) the composite containing 20 wt% HAF, (c) the composite containing 35 wt% HAF, and (d) the composite containing 60 wt% HAF.
composites are influenced strongly by those of the matrix phase. With increasing HAF content, the maximum strain decreases and the specimen is apt to show a brittle fracture. This result implies that HAF in the composites can share the applied load efficiently due to the formation of a bond between HAF and PLA. For example, the maximum strain of the composite containing 35 wt% HAF is \( \approx 1 \times 10^{-2} \), and it is one order of magnitude larger than that [19] of a dense HA ceramic.

Fig. 4 shows SEM photos of fracture faces of the composites containing 20, 35 and 60 wt% HAF. HAF was found to be successfully integrated into the PLA matrix phase. PLA was reported to be linked chemically with calcium orthophosphates; O in a C–O ester group double bond can form weak ionic bond with Ca in the orthophosphates such as TCP or HA [20]. When a load is applied to the composites, cracks would be propagated efficiently through HAF; the modulus of elasticity of the composites can be improved even by introducing a small amount of HAF. Numerous broken fibers and traces of fiber pull-out are seen in each photo in Fig. 4. Due to these mechanisms, a large energy is consumed in their fracture.

To our knowledge, this is the first work on PLA composites prepared using fibrous hydroxyapatite. The modulus of elasticity of the composite increased with increasing fiber content. Almost no degradation in the bending strength originated from introducing the fibers occurred. It is very important for practical applications that the materials have a large surface fracture energy. Experiments of compatibility in vivo are in progress.

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