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Nano-composite of poly(L-lactide) and surface grafted hydroxyapatite: Mechanical properties and biocompatibility

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Abstract

In order to improve the bonding between hydroxyapatite (HAP) particles and poly(L-lactide) (PLLA), and hence to increase mechanical properties of the PLLA/HAP composite as potential bone substitute material, the HAP nano-particles were surface-grafted with PLLA and further blended with PLLA. The structure and properties of the composites were subsequently investigated by the mechanical property testing, the differential scanning calorimeter measurements (DSC), the scanning electron microscopy (SEM), the polarized optical microscopy (POM), and the cell culture. The PLLA molecules grafted on the HAP surfaces, as inter-tying molecules, played an important role in improving the adhesive strength between the particles and the polymer matrix. At a low content (~4 wt%) of surface grafted-HAP (g-HAP), the PLLA/g-HAP nano-composites exhibited higher bending strength and impact energy than the pristine PLLA, and at a higher g-HAP content (e.g., 20 wt%), the modulus was remarkably increased. It implied that PLLA could be strengthened as well as toughened by g-HAP nano-particles. The results of biocompatibility test showed that the g-HAP existing in the PLLA composite facilitated both adhesion and proliferation of chondrocytes on the PLLA/g-HAP composite film.

Keywords: Polylactide; Hydroxyapatite; Composite; Mechanical properties; Biocompotibility; Cell culture

1. Introduction

In order to avoid the second operation imposed on bone defect patient for taking out traditional metallic implants made of stainless steel, titanium and its alloy, many attempt have been made to obtain a novel material for bone repairing in the last 20 years. Poly(lactic acid) (PLA), poly(glycolic acid), poly(ε-caprolactone), and their copolymers have attracted wide attention for their biodegradability in the human body. However, the mechanical strength, toughness, and elastic modulus of these polymers were lower than those of natural cortical bones. Thus, for preparing a desired material that presents high mechanical performance to match natural bones, inorganic fillers were introduced into biodegradable polymers to fabricate filler/polymer composites, such hydroxyapatite (HAP), β-tricalcium phosphate, or bio-ceramics [1–8]. Among them, composites of HAP particles and biodegradable polymers have been used clinically in various forms due to the good osteoconductivity and osteoinductivity of HAP and biodegradability of poly(L-lactide) (PLLA) in the composites. But in an ordinary PLA/HAP blending system, only physical adsorption is achieved between HAP particles and PLA matrix, consequently, its mechanical properties are low and its load-bearing applications are limited.

The interface adhesion of HAP particles and polymer matrix plays a very important role among the major

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factors affecting the properties of the PLA/HAP composites. In order to increase the interfacial strength between the two phases, various methods have been tried in the past [9–21].

The major objective of this paper is to explore a novel approach to high mechanical properties of PLA/HAP composites, i.e. the hydroxyl groups on the surface of the HAP nano-particles are grafted with PLLA by chemical bond and the g-HAP were further blended with PLLA. In this way, the g-HAP particles can be easily dispersed in the PLLA matrix and strongly tethered to the molecular chains of PLLA matrix. Thus, improved mechanical properties would be expected.

2. Materials and methods

2.1. Chemical reagents

PLLA was prepared according to the literature [22]. Its molecular weight (Mw) was about 300,000. The HAP nano-particles with the atomic ratio Ca/P$\approx$1.67 were acicular crystals of about 100 nm in length and 20–40 nm in width.

The preparation and the surface grafting of HAP particles, and the preparation of the PLLA/g-HAP and the PLLA/HAP composites have been described in our previous paper [22] and are briefly depicted in Fig. 1. The amount of grafted polymer determined by thermal gravimetric analysis was about 6 wt%.

2.2. Measurements of mechanical properties

2.2.1. Tensile strength

Dumbbell-shaped tensile test specimens with effective dimensions of 75 mm × 5 mm × 1 mm were prepared by press-molding under 10 MPa pressure at 175 °C. One batch of these specimens was tested as molded; another batch was subsequently annealed at 115 °C for 1 h and then tested. Normal tensile tests were conducted on an Instron 1121 machine at a crosshead speed of 1 mm/min. The tensile strength and modulus data were both obtained by averaging over five specimens.

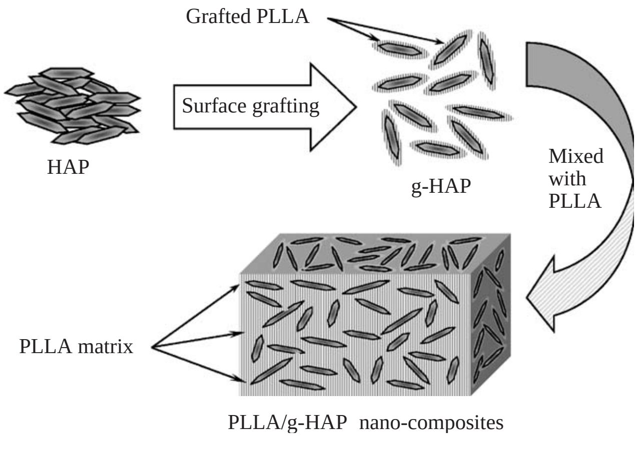

Fig. 1. Method for preparing of the PLLA/g-HAP nano-composites.

2.2.2. Bending strength and impact strength

Rectangular bars having effective dimensions of $55 \times 6 \times 4$ mm for bending and impact tests were cut from a 4-mm-thick plate which was compressed under 10 MPa at 175 °C and subsequently annealed at 115 °C for 1 h and naturally cooled to room temperature. A rectangle groove was made on one side of the specimens for notched Charpy impact strength measurement. The 3-point bending strength was measured by a universal testing machine (Instron 1121, UK) at a crosshead speed of 5 mm/min with a span of 40 mm, while measurement of impact strength was performed on impact testing machine (JJ-20, China).

2.3. Differential scanning calorimeter measurements (DSC)

The thermal properties of PLLA and the PLLA/g-HAP nano-composites were measured by the differential scanning calorimetry (DSC-7, from Perkin–Elmer) at a heating rate of 10 °C/min from 20 to 200 °C. Before the measurement, each sample was annealed at 115 °C for 1 h and about 10 mg sample was used.

Crystallinity of the PLLA in the composites was calculated from the following formula:

$$\text{Crystallinity}\ (\%) = (\Delta H_{\mathrm{m}}/93.7)100\%,$$

where ΔH_{m} indicates the melting enthalpy (J/g) that was calculated from the fusion peak in DSC curve. And the value 93.7 (J/g) is the theoretical enthalpy of completely crystalline PLLA [23].

2.4. Polarized optical microscopy (POM)

The crystal morphology of PLLA and the PLLA/g-HAP composites were observed by POM (Linkam TM 600). The samples used for POM observation were prepared by casting 1 wt% chloroform solution on a clean microscope cover-slide and drying at room temperature for 3 days to remove the residual solvent. The dried samples were melted at 180 °C for 3 min and then cooled to 115 °C at a rate of 40 °C/min. The POM observation was carried out as soon as the sample was cooled to 115 °C.

2.5. Scanning electron microscopy (SEM)

SEM (XL30 ESEM FEG, PHILIPS) was used to examine the selected impact fracture surface of PLLA and the PLLA/g-HAP nano-composites, and to investigate the dispersion of the fillers in the PLLA matrix.