



Effect of hydroxyapatite with different morphology on the crystallization behavior, mechanical property and *in vitro* degradation of hydroxyapatite/poly(lactic-co-glycolic) composite



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ABSTRACT

This work describes the effect of hydroxyapatite with different morphology of nano-particle (n-HA) and whisker (w-HA) on the properties of hydroxyapatite/poly-lactic-co-glycolic acid (HA/PLGA) composite. The crystallization behavior, mechanical property and *in vitro* degradation of HA/PLGA composite were studied by scanning electron microscope, differential scanning calorimeter, polarized optical microscopy, electromechanical universal tester and soaking in simulated body fluid (SBF) at 37 °C for 2, 4, 8, 12 and 16 weeks, comparing with pure PLGA. The results showed that n-HA had better mechanical increment effect for PLGA than w-HA, because of the more uniformly dispersion in PLGA matrix without any cavities and the better promotion crystallization effectiveness in HA/PLGA composite than w-HA. However, the *in vitro* degradation showed that w-HA could keep denser microstructure so that the w-HA/PLGA composite had lower bending strength reduction percent than the n-HA/PLGA composite, owing to the higher crystallinity of w-HA and the more perfectly microcrystalline of PLGA (PLGA/w-HA) than n-HA. The study would be of guidance to select the suitable filler for poly(lactic acid) (PLA) or PLGA polymers in manufacturing bone fracture internal fixation material in future.

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1. Introduction

Poly-lactic-co-glycolic acid (PLGA) has been widely investigated as bone fracture internal fixation materials. However, some inherent disadvantages are expected to be improved, including the mechanical properties, degradation behavior and the chemically bond ability with bone tissues [1,2]. Nano-Hydroxyapatite (n-HA) has similar inorganic component of bone and teeth in vertebrates, so it has received increasing attention in bone implant materials, owing to its good biocompatibility and osteoconductivity [3,4]. Therefore, to achieve a more ideal absorbable bone fracture internal fixation material, n-HA was generally selected as filler for PLGA to obtain n-HA/PLGA composite [5–7]. In our previous study, we have also systematically studied the effect of many factors on the mechanical property of n-HA/PLGA composite, including different new surface modification methods for n-HA, different n-HA loading contents, different grain size range of n-HA, different precipitation methods and different annealing conditions for n-HA/PLGA composite [8–10]. The results showed that the incorporation of n-HA particle into PLGA significantly increased the mechanical

property of PLGA, and the mechanical properties of n-HA/PLGA composite depend not only on filler–matrix interface adhesion, but also on particle size and morphology of filler.

Nano-scale needle-like HA (n-HA) has different structural crystallinity and specific surface areas, compared to conventional powders HA, so it had better mechanical increment effect for PLGA due to the promoting the crystallization for PLGA. However, it is well known that whisker-shaped reinforcements is also an important category to reinforce mechanical properties of polymer [11], so synthetic hydroxyapatite whiskers (w-HA) with long rod-like with higher aspect ratio has been utilized as a new and biocompatible reinforcement for orthopedic biomaterials [12–14], and it was reported that w-HA could improve tensile and fatigue properties than conventional HA powders, due to the orientation of w-HA dispersed within the polymer matrix [15–17]. However, to our best knowledge, mechanical increment effect for PLGA depended on not only the dispersion of HA into PLGA matrix, but also the promoting the crystallization for PLGA by nucleating agent of HA particles. So n-HA might had different mechanical increment effect for PLGA in comparison with w-HA, and there is no report on the difference of dispersion and promoting crystallization for PLGA between n-HA and w-HA.

In addition, as we know, it is very important for bio-absorbable bone fracture internal fixation materials to investigate the

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desirable degradation rate [18,19]. In our previous study, we found that the degradation rate of PLGA (95:05 of LA and GA) was too slowly, while n-HA/PLGA composite with 3 wt% n-HA had a much faster degradation rate, whose bending strength decreased nearly 50% after being soaked for 6 months, which was expected to be slowed a little. Luckily, w-HA has a bigger aspect ratio and higher crystallinity than the n-HA. Theoretically, it could be more difficult for w-HA to dissolve in w-HA/PLGA than n-HA, so that w-HA/PLGA composite might have a little less slowly degradation rate than that of n-HA/PLGA composite. However, up to now, the effect of n-HA and w-HA on the degradation behavior of PLGA has not been reported.

Based on these, in this present work, we attempted to study the dispersity of n-HA and w-HA in PLGA matrix, isothermal crystallization behaviors, spherulitic growth process and the increment effect of bending strength for PLGA. Moreover, after being soaked, the mechanical property reduction, fracture surface microstructure and thermal analysis of the two HA/PLGA composites with the same amount of n-HA or w-HA were also investigated. The main purpose is to make clear the effect of n-HA and w-HA on crystallization behavior, mechanical property and *in vitro* degradation of HA/PLGA composite as well as the correlation between properties and the microstructure. The study is expected to be of guidance to select the suitable filler for poly (lactic acid) (PLA) or PLGA polymers in manufacturing bone fracture internal fixation material in future.

2. Experimental

2.1. Materials

Hydroxyapatite nano-particle (n-HA) and whisker (w-HA), whose mean size were 80–100 nm in length and 20–40 nm in width, and 10–20 μm in length and 1–2 μm in width, respectively, were prepared in our laboratory. PLGA (95:05) with intrinsic viscosity of 4.0–4.2 Pa s was also prepared in our laboratory. Other agents were all analytical reagents.

2.2. Composite preparation

The two HA/PLGA composites with 4.5 wt% n-HA or w-HA taken as an example were prepared by solution mixing method [8]. First, n-HA or w-HA was separately dispersed highly in absolute ethanol and dichloromethane mixture solution with the volume ratio of 1:1 by ultrasonic treatment (BILON-500DL, China) at the frequency of 25 kHz and the used power of 200 W for 30 min. Then, pre-calculated dispersed n-HA or w-HA was slowly added into PLGA dichloromethane solution of 2% (w/v) with the help of magnetic stirring and the same above ultrasonic treatment process for 4 h. Finally, the two mixture solution were separately precipitated and washed with an excess of absolute ethanol, and dried in a vacuum oven at 40 °C for 48 h.

2.3. Characterization

The morphologies of n-HA and w-HA before compounding and the fracture surfaces of the two HA/PLGA composites with 4.5 wt% n-HA or w-HA were observed by scanning electron microscope (SEM) (KYKY-2800 KYKY, China), after being uniformly sputtered with a gold layer.

The isothermal crystallization behaviors of pure PLGA and the two HA/PLGA composites with 4.5 wt% n-HA or w-HA were performed with a differential scanning calorimetric (DSC) analyzer (Q20, TA Instruments-Waters, USA) under nitrogen atmosphere at the gas feed rate of 20 ml/min. The samples were heated from

room temperature to 190 °C with a rapidly heating rate of 200 °C/min and kept at this temperature for 5 min to eliminate previous thermal history, then cooled to predetermined crystallization temperature (T_c) (105, 110, 115, 120 °C) at cooling rate of 200 °C/min, and maintained at T_c for necessary time till the crystallization of the polymer matrix completed. The heat enthalpy of crystallization (ΔH_c) evolved during the isothermal crystallization was recorded as a function of time (t) at different T_c .

The spherulitic morphology and growth process of pure PLGA and two HA/PLGA composites with 4.5 wt% n-HA or w-HA were observed by polarized optical microscopy (POM) equipped with a hot stage (model XPN-203). The samples were melted at 190 °C for 5 min, and then cooled at a rate of 30 °C/min to predetermined crystallization temperature (120 °C) as an example.

Pure PLGA and the two HA/PLGA composites with 4.5 wt% n-HA or w-HA were fabricated into rectangular bars of 4 mm \times 6 mm \times 60 mm by hot compression molding at 190 °C for 10 min, then the original bending strength of samples were tested by an electro-mechanical universal testing machine (CMT6000, Sans, China) in accordance with GB/T6569-1986, at a crosshead speed of 20 mm/min at 19 °C (test room temperature), according to the calculation formula of $\sigma_b = 3PL/2wd^2$, where σ_b is the bending strength of sample, P , L are the maximum load peak and the span, and w and d are the width and thickness of sample, respectively.

The *in vitro* degradation of samples with the size of rectangular bars of 4 mm \times 6 mm \times 60 mm of pure PLGA and the two HA/PLGA composites with 4.5 wt% n-HA or w-HA were carried out by soaking in simulated body fluid (SBF) in a rocking water bath at 37 °C for 2, 4, 8, 12 and 16 weeks. After being soaked, the specimens were removed from SBF at the interval time, gently rinsed with deionized water several times, absorbed the water on the surface with filter paper, and dried completely in a vacuum oven at 40 °C. The fracture surfaces microstructure of pure PLGA and the two HA/PLGA composites after being soaked for 16 weeks were observed by SEM, and their thermal properties were measured with DSC, the samples were heated from room temperature to 190 °C at a rate of 10 °C/min. The bending strength reduction of pure PLGA and the two HA/PLGA composites at interval time were tested according to the previous procedure, and five parallel specimens of each sample were tested and the mean values were given.

3. Results and discussion

3.1. SEM observation

The morphologies of n-HA and w-HA before compounding and the fracture surfaces of the two HA/PLGA composites with 4.5 wt% n-HA or w-HA were given in Fig. 1. From the micrographs, it can be found that the n-HA was needle-like nano-particle with the size of 80–100 nm in length and 20–40 nm in width, and the w-HA was long rod-like with the aspect ratio of about 10 and 10–20 μm in length. After n-HA or w-HA were separately compounded into PLGA as fillers, it can be seen that n-HA was well-distributed in PLGA without any cavities. However, w-HA was not completely embedded into PLGA, even there existed some cavities between w-HA and PLGA. Obviously, the fracture surfaces microstructure of the two HA/PLGA composites had obvious difference, which would have an important influence on the original mechanical property [20].

3.2. Isothermal crystallization behavior

The isothermal crystallization behaviors of PLGA and the two HA/PLGA composites were analyzed by DSC at different crystallization temperature, which is conducive to understand the effect of

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