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Synergistic reinforcing and toughening of poly(L-lactide) composites with surface-modified MgO and chitin whiskers

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ABSTRACT

In order to improve the mechanical properties of poly(L-lactide) (PLLA), two types of whiskers, rod-like MgO whiskers (MgO-Ws) and needle-like chitin whiskers (CHN-Ws), were prepared and then surface modified with L-lactide to obtain grafted MgO-Ws and CHN-Ws (*g*-MgO-Ws and *g*-CHN-Ws), respectively. Subsequently, the initial and grafted MgO-Ws and CHN-Ws were introduced into a PLLA matrix together or singly to prepare PLLA/MgO-Ws/CHN-Ws and PLLA/*g*-MgO-Ws/*g*-CHN-Ws composites via injection molding. As compared to pure PLLA, the increase in the degree of crystallinity and hydrophilicity and decrease in the thermal stability of the resulting composites were confirmed by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and water contact angle (WCA) testing. After surface modification, the dispersion of the whiskers and the interfacial adhesion between the whiskers and the PLLA matrix were significantly improved, which was clearly observed by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). As a result, higher values for tensile strength (84.2 ± 0.9 MPa), flexural strength (102.7 ± 0.6 MPa), notch impact strength (36.7 ± 0.8 J/m), and fracture energy (576 ± 31 J/m^2) were obtained for the PLLA/*g*-MgO-Ws/*g*-CHN-Ws composites as compared to those for pure PLLA and PLLA/MgO-Ws/CHN-Ws composites. Moreover, the crystallization ability and mechanical properties of PLLA were more improved by loading both types of whiskers as compared to loading only one.

1. Introduction

Bone defects or trauma has become a worldwide and frequently occurring disease. In order to promote the bone-healing process, bioresorbable or non-bioresorbable internal fixation materials are often needed [1–3]. Owing to their incomparable advantages over non-bioabsorbable internal fixation materials, bioabsorbable internal fixation materials have attracted more attention in the past 30 years [4,5]. Poly(L-lactide) (PLLA), a bioresorbable material with good biocompatibility, mechanical properties, and processibility, has been widely explored as an internal fixation material and studied extensively [6–8]. However, PLLA as a bone repair material still has some shortcomings, such as insufficient strength and toughness, and its degradation products can easily lead to a noninfectious inflammatory response, etc. One solution is to reinforce PLLA with harder and stronger fillers such as nanoparticles, nanotubes, or fibers to obtain PLLA-based composites [9–11]. However, increasing the strength of a material by loading it with fillers often causes a decrease in toughness. The toughness of an internal fixation material is very important for its clinical application.

Whiskers, a type of short, fiber-shaped single crystal, exhibit high mechanical strength and elastic modulus owing to their highly ordered atomic structure and structural integrity. According to the literature [12], when whiskers are added to a matrix, the force applied to the resulting composite is often transferred to the whiskers, bypassing the matrix; meanwhile, the whiskers consume

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a large part of the force, which leads to an increase in both the strength and toughness of the composite matrix. Thus, whiskers have been used as the most promising reinforcing and toughening agents for various types of matrices in recent years [13]. Two types of whiskers have attracted wide attention and been used as fillers for polymer-based composites. One is magnesia whiskers (MgO-Ws) and the other is chitin whiskers (CHN-Ws) [14,15]. As easily available and low-cost inorganic whiskers, MgO-Ws have a high tensile strength of 980 MPa and an elastic modulus of 310.1 GPa. As natural polysaccharide whiskers, CHN-Ws exhibit longitudinal and transverse moduli of 150 and 15 GPa, respectively. In our previous study, MgO-Ws and CHN-Ws were introduced into a PLLA film or an electrospun fiber membrane. The reinforcing and toughening effects of MgO-Ws and CHN-Ws on the PLLA matrix were proven despite their rigid nature [16,17].

The major objective of this study was to obtain better mechanical properties for PLLA by adding both MgO-Ws and CHN-Ws at the same time and to clarify whether there are synergistic effects between the two types of whiskers. MgO-Ws and CHN-Ws were also chosen because they have favorable biological characteristics and can promote bone fracture healing. Moreover, owing to their alkaline characteristics, MgO-Ws and CHN-Ws can not only neutralize the acidic degradation products of PLLA, thereby reducing the chance of non-infectious inflammation but also regulate the degradation rate of PLLA. In addition, the effective dispersion of fillers in polymer matrices remains a challenge for injection-molding technology. Thus, another objective of this study was to improve the dispersion of whiskers and the interfacial adhesion between the whiskers and the matrix during the injection-molding process [18].

For this purpose, MgO-Ws and CHN-Ws were first prepared and then surface modified with L-lactide to obtain grafted MgO-Ws and CHN-Ws (*g*-MgO-Ws and *g*-CHN-Ws). Then, the initial and grafted whiskers were added into the PLLA matrix together or singly via injection molding. The thermal and crystalline properties, hydrophilicity, morphologies, and mechanical properties of the resulting composites were studied. To our knowledge, there are few reports about PLLA/MgO-Ws/CHN-Ws and PLLA/*g*-MgO-Ws/*g*-CHN-Ws ternary composites.

2. Experiment section

2.1. Materials

PLLA was obtained from Nature Works (USA, Grade 3052D, M_n = 200,000). The L-lactide was supplied by Jinan Daigang Biological Engineering Co. Ltd. Stannous octoate [$Sn(Oct)_2$] was provided by Sigma-Aldrich, USA. Chitin was supplied by Jinan Haidebei Biological Material Co. Ltd. $Na_2CO_3 \cdot 10H_2O$, $MgCl_2 \cdot 6H_2O$, and other reagents were purchased from Guangzhou Chemical Reagent and used without further purification.

2.2. Preparation of the initial and grafted whiskers

The initial and grafted MgO-Ws and CHN-Ws were prepared according to our previous report [16,17]. The process is briefly depicted in Fig. 1. The characterization and corresponding results of the initial and grafted whiskers are given in the Supporting Information.

2.3. Preparation of the composites

The PLLA/MgO-Ws/CHN-Ws and PLLA/*g*-MgO-Ws/*g*-CHN-Ws composites with different whisker contents were prepared by injection molding. The compositions of the resulting composites in mass fraction are listed in Table 1. Briefly, the *g*-MgO-Ws and *g*-CHN-Ws were uniformly mixed, and further kneaded with PLLA particles using a two-roll mill at a temperature of 165 °C for 8 min to prepare a *g*-MgO-Ws/*g*-CHN-Ws/PLLA blend, which was further crushed into small pellets. The pellets were then dried under vacuum at 50 °C for 24 h before injection molding. Finally, the PLLA/*g*-MgO-Ws/*g*-CHN-Ws composites were prepared by injection molding at a melting temperature of 165 °C. The PLLA/MgO-Ws/CHN-Ws composites were prepared the same way.

2.4. Characterization

The thermal stability of the composites was measured on a TG system (209F3-ASC, Germany, Netzsch) under N_2. The samples were heated from 25 to 500 °C at a heating rate of 10 °C/min. The corresponding DTG curves were obtained accordingly.

The thermal properties were further tested by a TA Q20 differential scanning calorimeter (DSC, TA Company, USA). The samples were heated from 20 to 200 °C at a rate of 10 °C/min under N_2 and kept in the molten state for 3 min. They were then cooled to 0 °C at a rate of 10 °C/min. Subsequently, the samples were heated to 200 °C, again at a rate of 10 °C/min. The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_{m1}, T_{m2}), and cold crystalline enthalpy (ΔH_{cc}), as well as melting enthalpy (ΔH_m), were determined from DSC thermograms. The degree of crystallinity (X_c) of the samples was measured based on Eq. (1).

$$X_c = \Delta H_m \times 0.95/\Delta H_0 \times 100\% \quad (1)$$

where ΔH_m is the melting enthalpy for the PLLA-based composites, 0.95 is the PLLA composition ratio in the PLLA composites, and ΔH_0 is the melting enthalpy for 100% crystalline PLLA (93 J/g) [19].

X-ray diffraction (XRD) analysis was conducted using a Dmax-1200 X-ray diffractometer (Japan) with Cu Kα radiation at a scanning speed of 8°/min, the operating voltage and current are 40 KV and 15 mA, respectively.

The static water contact angle (WCA) of the composites was measured by a contact angle meter (DSA100, Germany, Kruss). At least five points for each sample were recorded and averaged to determine the contact angle.

The tensile fracture morphologies of the composites were observed by field-emission scanning electron microscopy (FESEM, ULTRA 55, Carl Zeiss, Germany). A layer of gold was sprayed over the surface before observation.

The dispersion of the whiskers in the composites was observed by TEM using a Philips CM-120 instrument (Holland). The composites were trimmed to sheets with a thickness of approximately 100 nm, which were coated on copper grids for TEM observation.

The tensile, flexural, and notch impact properties of the composites were measured. Following ISO 527: 1993, the composites were injection molded into dumbbell-shaped samples with a dimension of 75 × 5.0 × 2.5 mm for tensile testing. The tensile testing was carried out using a universal testing machine (Zwick/Roell Z005, Japan, 30 KN load cell) with a 50 mm/min crosshead speed at ambient temperature. The same instrument was used to measure the flexural property of the specimens (80 × 10 × 4 mm). Following ISO 180: 1993, the Izod notch impact strength of the composites was measured with the help of a digital pendulum impact tester (MTS ZBC50, Japan) equipped with automatic correction for pendulum deviation and pendulum-bearing friction. The depth of the notch on these samples was 1.7–2.0 mm. Every specimen was parallel measured six times to obtain the averages with standard deviations.