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Effect of surface modified hydroxyapatite on the tensile property improvement of HA/PLA composite

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ABSTRACT

In this study, we modified the surface of hydroxyapatite (HA) particle by ring-opening polymerization of lactide (LA). The modified HA particles were characterized by IR and TGA. It was shown that LA could be graft-polymerized onto the surface of HA. A series of composites based on modified HA/PLA were further prepared and characterized. It indicated that the modified HA particles were well dispersed in PLA matrix than unmodified HA particles and the adhesion between HA particle and PLA matrix was improved. The modified HA/PLA composites showed good mechanical properties than that of unmodified HA/PLA.

1. Introduction

Among the numerous polymers studied so far, polylactide (PLA) have proven to be the most attractive biodegradable polyesters [1,2]. PLA possesses excellent mechanical properties and can be broken down into non-toxic metabolites by bio-organisms. However, the ranges of its application are limited because of the difficulty in controlling the hydrolysis rate and poor hydrophilicity. To overcome these problems, various blends of PLA with other materials have been studied, e.g. starch [3], poly(ε-caprolactone) (PCL) [4]. Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is an inorganic part of the naturally occurring bone. Recently, HA/PLA composite has been studied by many scientists, since HA particle can reinforce the materials and decrease the degradation rate of PLA [5]. However, as the filler, HA was in lack of adhesion with PLA matrix. Consequently, an improvement of the interfacial adhesion between particles and matrix has become the key technique in preparing HA/PLA composites. Various methods have been developed to improve adhesion between HA and the particular polymeric matrix [6–8]. However, because the number of active hydroxyl groups on the HA particles was limited and the reactivity of these groups was reasonably low, only a little amount of grafted organic molecules was obtained. Moreover, most of the grafted organic molecules mentioned above are usually noxious.

In this paper, we tried to prepare surface-grafted HA (*g*-HA) particles by ring-opening polymerization of *l*-lactide, and study the mechanical property improvement of the *g*-HA/PLA composites.

2. Materials and methods

2.1. Materials

HA were purchased from Crystal Advanced Materials Co., Ltd. *l*-Lactide (LA) was synthesized from *l*-lactic acid (Purac, The Netherlands) according to literature [9]. PLA was prepared with ring-opening of LA with stannous octanoate ($Sn(oct)_2$) as catalyst. The molecular weight of PLA is about 100,000 (M_n) indicated by GPC.

2.2. Surface modification of HA and preparation of composites

10 g HA each was uniformly dispersed in tetrahydrofuran with stirring and *l*-lactic acid (5, 10, 20 g, respectively) were dropped in. After the toluene was added, the mixture was preserved at 85 °C

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for 6–8 h. Then particles were washed by ethyl acetate and vacuum-dried, and denoted by *m*-HAs (*m*-HA-1, *m*-HA-2, *m*-HA-3).

The above three *m*-HA particles and LA were put into $Sn(oct)_2$/toluene solution ($LA:Sn(oct)_2 = 3000:1$ (mol%)), respectively, and kept under vacuum at 130 °C for 24 h. After washed with chloroform and vacuum-dried, three corresponding *g*-HA samples (*g*-HA-1, *g*-HA-2, *g*-HA-3) were obtained.

HA or *g*-HA samples were uniformly suspended and 10% PLA/chloroform solution was added into to achieve HA content of 0–20 wt.% in the composites. Then chloroform was removed by evaporation and the HA/PLA and g-HA/PLA composites were vacuum-dried.

2.3. Characterization of the samples

All samples were used directly for IR measurement in KBr disks using a PE 100 spectrometer. Thermogravimetric data were obtained using a Mettler Toledo TGA/SDTA851e in N_2 at a heating rate of 10 °C/min.

The stress–strain data were obtained with an ElectroForce 3200 test instruments by applying a 200 N load cell at a cross-head speed of 10 mm/min. Mini dumb-bell-shaped tensile specimens with dimensions of 50 mm × 8.0 mm × 1 mm were cut from the sheets of the composites. A scanning electron microscope (FEI Sirion 200, Philips) was used to observe the morphology of particles.

3. Results and discussion

The FTIR spectra of HA, *m*-HA, *g*-HA and PLA are presented in Fig. 1. For three HA particles, the bands at 3440 cm^{-1} (–OH), 1040 cm^{-1} (phosphate group) are similar. Some small peaks are observed at 3000–2840 cm^{-1} contributing to C–H stretching of CH_3– and CH_2– of lactic acid and PLA. After surface grafting, a new absorption band appears at 1750 cm^{-1} belonging to –C=O group of PLA on the *g*-HA (Fig. 1c).

The weight losses of HA, *m*-HA-1, *m*-HA-2, *m*-HA-3, *g*-HA-1, *g*-HA-2 and *g*-HA-3 were 1.63%, 7.49%, 14.91%, 25.36%, 16.23%, 29.21% and 36.40%, respectively. The amounts of surface-grafted lactic acids on *m*-HA or LA on the surface of *g*-HA were calculated by the equation, the grafting ratio (%) = W_1 (%) − W_0 (%), where W_1 is the weight loss of HA and W_0 is the weight loss of *m*-HA or *g*-HA.

Fig. 2 presents the grafting ratio of lactic acids on *m*-HA and that of LA on *g*-HA. The grafting ratio of *l*-lactic acid and LA could be easily dominated. The increasing trend of LA-grafting ratios get weaker than that of the grafting ratios of lactic acid on *m*-HA, due to the increasing space steric hindrance of *g*-HA.

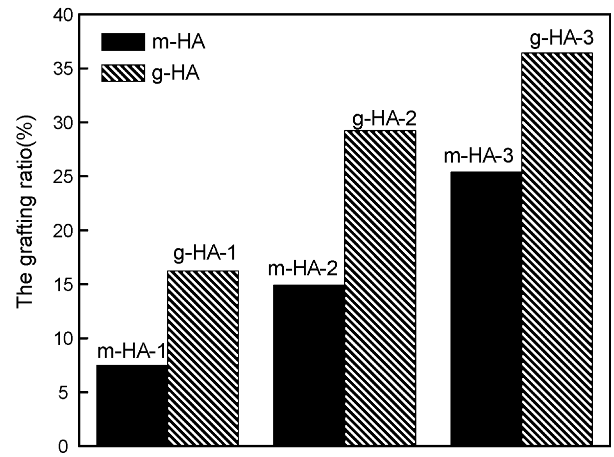

Fig. 2. The grafting ratio of lactic acid or LA for *m*-HA and *g*-HA.

The thermal stability of HA, *m*-HA-3 and *g*-HA-3/PLA composites (10 wt.%) was investigated with TGA. The 5% and 50% weight-loss temperatures (T_5 and T_{50}, respectively) are listed in Table 1 for three specimens. It indicates that the presence of *g*-HA and *m*-HA affect the pyrolysis process significantly. The improvement in T_5 and T_{50} of three composites could be attributed to the enhancement of the interaction and adhesion between the modified HA fillers and the PLA matrix as a result of the surface modification of HA.

The SEM micrographs of HA, *m*-HA-2 and *g*-HA-2 are presented in Fig. 3. It can be seen that HA particles are needlelike shape with dimensions of about 100 nm × 40 nm. *m*-HA and *g*-HA particles do not make appreciable difference in shape and size from HA particles.

The representative stress–strain curves are shown in Fig. 4A. The stress–strain behavior of PLA and composites exhibit the characteristic of brittle materials, all specimens break at certain points shortly after the yielding stage. The relationship between the filler content and the tensile properties of the composites was shown in Fig. 4B and C. The *g*-HA/PLA composites showed more enhancement of tensile strength and elastic modulus in comparison with HA/PLA composites. The higher the *g*-HA content, the larger the difference between them because the tensile strength of the HA/PLA composite decreased more rapidly with the filler content than that of the *g*-HA/PLA composite. The tensile strength of *g*-HA/composites increases with *g*-HA content and shows a maximum at 5–10 wt.% *g*-HA addition. Then the tensile strength of g-HA/composites decreases as g-HA content increases further. During the preparation of the composites, the *g*-HA particles could be easily dispersed in PLA, whereas the unmodified HA particles would be agglomerated and were difficult to disperse. Significant aggregation occurring in the HA particles within PLA matrix results in the deterioration of tensile strength. The *g*-HA particles show an improved adhesion with PLA matrix and *g*-HA/PLA composites exhibit better mechanical properties than HA/PLA blends. Similarly, the deterioration of

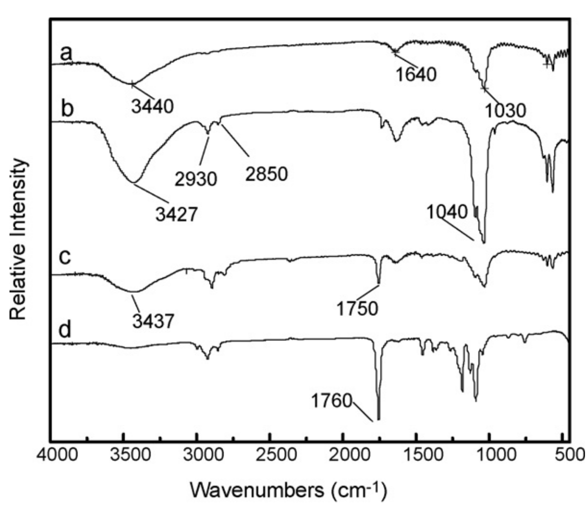

Fig. 1. FTIR spectra for HA (a), *m*-HA (b), *g*-HA (c) and PLA (d).

Table 1
The T_5 and T_{50} of 10 wt.% HA or modified HA/PLA composites

	10 wt.% HA/PLA	10 wt.% *m*-HA-3/PLA	10 wt.% *g*-HA-3/PLA
T_5 (°C)	333	335	339
T_{50} (°C)	354	360	365