

Poly lactide (PLA)/layered double hydroxides composite fibers by electrospinning method

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Received 28 June 2007; received in revised form 29 September 2007; accepted 30 October 2007

Abstract

Inorganic nanosized layered double hydroxides (LDHs) modified with dodecyl sulfate (DS) ions were incorporated into semi-crystalline poly lactide (PLA) nanofiber non-woven membranes by combining a nanocomposite technique and the solution electrospinning process. The structure, morphology and thermal property of the electrospun membranes were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and differential thermal analysis (DTA). It was found that the melting point of PLA decreased upon the increase of LDHs content in the membranes.

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Keywords: A. Inorganic compounds; A. Polymers; C. Electron microscopy

1. Introduction

Poly lactide (PLA) is often used as the base materials for implant devices, such as suture fibers and scaffolds for tissue engineering [1–3]. It is biocompatible and biodegradable, and they can provide high efficiency of drug loading. Many different techniques have been developed to produce nanostructured biodegradable materials such as microspheres, foams and films. It has been demonstrated that the molecular structure and morphology of PLA play major roles in the degradation and mechanical properties of the final products [4].

Recently, the electrospinning method has attracted much attention to produce non-woven membranes of nanofibers. This technique, invented in 1934, makes use of an electrical field that is applied across a polymer solution and a collector plate, to force a polymer solution jet out from a small hole [5]. As particular interests have been addressed in the tissue engineering, great efforts have been made to study electrospinning of biodegradable polymers [6–10]. Several investigations for producing

PLA nanofiber scaffolds have been performed using electrospinning method, and the solvents generally used are chloroform, chloromethane and *N,N*-dimethyl formamide [2,3,10].

However, it should be mentioned that the electrospinning fibers have difficulty in being utilized as a hard tissue scaffold system like bone regeneration application, because they are too soft. Polymer/layered crystal nanocomposites have been recognized as one of the most promising research fields in materials chemistry because of their unique properties, such as enhanced mechanical property, increased thermal stability, improved gas barrier property and reduced flammability [11–15]. Recently, it has been reported that adding a small quantity of nanosized montmorillonite (MMT) platelets can increase mechanical and physical properties of PLA fibers including higher strength and greater stiffness [16].

To the best of our knowledge, the layered double hydroxides (LDHs) systems of polymer/layered crystal nanocomposites have been much less reported in the literature [17–20]. The LDHs can be represented by the ideal formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}A_{x/n}^{n-} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, such as Mg^{2+} , Al^{3+} , respectively; A is an anion, such as CO_3^{2-} ,

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SO_4^{2-} , and NO_3^- . LDHs are important layered crystals due to their wide applications as catalysts, flame retardants, stabilizers, medical materials, etc. [21]. Due to their highly tunable properties, LDHs are considered as a new emerging class of the most favorable layered crystals for preparation of multifunctional polymer/layered crystal nanocomposites [17]. Some organic or polymeric anions, such as alkyl carboxylates, alkyl sulfates, polyacrylates and poly(styrene sulfates) have been intercalated into the interlayer region of LDHs by ion-exchange reaction or in situ polymerization [21–24].

In the present study, dodecyl sulfate (DS) ions were intercalated into the MgAl layered double hydroxide (MgAl-LDH) to improve the hydrophobicity of LDH layers and compatibility with the organic solvents. The organomodified MgAl layered double hydroxide (OMgAl-LDH) was added into the PLA solution which was electrospun to provide LDHs-reinforced PLA nanofibers. The structure, morphology and thermal property of the electrospun membranes were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and differential thermal analysis (DTA).

2. Experimental section

2.1. Preparation

MgAl-LDH (also known as hydrotalcite) was obtained by adding 100 mL of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.075 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.025 mol) aqueous solution into 100 mL of Na_2CO_3 (0.025 mol) and NaOH (0.2 mol) aqueous solution. The slurry was then aged for 12 h at 65 °C keeping the pH at 9.0–9.5 by adjusting with 1 mol/L NaOH. The precipitate was washed with distilled water and dried at 70 °C for 12 h. The OMgAl-LDH sample was obtained from the reaction of MgAl-LDH with a 4-fold excess of DS in aqueous solution at 65 °C for 2 h under a nitrogen atmosphere. The pH value was kept 4.0–4.5 by adding 0.1 mol L⁻¹ HCl solution during reaction. The product was washed with ethanol, centrifuged and dried at 70 °C for 8 h.

The non-woven membranes were prepared by electrospinning method. A viscous polymer solution with a concentration of 0.1 g ml⁻¹ was prepared by dissolving PLA polymer in chloroform. OMgAl-LDH clays without delamination were added to the PLA solution and thoroughly mixed by ultrasonic waves. The content of OMgAl-LDH clay to PLA were 2.0, 5.0, 10.0 and 15.0 wt%, respectively. For the electrospinning process, the PLA/LDHs solution was placed into the syringe by the needle with inner diameter of 0.9 mm. Randomly oriented nanofibers were electrospun by applying the voltage of 22 kV to the needle using a high voltage supplier. The grounded plate collector was located at distance from 13 cm and the polymer solution was loaded at feed rate from 1.5 ml h⁻¹. All electrospun fibers collected were stored

in vacuum for at least 24 h to ensure that the solvents were completely vaporized.

2.2. Characterization

Powder XRD measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu K α radiation ($\lambda = 0.15406$ nm, Ni-filter) at 40 kV, 30 mA. The samples without preferred orientations were scanned in steps of 0.02° in the 2θ range 3° to 70° using a count time of 4 s per step. The Fourier transform infrared (FTIR) spectra were recorded using a Vector 22 (Bruker) spectrophotometer in the range 4000–400 cm⁻¹ with 2 cm⁻¹ resolution. The standard KBr disk (1 mg of sample in 100 mg of KBr) was used. DTA curve was measured on a PCT-1A thermal analysis system with a heating rate of 10 °C min⁻¹ under air atmosphere. The morphology of the electrospun PLA fibers was examined by a Hitachi S-4700 SEM. The degree of dispersion of OMgAl-LDH in PLA matrix was observed by a Hitachi H-800 TEM operated at 200 kV. The as-cast film specimens were embedded in epoxy resin and subjected to ultramicrotoming into ultrathin section.

3. Results and discussion

3.1. Organomodification of Mg-Al-CO₃²⁻ LDH

The XRD patterns in the range $2\theta = 3\text{--}70^\circ$ for Mg-Al-CO₃²⁻ LDH and OMgAl-LDH samples are shown in Fig. 1. Fig. 1a represents a typical XRD pattern of Mg-Al-CO₃²⁻ LDH sample, with the (003) reflection at $2\theta = 11.0^\circ$ corresponding to a basal spacing of 0.78 nm. As shown in Fig. 1b, the (003) and higher-order reflections of the OMgAl-LDH shift to lower 2θ angles compared to those of the Mg-Al-CO₃²⁻ LDH. After the intercalation of DS anions, the basal spacing (d_{003}) increases from 0.78 to

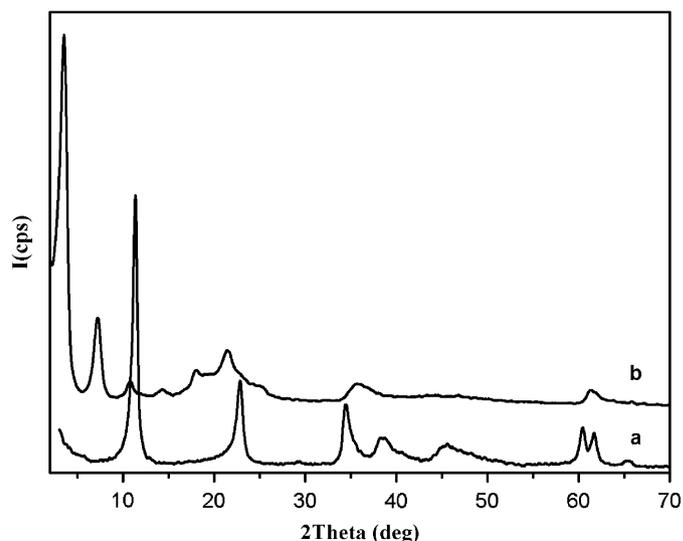


Fig. 1. XRD patterns for (a) pristine Mg-Al-CO₃²⁻ LDH and (b) modified LDHs by DS.

2.54 nm. As a result, the gallery height of the OMgAl-LDH increases to 2.06 nm when the thickness of the mixed aluminum/lithium hydroxide layers (0.48 nm) is subtracted [25], which strongly indicates the intercalation of DS anions into the MgAl-LDH.

The FTIR spectra of the Mg-Al-CO₃²⁻ LDH and OMgAl-LDH samples are presented in Fig. 2. The spectrum of Mg-Al-CO₃²⁻ LDH sample (Fig. 2a) shows a strong and broad absorption band at about 3500 cm⁻¹ due to O-H stretching vibration. The band at about 1640 cm⁻¹ is due to the δ(H-OH) vibration. The carbonate stretching vibration appears at 1360 cm⁻¹. The band at 1224 cm⁻¹ is assigned to the stretching vibration of sulfate in the OMgAl-LDH sample (Fig. 2b). The stretching vibration bands of -CH₂- or -CH₃ in the aliphatic chains of DS appear at 2845–2960 cm⁻¹. By the reaction of MgAl-LDH with DS anions, organomodified layered compounds were obtained.

3.2. Characterization of PLA/LDHs fibers

Fig. 3 displays the XRD patterns in the range $2\theta = 2\text{--}70^\circ$ for the pristine PLA fibers and the PLA/LDHs fibers. Fig. 3a exhibits a broad peak which is attributed to the reflection of semi-crystalline PLA, while the XRD pattern of PLA/LDHs fibers (Fig. 3b) shows two characteristic reflections of OMgAl-LDH at 2θ 3.00° (003) and 7.46° (006), besides the broad peak of pristine PLA similar to Fig. 3a. This confirms the hybridization of PLA and LDHs through the method of electrospinning.

The SEM micrograph of the PLA/LDHs composite fibers containing 15 wt% of OMgAl-LDH formed by electrospinning is shown in Fig. 4. Fig. 4A exhibits rather uniform and slick fibers of pristine PLA with the average diameter smaller than 1 μm. However, the surface of the

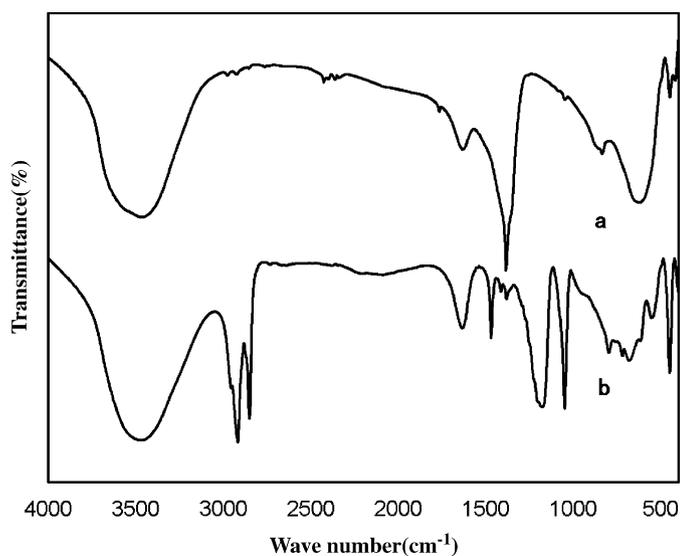


Fig. 2. IR spectra for (a) pristine Mg-Al-CO₃²⁻ LDH and (b) modified LDHs by DS.

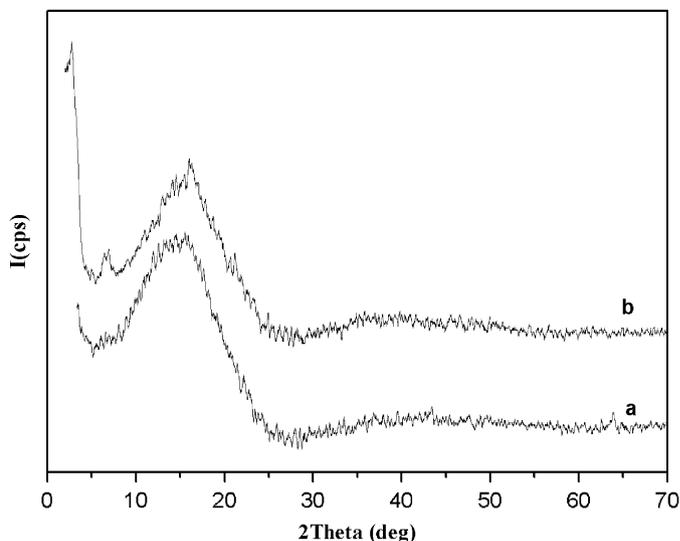


Fig. 3. XRD patterns for the fibers of (a) pristine PLA and (b) PLA/LDHs.

PLA/LDHs composite fibers (Fig. 4B) is much rougher, with knobs observed (Fig. 4C). These knobs are possibly due to the conglomeration of OMgAl-LDH nanoparticles which have not dispersed completely in the PLA. The effects of OMgAl-LDH nanoparticle contents, temperature, pH value, solvent and atmospheric conditions on the preparation of PLA/LDHs composite fibers are under investigation to increase the dispersion of LDHs in PLA.

Fig. 5 exhibits the TEM micrograph for the transect of PLA/LDHs composite fibers containing 15 wt% of OMgAl-LDH formed by electrospinning. The bright and dark regions correspond to PLA matrix and OMgAl-LDH particles, respectively, which confirms the embedment of LDH particles by PLA fibers with high degree of dispersion and uniformity.

Fig. 6 illustrates the DTA curves of the PLA nanofibers with different LDHs contents and the corresponding number average molecular weight M_n of these fibers. It was found that the value of M_n did not change remarkably with increase of LDHs content in the membranes, indicating that the incorporation of OMgAl-LDH nanoparticles into PLA through electrospinning does not induce molecular scission.

It can be seen from Fig. 6 that the melting point of pellet PLA is about 150 °C, while it decreased to about 145 °C after the formation of fibers. Moreover, the melting point decreased upon the increase of OMgAl-LDH content in the fibers. This result is unexpected because the molecular weight did not change remarkably with the increase of LDHs content; therefore, the decrease in melting point might be due to the change in crystalline orientation of PLA fibers resulted from the addition of LDHs. In addition, this phenomenon implies that the degradation of the polymer becomes easier upon the hybridization with LDHs nanoparticles, and this deserves further research in the field of environmental friendly applications.

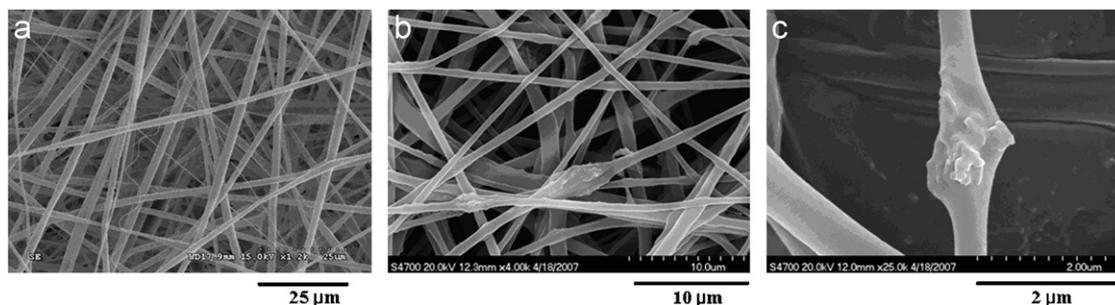


Fig. 4. SEM images of PLA fibers: (A) the fibers of pristine PLA; (B) (C) the fibers of PLA/LDHs containing 15 wt% of OMgAl-LDH.

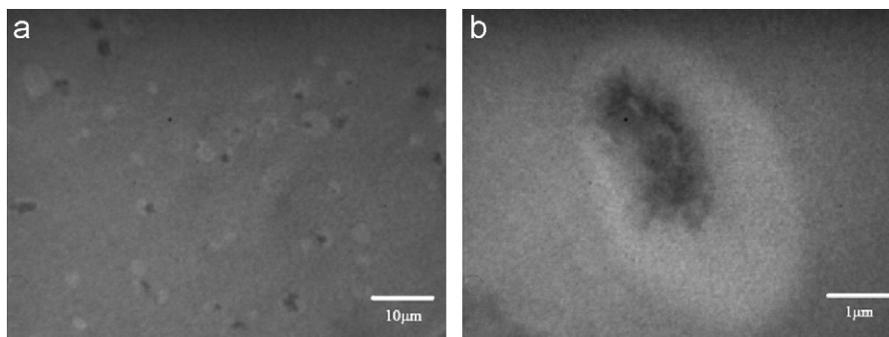


Fig. 5. TEM images of PLA/LDHs fibers containing 15 wt% of OMgAl-LDH: (A) low magnification and (B) high magnification.

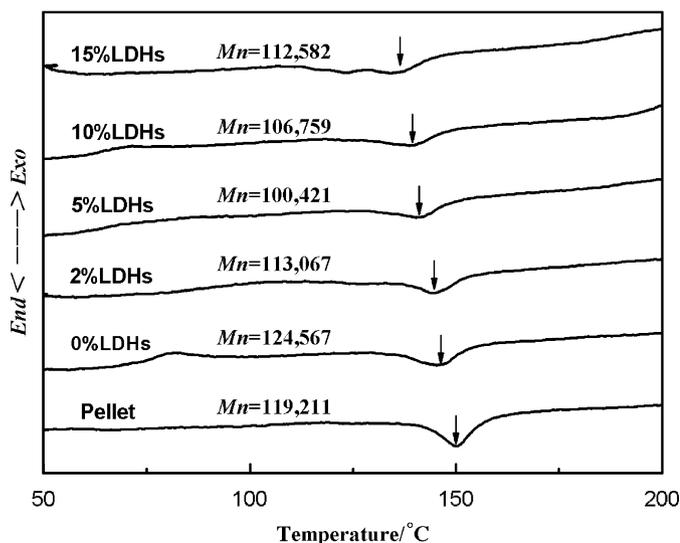


Fig. 6. DTA curves for PLA fibers with different OMgAl-LDH contents.

4. Conclusions

PLA/LDHs composite fibers were successfully prepared by the method of electrospinning. TEM shows the embedment of LDH particles by PLA matrix with high degree of dispersion and uniformity. It has been found that the number average molecular weight M_n of the electrospun PLA fibers did not change remarkably while the melting point of PLA decreased upon the increase of LDHs content in the membranes, which suggests that this polymer/LDHs composite material may have prospective application as the basis of environmental friendly systems.

Acknowledgments

This project was supported by the National Natural Science Foundation Major International Joint Research Program (Grant no.: 20620130108), National Natural Science Foundation Key Project (Grant no.: 20531010), National Natural Science Foundation of China (Grant no.: 20601001), the Program for New Century Excellent Talents in University (Grant no.: NCET-05-121), the 111 Project (Grant no.: B07004) and the Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT).

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