



Full Length Article

Crystallization, rheology behavior, and antibacterial application of graphene oxide-graft-poly (L-lactide)/poly (L-lactide) nanocomposites

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ABSTRACT

Poly L-lactide nanocomposites with graphene oxide (GO) were prepared via solution casting in this work. With the aim of improving the interface compatibility, the GO grafted with poly L-lactide (GO-g-PLLA) was synthesized by the ring-opening polymerization of L-lactide on the surface of lyophilized GO. The chemical structure, morphology and thermal properties of GO and GO-g-PLLA were compared by X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM) and thermal gravimetric analysis (TGA), respectively. Based on the isothermal and non-isothermal crystallization of PLLA/GO-g-PLLA blends, the added GO-g-PLLA acted as nucleating agents to enhance the crystallization rate of PLLA, with its special surface grafted with the PLLA matrix. The introduced GO-g-PLLA sheets also improved the viscosities of PLLA as rheological enhancers, which is favorable for the processibility of PLLA. The added GO-g-PLLA also endow PLLA nanocomposites with significantly improved electrical conductivity. More interesting, this work presented the antibacterial activity of PLLA/GO and PLLA/GO-g-PLLA nanocomposites electrospinning membrane for Escherichia coli and Staphylococcus aureus, which further widen the biomedical application of PLA.

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1. Introduction

Poly (L-lactic acid) (PLLA), an aliphatic polyester produced from renewable biomass such as corn and sugar beet, has been recently spotlighted as a biodegradable, sustainable, and eco-friendly substitute for petroleum-based polymers [1–4]. It has broad applications in the field of medicine, agriculture and packaging materials [5,6].

Although PLLA has been researched for several years, its commercial usage has been limited to certain low value applications because of high synthesis cost. The nanocomposition technology is a traditional method to endow the polymeric matrices with enhanced thermo-mechanical, optical and electrical properties [7–9]. Therefore, several works have been focused on the preparation and study of biodegradable PLLA-based nanocomposites. PLLA has been modified by various nanomaterials such as nanofillers like nanoclays [10], carbon nanotubes [11], graphene nanoplatelets [12–14], and nanofibers [15]. However, the properties of the

prepared polymeric nanocomposites are strongly related to the nanoparticle-polymer compatibility and also the spatial separation of nanoparticles. The as-prepared PLLA nanocomposite has enhanced crystallization behavior compared with traditional modified PLLA composites. For instance, Cao and co-workers [16] successfully improved the mechanical and thermal properties of PLLA via adding lyophilized graphene nanosheets. Carson [17] prepared PLLA/CNTs nanocomposites, and they showed the crystallization of PLLA could be promoted apparently due to the CNTs acted as a nucleating agent in the PLLA matrix. Qiu and Pan [18] reported the introduction of POSS significantly enhanced the crystallization rate, improved the mechanical properties and accelerated the hydrolytic degradation of PLLA in the nanocomposite with respect to pristine PLLA.

Graphene oxide nanosheets have been widely reported to be applied in the polymer composites with developed high performance due to its large specific surface area, high aspect ratio and rich oxygen-containing groups on the surface [19–21]. However, one of the prerequisites for achieving the desired reinforcing effect of GO nanosheets is to have homogeneous distribution of GO nanosheet in the polymer and furthermore to have good polymer matrix/GO compatibility. Thus, a suitable surface modification on GO with grafting polymer could be good strategy for their

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extensive applications in polymer blends. Besides, due to its edges of graphene nanosheets with extremely high aspect ratio. GO is reported can be proposed as one of the ideal nanostructures for an effective direct contact interaction with microorganisms [22–24]. Akhavan [23] has found the cell membrane damage of bacteria was caused by direct contact of bacteria by the extremely sharp edges of GO. Subsequently, the GO nanosheets will oxidize glutathione of bacterial, which serves as redox state mediator in bacteria.

In this work, the functionalized GO, GO-g-PLLA has been synthesized and characterized by XPS, TGA and FTIR. Furthermore, GO-g-PLLA and GO composites based on PLLA were prepared through solution casting. The related crystallization and melting behavior of PLLA/GO-g-PLLA and PLLA/GO composites were also evaluated by DSC and POM. In addition, we proposed a strategy of fabricating PLLA/GO and PLLA/GO-g-PLLA electrospinning mats with enhanced antibacterial performance. And the antibacterial activities of the mats against Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* was investigated.

2. Experimental section

2.1. Materials and reagents

Graphite powder was supplied by Nanjing Xianfeng Nanomaterial Science and Technology Co. Ltd, China; PLLA ($M_w = 1.75 \times 10^5 \text{ g mol}^{-1}$) used in this study was supplied from Purac Co. (Gorinchem, Netherlands); l-lactide was purchased from Changchun Shengboma Biological Co, LTD; Dichloromethane and stannous octoate ($\text{Sn}(\text{Oct})_2$) were acquired from Sinopharm.

2.2. Preparation of GO

GO was prepared according to a modified Hummer's method widely reported in the previous reports [25–27]. In detail procedure, graphite powder (3g) was puffed in muffle furnace at 960 °C for 15min, then the fluffy powder and KMnO_4 (18 g) were put into a cold (0 °C) concentrated H_2SO_4 (120 mL), where KMnO_4 was added to the mixture in five times under stirring. Subsequently the mixture was intensely stirred in an ice bath to maintain a temperature below 40 °C for 5 h. Once the reaction was complete and a pasty mixture had formed, the mixture was diluted with deionized water (300 mL) in an ice bath and stirred for 2 h while the temperature was kept below 30 °C. After that, additional deionized water (1000 mL) was added to the mixture to reduce the temperature value. Subsequently, 30% H_2O_2 (15 mL) was gradually added into the mixture and stood for overnight, the aqueous GO was washed by HCl dilute solution to remove metal ions and acid until the PH value of the liquid became 7. After that, the resultant product was dried in lyophilization for 72 h and GO powder was finally obtained.

2.3. Preparation of GO-g-PLLA

To prepare GO-g-PLLA by ring-opening polymerization, l-lactide monomers (10 g) mixed GO (1g) were added into a reactor, where GO used as initiator. Under the protecting of nitrogen atmosphere, the polymerization was started by adding $\text{Sn}(\text{Oct})_2$ as the polymerization catalyst to toluene solution (the weight of $\text{Sn}(\text{Oct})_2$ was 1.0 wt% of l-lactide). Then the reaction remained for 48 h at 130 °C under stirred. After that, the product was dissolved in excess chloroform and precipitated through the Teflon membrane for several times to remove the unreacted l-lactide monomers and PLLA homopolymer [28]. Finally, the resulting solid was dried for 24 h at 45 °C in vacuum to obtain GO-g-PLLA powder.

2.4. Preparation of PLLA/GO-g-PLLA and PLLA/GO nanocomposites

The integrated preparation scheme of PLLA composites was shown in Fig. 1. PLLA/GO-g-PLLA nanocomposites were prepared through the solution-casting method with chloroform as the solvent. GO-g-PLLA and PLLA (1.0 g) were mixed, when the weight ratio of GO-g-PLLA to PLLA was set to be 0.1%, 0.5%, 1%, 2%, and 3%. For PLLA/GO nanocomposite, the weight percent of GO was 0.5%. After mixed with mechanical stirring for 3 h, the mixtures were poured into surface dishes and kept for 24 h at room temperature to remove the solvent. Finally, the dried GO-g-PLLA/PLLA and GO/PLLA composite films were obtained by drying them in a vacuum oven at 50 °C for 48 h.

2.5. Instruments and characterization

XPS and TGA measurements were carried out for the chemical structural characterization of GO and GO-g-PLLA. XPS measurements were performed using an X-ray photoelectron spectrometry (Kratos Axis Ultra DLD Shimadzu, Japan) equipped with a scanning monochromatic Al K α ($h\nu = 1486.6 \text{ eV}$) X-ray source. The morphology of GO, GO-g-PLLA and their dispersion in PLLA was observed by TEM (Tecnai G2 F20 S-TWIN, USA).

TGA curves were obtained from an instrument, TGAQ600, USA. The samples were heated from 25 °C to 800 °C at a rate of 10 °C/min under 60 mL/min of nitrogen purging.

The isothermal and non-isothermal crystallization behavior of the blends were investigated by DSC (Stare DSC-1, Mettler Toledo, Switzerland). For non-isothermal crystallization samples, the program was set heated from 25 °C to 220 °C and kept 5 min to erase previous thermal history. After that, the melt was cooled back to 25 °C and reheated to 220 °C again. Both the heating and cooling rates were set to be 10 °C/min, and the first cooling and second heating scan curves were recorded. The isothermal crystallization samples were heated from room temperature to 220 °C quickly and kept 5 min to erase the thermal history. Then the samples were cooled down to different crystallization temperature (100 °C, 110 °C, 120 °C) at the cooling rate of 50 °C/min and maintained enough time for the completely crystallization of the blends. After finished crystallization, the samples were reheated to 220 °C at the heating rate of 10 °C/min. All the DSC test were carried out under the protection of nitrogen atmosphere. The values of the crystallinity were calculated according to the follow Eq. (1):

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f(1 - M)} \times 100\% \quad (1)$$

where ΔH_m (J/g) and ΔH_{cc} (J/g) are melting enthalpy and the cold crystallization enthalpy obtained during the DSC heating process, respectively. ΔH_f is the fusion enthalpy of the completely crystalline PLLA. M represents the weight fraction of added GO-g-PLLA or GO in the sample. Here, the value of ΔH_f of PLLA was selected as 93 J/g.

Rheological measurements were carried out by a rheometer (DHR-1, TA instruments, USA) with a parallel plate. During the rheological measurements, a frequency sweep from 0.1 to 100 rad/s was performed with constant 1% strain under dry nitrogen atmosphere.

The electrical conductivities of composite samples with 100 mm diameter and 1 mm thickness were measured using A PC69 digital high resistance test fixture. (Shanghai Precision Instrument Manufacture, China)

The morphology of the electrospun mats and the distribution of cells in fibers was examined using scanning electron microscopy with an accelerating voltage of 10 kV (SEM, Tescan Vega3, Czech).

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