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# A facile method to produce graphene oxide-g-poly(L-lactic acid) as an promising reinforcement for PLLA nanocomposites

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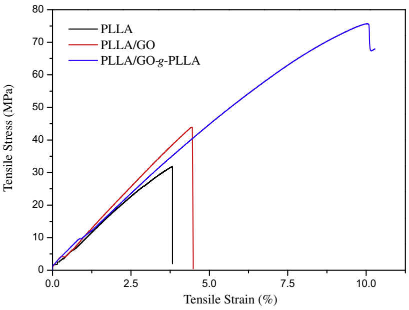
## HIGHLIGHTS

- GO grafted with PLLA (GO-g-PLLA) was synthesized by in situ polycondensation.
- The weight percent of PLLA chains in obtained GO-g-PLLA was as high as 30.8%.
- The mechanical property of PLLA/GO-g-PLLA composites was enhanced significantly.
- It is owing to the improvement of interfacial adhesion between GO-g-PLLA and PLLA.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Poly(L-lactic acid) (PLLA) nanocomposites reinforced with graphene oxide (GO) or GO grafted with PLLA (GO-g-PLLA) were prepared by solution blending and then compression molding method, where GO-g-PLLA was synthesized via one step based on in situ polycondensation of the L-lactic acid monomers initiated by lyophilized GO. The average thickness of GO was increased by about 2 nm and the weight percent of grafted PLLA chains in obtained GO-g-PLLA was as high as 30.8%. It was clearly evidenced that the functionalization of GO with this method enhanced its dispersion and interfacial interactions with the PLLA matrix and thus improved the final thermostability and mechanical properties of nanocomposites. The flexural and tensile strength of PLLA/GO-g-PLLA nanocomposites were increased by 114.3% and 105.7%, respectively, compared with neat PLLA.

## 1. Introduction

Compared with traditional composites, polymer nanocomposites exhibit dramatic changes in some properties at very low loadings (generally $\leqslant$2 wt%) of nanofillers like cellulose nanofibers [1], carbon nanotubes [2], graphite nanoplatelets [3–5], and nanoclays [6]. However, the optimal performance conferred by these nanofillers can be achieved only when the homogeneous dispersion of nanofillers and strong interfacial adhesion between nanofillers and polymer matrix are realized. Graphene, a single-atom-thick sheet of hexagonally arrayed $sp^2$-bonded carbon, chemically similar to carbon nanotubes and structurally analogous to silicate layers [7], has drawn the attention of researchers in various fields due to its remarkable mechanical, thermal [8], and electrical properties [9]. With such outstanding properties, graphene nanosheets can be usefully applied as a reinforcing material in polymers using a variety of methods including solution (or melt) blending [3,10,11] and in situ polymerization [12]. However, to improve the solubility of graphene nanosheets in various organic and aqueous solvents, as well as their miscibility with polymer materials, the preparation of graphene derivatives by chemical modification has been the subject of intense interest recently [13,14].

Poly(L-lactic acid) (PLLA), an aliphatic polyester produced from renewable biomasses such as corn and sugar beet, has been recently spotlighted as a biodegradable, sustainable, and eco-friendly

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substituent for petroleum-based polymers [15,16]. PLLA has balanced properties of mechanical strength, thermal plasticity and transparency [17]. Nevertheless, its crystallization rate, thermal and mechanical properties need to be improved for long-term high performance applications [18]. Many reports have verified that the addition of functionalized carbon nanomaterials can increase the crystallization rate, and promote the thermal stability and mechanical strength of PLLA. For instance, Cao and co-workers [19] made successful use of lyophilized graphene nanosheets to improve the mechanical and thermal properties of PLLA in some degree. The graphene nanosheets were in the form of chemically reduced graphene oxide which were prepared by a modified Hummers method and then chemically reduced with hydrazine. Yang et al. [20] prepared a series of PLLA/thermally reduced graphene oxide composites via the in situ ring-opening polymerization of lactide, using thermally reduced graphene oxide as the initiator. The thermal stability, crystallization rate and electrical conductivity of PLLA were increased. Although in situ polymerization is an effective way to disperse the fillers in the matrix uniformly and generate better interfacial interactions with the host polymer, the synthesis of high molecular weight PLLA requires severe conditions [21] and expensive precursor (lactide) [22]. In the works of Song et al. [23] and Yoon et al. [24], PLLA was successfully covalently grafted onto the convex surfaces and tips of the multi-walled carbon nanotubes (MWNTs) via one step based on in situ polycondensation of the commercially available L-lactic acid monomers. They prepared MWCNTs with carboxylic functional groups (MWCNTs–COOH) via a mixture of concentrated sulfuric and nitric acids oxidation. Subsequently, the MWCNTs–COOH acted as an initiator, and PLLA was grafted onto the MWCNTs–COOH surface. The resulting MWNTs-g-PLLA were mixed with commercially available neat PLLA to prepare PLLA/MWCNTs-g-PLLA nanocomposites and improved the initial modulus, tensile strength and crystallization rate of PLLA. Graphene oxide (GO) has a higher content of oxygen-containing functional groups [25,26] and higher specific surface area [27] than MWCNTs–COOH, thus it is expected to be more promising than MWCNTs–COOH in polycondensation of L-lactic acid. Besides, the preparation of GO is based on a frequently-used method to prepare graphite oxide by using strong oxidizing agents, which is then exfoliated to single or few platelets via sonication in water [19,28], without any other further treatment. But the facile one-step polycondensation method has not been applied to the functionalization of GO. It is desirable to use GO as the reactants or initiators in the in situ polymerization of L-lactic acid monomers to prepare GO grafted with PLLA (GO-*g*-PLLA). Moreover, the grafted polymer chains can also act as compatibilizer when graphene sheets are mixed with polymer, particularly when they are of the same nature as matrix, which can improve the interfacial adhesion and maximize the compatibility between the partners [29,30]. So it is estimated that GO-*g*-PLLA would exhibit excellent performance in the reinforcement of PLLA.

We herein described an in situ polycondensation approach, to functionalize the pristine GO with PLLA via one step from commercially available polycondensation-type monomers, L-lactic acid, as shown in Scheme 1. In our work, in order to prevent GO aggregation, we used lyophilization method to prepare GO powder, which was shown to be extremely light and macroporous, so that the functionalization of GO was facilitated and its dispersibility with polymer was improved [31]. GO-*g*-PLLA was successfully prepared judging from the results of Fourier transform infrared spectroscopy (FTIR) , X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and atomic force microscopic (AFM), and it was proved that the oxygen-containing functional groups on GO could initiate the polycondensation reaction of L-lactic acid. In addition, we prepared neat PLLA, PLLA/GO and PLLA/GO-*g*-PLLA nanocomposites by solution blending and compression molding and then made a comparative study on these three samples to clarify the important role of PLLA chains on GO surface in the enhancement of host polymer.

## 2. Experimental

### *2.1. Materials*

Natural graphite powder was provided by Nanjing Xianfeng Nanomaterial Science and Technology Co., Ltd., China. PLLA (biopla 6202F) was purchased from Ningbo Global Biological Material Co., Ltd. Its number-average molecular weights is $Mn = 1.1 \times 10^5$ g/mol.

L-lactic acid [$CH_2O(CH_3)COOH$] (85 wt% aqueous solution) was purchased from Tianjin Reagents Co., Ltd., which was dehydrated with magnetic stirring for 8 h at 110 °C under a vacuum distillation unit to remove the water before used as the monomer for polycondensation. Potassium permanganate ($KMnO_4$), sulfuric acid ($H_2SO_4$, 98%), phosphoric acid ($H_3PO_4$), hydrogen peroxide ($H_2O_2$), and Tin octoate ($Sn(oct)_2$) of reagent grade were purchased from Tianjin Reagents Co., Ltd. These chemicals were used as received.

### *2.2. Preparation of GO*

Graphite oxide was synthesized from commercial graphite powder according to a improved Hummer's method [25]. In detail, a 9:1 mixture of concentrated $H_2SO_4/H_3PO_4$ (360:40 mL) is added to a mixture of graphite flakes (3.0 g, 1 wt equiv.) and $KMnO_4$ (18.0 g, 6 wt equiv.), and then the mixture was stirred for 12 h at 50 °C. After that it was poured into ice water (400 mL) with 30% $H_2O_2$ (3 mL) and stood for one night. The resultant product was washed on the centrifuge until the pH value of the supernatant fluid became 7 and then was dried in a vacuum oven at 45 °C forming graphite oxide powder.

The solid was suspended in deionized water (1 mg/mL) and sonicated for 2.5 h [28,32] to generate a GO suspension. Subsequently, the aqueous GO suspension was frozen into an ice cube in a refrigerator (−15 °C) for 8 h and then was freeze-dried using a FD-1A-50 lyophilizer (Boyikang Co., Ltd., China) with a condenser temperature of −50 °C at a inside pressure of less than 20 Pa. After 48 h lyophilization and 48 h vacuum drying (45 °C) process, low-density, loosely packed GO powder was finally obtained.

### *2.3. Preparation of GO-g-PLLA*

To prepare GO-*g*-PLLA by melt polycondensation, GO (1.0 g) was mixed with dehydrated L-lactic acid (200 mL). The mixture was sonicated for 30 min to obtain a homogeneous dispersion of GO in the L-lactic acid. Then, $Sn(oct)_2$ (0.2 g) as the polycondensation catalyst was added into the viscous mixture. Melt-polycondensation of L-lactic acid with GO was carried out in 500-mL Florence flask for 5 h at 180°Cwith magnetic stirring under vacuum. The internal pressure in the polymerization reactor was about 100 Pa. The scheme of melt-polycondensation to prepare GO-*g*-PLLA is shown in Scheme 1. After melt-polycondensation, the final product was dissolved in excess chloroform and then filtered through the PTFE membrane to remove the unreacted monomer, PLLA homopolymer and PLLA ungrafted to graphene nanosheets [23,29]. The dissolution and filtration process were repeated several times until no PLLA in the filter liquor could be detected. The resulting solid was dried for 24 h at 50 °C under vacuum to obtain GO-*g*-PLLA.