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Fabrication of graphene/polylactide nanocomposites with improved properties

Xiao-Zuo Tong [a], Fei Song [a,*], Mao-Qin Li [a], Xiu-Li Wang [a,*], In-Joo Chin [b], Yu-Zhong Wang [a]

[a] Center for Degradable and Flame-Retardant Polymeric Materials (ERCPM-MoE), College of Chemistry, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Sichuan University, 29 Wangjiang Road, Chengdu 610064, China
[b] Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

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ABSTRACT

For the purpose of development of graphene/polylactide composites with good performance, a compatibilizer functionalized with pyrene was synthesized by one-step ring-opening polymerization, which presented strong π–π interaction with graphene. The dispersing stability of graphene in organic solvents facilitated the fabrication of composites with uniformly distributed graphene by a solution-cast method. For the resultant composites of graphene and polylactide, the compatibilizer showed positive effects of enhancing crystallization, thermal stability and mechanical property of the composites. Moreover, electrical conductivity of the polymer matrix was greatly increased with the incorporation of graphene, and the addition of the compatibilizer did not cause an obvious change in the electrical conductivity of the resultant composites. The results implied that the compatibilizer, which was obtained by the simple and facile synthetic strategy presented herein, had great potential in the field of composites based on polymer and carbon allotropes.

1. Introduction

Recently, polymer composites containing carbon allotropes are new class of materials, noteworthy among which graphene, a single sheet of graphite, holds remarkable thermal, electrical, and mechanical properties due to its 2D as well as one-atom-thick crystal structure [1]. With incorporation of graphene into polymer matrix, significant enhancement of properties such as electrical and thermal conductivity, mechanical strength, and flame retardancy can be achieved for prepared composites [2–5]. However, how to realize the uniform distribution and dispersion of graphene in polymer matrix without losing practical performances is a big problem we need to deal with. For this purpose, derivatives of graphene with alkyl or polymer chains have been synthesized, which can disperse or dissolve in organic solvents without aggregation for several months [6–8]. Generally, these chemical modifications of graphene were mainly conducted on the active groups of graphene, however, the definite amounts of the groups on graphene were hard to be confirmed and thus the molecular structure of synthesized derivatives of graphene was difficult to be well controlled and defined, which were not favorable to understand the structure–property relationship as well as to accurately modulate properties of prepared graphene/polymer composites. Compared with the chemical routes, physical decorations are easy to be handled without complicated modification of graphene. Different stabilizers, up to now, have been used to inhibit aggregation of graphene in aqueous solutions through π–π stacking or electrostatic stabilization [9–13], and very recently, an aromatic amphiphile based on an aromatic molecular sheet was synthesized for stabilizing graphene in aqueous solution [14]. Nevertheless, the synthesis route to this stabilizer is too complex and it has not been discussed whether graphene can be dispersed in organic solvents other than water, which is particularly more important for fabrication of graphene/polymer composites, because most engineering polymers are soluble in organic solvents. These existed issues stimulus us to explore a simple method to synthesize a novel stabilizer with well-defined structure for stabilizing graphene in organic solvent and making it convenient to prepare graphene/polymer composites with uniform graphene distribution.

In the present report, a molecule containing a pyrene fragment and a poly (L-lactide) (PLA) chain was synthesized by a simple one-step ring-opening polymerization strategy in the presence of 1-pyrenemethanol as an initiator. The resultant molecule was used as a stabilizer for graphene as well as a compatibilizer for development of composites based on graphene and PLA. Moreover, the interactions among PLA, graphene and the compatibilizer were investigated, and the mechanical property and electrical conductivity of the obtained composites were studied.

* Corresponding authors. Tel./fax: +86 28 85410755.
E-mail addresses: songfei520@gmail.com (F. Song), xiuliwang1@163.com (X.-L. Wang).

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2. Experimental

2.1. Materials

PLA resin (4032D) was supplied by Nature Works Co. (USA). Thermally reduced graphene (TRG) was supplied by XFNANO Materials Technology Co. Ltd. (Nanjing, China). L-lactide (purity ⩾ 99%) was purchased from Daigang Biomaterial Co. Ltd. (Jinan, China). 1-pyrenemethanol (analytical grade) was purchased from Alfa Co. and stannous octoate, $Sn(Oct)_2$, was obtained from Sigma Co. (USA). Other reagents were purchased from Zhenxing Chemical Co. (Chengdu, China) and used as received.

2.2. Synthesis of poly (L-lactide) functionalized with pyrene (Py-PLA-OH)

A graphical illustration of the synthesis route to Py-PLA-OH is shown in Fig. 1. In a typical experiment, 1-pyrenemethanol and L-lactide with a molar ratio of 1:14 were added in a glass flask and then the reactor was immersed in an oil bath at 100 °C under rigorous stirring. $Sn(Oct)_2$ was injected with a syringe under nitrogen, and the reaction was performed at 140 °C for 24 h. The polymerization was then quenched by cooling the reactor to 0 °C. The crude product was dissolved in chloroform and precipitated with excess methanol. After filtration, the obtained product was dried at 60 °C under vacuum for 24 h.

2.3. Preparation of TRG/PLA composite films

For the preparation of TRG/PLA composite films, a common method reported previously was used [2,20]. Py-PLA-OH and TRG with a weight ratio of 10:1 were first dispersed in *N*,*N*-dimethylformamide (DMF) under agitation and sonification at room temperature, and then the dispersion was mixed with PLA in DMF solution at 60 °C. After coagulation with methanol, the obtained product, which was denoted as TRG/PLA/Py-PLA, was vacuum-dried at 80 °C for 24 h and hot-pressed into sheets at 185 °C under 10 MPa and cut to the required dimensions for tests. For a comparison study, the TRG/PLA sheets without the compatibilizer, Py-PLA-OH, were also prepared by the same method.

2.4. Characterizations

The ^1H NMR measurement was performed on an NMR spectrometer (Varian Germini 400) by using $CDCl_3$ as a deuterated solvent. The fluorescence emission spectra were obtained from a VARIAN Cary Eclipse spectrophotometer (concentration of Py-PLA-OH, 2.0 mg/mL; Py-PLA-OH/TRG, 10:1; excitation wavelength, 340 nm). Raman spectra were recorded on a LabRAM HORIBA spectrophotometer at an excitation wavelength of 532 nm. Electron micrographs were acquired by using a transmission electron microscopy (TEM, Philips Model CM200 Netherlands) at an accelerating voltage of 120 kV. The composites were microtomed to slices of 60 nm thickness with RMC Ultra Microtome Model MTX (USA) and collected on standard TEM grids prior to test. The diffraction behavior of PLA and its composites was studied by using a DX1000 X-ray diffractometer (XRD) equipped with a Cu Kα radiation at a generator voltage of 40 kV and a current of 40 mA. The scans were carried out at a scan rate of 2°/min. Dynamic mechanical analysis (DMA) was performed on a Dynamic Mechanical analyzer (Rheometric scientific Co.) under tension mode. The samples with a thickness of 0.3 mm were scanned from −30 to 160 °C at a heating rate of 3 °C/min. The strain amplitude and frequency of dynamic oscillatory loading was 0.02% and 1 Hz, respectively. The tensile strength (TS) and elongation at break (ε_b) of the samples were investigated using a universal testing machine (Model 4302, Instron Engineering Corporation) with a tensile rate of 5 mm/min. The testing temperature and relative humidity (RH) were 25 °C and 60%, respectively, and five parallel measurements were carried out for each sample. Thermal gravimetric analysis (TGA) was performed under a nitrogen atmosphere on a Netzsch TG 209 F1 apparatus using a heating rate of 10 °C/min from 40 to 700 °C. The oxidation induction temperature (OIT) was evaluated in a dynamic mode described previously [15]. Samples (about 4 mg) were heated in the DSC from 40 to 550 °C at a rate of 10 °C /min with an oxygen flow of 50 mL/min, and OITs were determined by the onset of exothermic oxidation reaction of PLA shown in the calorimetric curves. A two-probe resistance measurement was carried out for determining the resistivity at room temperature with a Keithley 6517B digital electrometer when the resistance of the samples was lower than $10^8\ \Omega$ (thickness of sample: 2.0 mm). PC68 Digital High Resistance Test Fixture (Shanghai Precision Instrument Co., China) was used to determine the resistance of samples higher than $10^8\ \Omega$ (thickness of sample: 0.3 mm).

3. Results and discussion

Generally, the Py-PLA-OH molecule was synthesized in a simple way, and its structure was characterized by NMR spectroscopy. The ^1H NMR spectrum of molecule showed that its chemical structure was in full agreement with that presented in Fig. 1, and its molecular weight was calculated to be 2600 g/mol based on the integration areas of H_a and H_c (Fig. 2).

To investigate the interaction between Py-PLA-OH and graphene as well as the capability of Py-PLA-OH to stabilize graphene in DMF, the purchased TRG was dispersed in DMF with or without Py-PLA-OH under sonication. The resultant dispersions were kept at room temperature and their stability was shown in Fig. 3b. It can be clearly seen that a partial precipitation was happened to pure TRG within 12 h and almost a complete precipitation occurred within 24 h. However, TRG can be well stabilized and no precipitation was observed in 24 h for the dispersion with the addition of Py-PLA-OH, which may be attributed to the interaction between TRG and Py-PLA-OH.

As a further investigation, fluorescence measurement was conducted for pure Py-PLA-OH and TRG/Py-PLA-OH in DMF solutions (Fig. 4a). Py-PLA-OH showed an obvious fluorescence emission

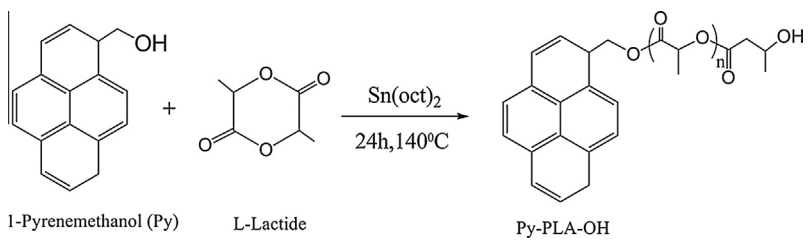

Fig. 1. Synthesis route to Py-PLA-OH.