Facile preparation of poly(p-phenylene benzobisoxazole)/graphene composite films via one-pot in situ polymerization

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ABSTRACT

Since being discovered, graphene shows promise as reinforcements in high-performance nano-composites. In the present study, we describe a novel strategy to design and prepare poly(p-phenylene benzobisoxazole) (PBO)/graphene composite. Graphene oxide (GO) was first modified by 4, 6-diaminoresorcinol (DAR) to improve the reactivity, solubility, and dispersivity of GO in polymer matrix. Without separation and purification, GO-DAR was further incorporated with PBO through in situ polymerization, and PBO/GO composite films were obtained by thermoforming process. The structure and morphology of GO-DAR and PBO/GO films were characterized and the mechanical and thermal properties were investigated. The incorporation of GO improved the thermal stability of PBO. Mechanical property measurements revealed that the PBO/GO films exhibited a tensile strength (148 MPa) and Young's modulus (6.2 GPa) at a GO loading of 1.5 wt%, corresponding to 39.6% and 72.2% increase compared to the PBO film, respectively. The one-pot in situ procedure wraps GO with PBO chains, improves the dispersion and alignment of GO in PBO matrix, enhances PBO chain packing order, which are considered to be the main reasons for the performance improvement of PBO.

1. Introduction

Rigid-rod polymers are attractive materials for use in high-performance structural applications, including aircraft components or fire protection garments. Poly(p-phenylene benzobisoxazole) (PBO), one of the representative rigid-rod polymers, is characterized by high tensile strength, high stiffness, high thermal stability, and good chemical resistance [1]. However, even for commercial high modulus PBO, there is still a large gap between the actual tensile modulus and the theoretical tensile modulus [2]. Many efforts have been made to increase the mechanical properties of PBO and to overcome this gap. The nanoscale materials such as carbon nanotubes (CNTs), graphene, silicates, nanoclays have been considered as effective reinforcing or functional fillers for polymeric materials including PBO.

Among the nanoscale materials, CNTs have been considered as good fillers for the reinforcement of PBO. During the past few years,

CNTs/PBO composites were prepared using in situ polymerization of PBO with etched CNTs [3], carboxylated CNTs [4—8], oligo-hydroxyamide functionalized CNTs [9], or solution blending of PBO and CNTs [10,11]. The reports suggest that the introduction of CNTs could significantly enhance the mechanical, electrical, magnetic, thermal resistance properties of PBO. Inspired by CNTs, graphene has moved into the spotlight as a novel reinforcing material for PBO. Since the discovery in 2004, graphene, a new member of the carbon nanomaterials' family, has drawn enormous research interest for its unique thermal, mechanical, and electrical properties [12]. The high special surface area (2630—2965 m^2/g) [13] and large aspect ratio (>2000) [14] of graphene sheets lead to outstanding reinforcement for polymer matrices [15,16]. However, graphene is difficult to dissolve or disperse in common organic solvents or polymeric matrices for making useful materials. As known from classic composites science, the fine dispersion of graphene in the matrix is one of the most important and challenging tasks towards maximizing the transfer of the graphene attributes into the composites. Recently, a variety of chemical and physical approaches have been reported to enhance the dispersion of graphene in PBO matrix. Similar with the CNTs, graphene/PBO composite fibres have been prepared via in situ polymerization of

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PBO with pristine graphene [17] or graphene oxide (GO) [18,19]. Furthermore, graphene/PBO (as well as graphene/poly-p-phenylene benzobisthiazole) composite films are fabricated by solution blending methods [20,21]. However, challenges still remain mainly from the difficult dispersion of the graphene in PBO media or the complicated preparation methods, which require large amounts of strong acid.

In comparison to the previous fabrication methods of graphene/PBO composites, the development of a simple, one-pot strategy for the preparation of the composites would represent a significant advance. To accomplish this goal, our strategy is to utilize the PBO monomer 4, 6-diaminoresorcinol (DAR) to modify the graphene at the very beginning of the polycondensation reaction. This design would improve the reactivity, solubility, dispersivity, and interfacial adhesion of graphene in polymer matrix. Without purification or separation, another PBO monomer terephthalic acid (TA) is then added into the reaction system for in situ polymerization. Finally, graphene/PBO composite films were fabricated using thermoforming process. The typical procedure for preparing graphene/PBO composite films is shown in Fig. 1.

2. Experimental section

2.1. Materials

The monomer for polymerizing PBO, DAR·2HCl, was synthesized in our laboratory from 1, 2, 3-trichlorobenzene by a modified method [22]. TA, phosphoric acid, and P_2O_5 were purchased from Shanghai Reagents Company. Graphite powder (500 meshes) was provided by Nanjing XFNANO Materials Tech Co. Ltd. Methanesulfonic acid (MSA) was purchased from Sigma−Aldrich Chemical Company.

2.2. Preparation of DAR functionalized graphene (GO-DAR)

GO was synthesized by using the modified Hummers method. In a 250 mL three-neck round-bottom glass flask, equipped with a mechanical stirrer and a nitrogen inlet/outlet, GO (0−1.5 wt%, based on the PBO polymer) and 21.60 g of H_3PO_4 (85 wt% in H_2O) were placed. After sonication for 2 h, 27.05 g P_2O_5 was added in three portions, then 10.65 g. DAR·2HCl was added. The reaction mixture underwent dehydrochlorination under a nitrogen atmosphere at 60 °C for 2 h and subsequently at 100 °C for 10 h. A condensation step was then carried out at 120 °C for 6 h, 140 °C for 2 h, and 180 °C for 2 h, in which GO was further modified by DAR. The reaction solution was used directly in the following polymerization. In order to characterize the GO-DAR, the reaction was terminated by the addition of water. The GO-DAR was isolated by filtration. The collected solid was washed with water and acetone for several times and then dried by vacuum freeze drying. XPS analysis: C 1s 71.4%, O 1s 18.1%, N 1s 11.5%. The degree of functionalization was

estimated from the XPS elemental composition to be 1 DAR group for every 8 carbons of the GO-DAR.

2.3. One-pot in situ polymerization of PBO with GO-DAR

The one-pot in situ polymerization was continuous prepared using the reaction solution obtained above. TA (8.30 g) was added into the above mixture, and the solution was further stirred at 120 °C for 4 h. Another 19.50 g of P_2O_5 was then added to the mixture to combine H_2O formed by the polycondensation reaction and bring the P_2O_5 concentration to 83.5 wt%. The resulting polymer solution was heated to 200 °C at 5−10 °C/h stepwise, and kept at 200 °C for 2 h with constant stirring. The concentration of PBO synthesized in PPA was controlled to be 14 wt% and the GO content in the graphene/PBO composites was adjusted to be 0.5, 1.0 and 1.5 wt%.

2.4. Fabrication of graphene/PBO composite films

The thick polymer composite solution was poured onto a flat plate covered with Teflon. Then, the composite films with thickness of 100−200 μm were prepared by compression moulding at 180 °C and at 10 MPa for 20 min, and subsequently cooled to 30 °C at 10 °C/min under pressure. The sample was immersed in deionized water for 1 day to remove PPA. The composite films were dried overnight under vacuum at 80 °C.

2.5. Characterizations and measurements

Fourier transform infrared spectra (FT-IR, Bruker, Tensor 27), Raman spectra (Horiba Jobin Yvon, France), Wide-angle X-ray diffraction (WAXD, D/Max-2550 PC rotating anode X-ray generator with Ni-filtered Cu Ka radiation operated at 350 mA and 40 kV), X-ray photoelectron spectroscopy (XPS, RBD upgraded PHI-5000C ESCA system, Lemans−Elmer), and Solid-state ^{13}C cross-polarization magic-angle-spinning nuclear magnetic resonance (^{13}C CPMAS NMR, 9.4 T on a Varian Infinity Plus 400 spectrometer operating at a ^{13}C Larmor frequency of 100.4 MHz) were used to characterize the chemical structure of the samples. Transmission electron microscopy (TEM, JEOL, JEM-2100F) and atomic force microscope (AFM, Sounding Housing SPA 400) were used to characterize the morphology and structure of the samples.

TG analyses were performed with a thermogravimetric analyzer (Netzsch STA449C) from room temperature to 850 °C at a heating rate of 10 °C min^{-1}. The tensile measurements were carried out with an Instron 5569 MicroTester at a crosshead speed of 1 mm/min. The sample thickness was measured using caliper.

3. Results and discussion

In recent years, graphene-based fillers are expected as promising reinforcements for polymer. In order to achieve optimal
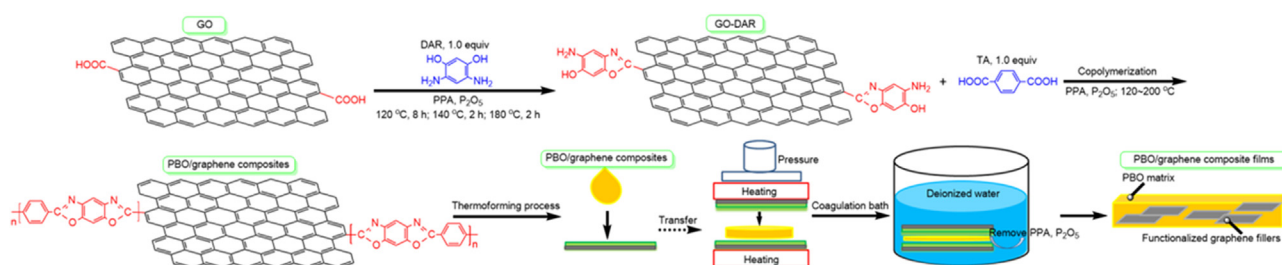

Fig. 1. One-pot synthesis of PBO/graphene composites and the procedure for composite films fabrication.