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Facile method to functionalize graphene oxide nanoribbons and its application to Poly(*p*-phenylene benzobisoxazole) composite

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ABSTRACT

Graphene oxide nanoribbons (GONRs), as a new member of carbon family, attracted extensive attention in industry and science field. It has considered to be as a promising nanomaterial for applications in the field of materials science, energy storage and optics science due to its extraordinary mechanical, electrical and thermal properties. Hence, in this study, we carried out a facile and efficient strategy for preparing poly (phenylene benzobisoxazole) (PBO)/GONRs(PGR) composite fibers via one-pot in situ polycondensation method for enhancement in mechanical and thermal properties. The GONRs sheets in this work were obtained by unwrapping multi-walled carbon nanotubes (MWCNTs) side walls, and then directly reacted with PBO monomer 4,6-diaminoresorcinol(DAR) and covalently grafted on PBO molecular chains. The structure and morphology of GONRs and modified GONRs were well demonstrated by the FT-IR, XPS and TEM analysis for confirming the formation of chemical bond between GONRs and PBO molecular chains. The mechanical and thermal properties of PGR composite fibers were also investigated. It was found that the performance of composite fibers about 32.1% improvement in tensile modulus, 24.2% in tensile strength and 10.5% thermal stability, respectively.

1. Introduction

During the recent years, polymer composite with nano-fillers have generated tremendous interest in industry and science due to its superior mechanical and thermal properties without sacrifices other valuable properties compared to neat polymer [1–5]. As a new carbon family nano-filler, graphene oxide nanoribbons (GONRs, the nanometre-wide strips of graphene oxide) also displays perfect mechanical and thermal properties due to its intriguing structure and characters [6]. It has attracted increasingly study as a reinforced nano-filler to improve the properties of polymer matrix [7–11], and showed a bright prospects application in electronic [12–14], energy storage devices [15–17] and catalyst fields [18]. However, as we know, for the most nano-fillers enhanced polymer composite, the poor dispersion as well as insufficient interfacial strength between nano-fillers and polymer matrix, are persistent problems for composite application. Hence some method should be developed and proposed to solve above problem. For example, Feng [19] et al. tried to modify GO sheet with different kinds of chemical reductants to improve the dispersion ability and enhance the interfacial strength between nano-fillers and polymer matrix. The results displayed that the performance of polymer composite has an obviously improvement after the incorporation the modified GO. Similar works such as improving the interfacial property between carbon fiber and poly(ether-ether-ketone) polymer by coating modified GO on the carbon surfaces or enhancing the mechanical and thermal properties of polybenzoxazines resins by adding the modified GO sheet into polymer matrix also have been studied by Zhao and Jian et al. [20,21]. Hence, the manufacture of such GONRs composite with optimized performance also requires the nano-filler homogeneously dispersion in polymer matrix as well as a strong interfacial interaction between the nano-filler and the polymer matrix.

GONRs' chemical structure unlike to other nano-fillers, such as carbon nanotube or fullerene, which is consists of oxygen functional groups on the basal planes and edges. These functional groups offer versatile sites for further group modification, improving compatibility and reinforcing efficiency of GONRs in polymeric matrix. Therefore, it is easy to design and prepare GONRs-polymer composite polymer using various modifying methods to modulate the interphase structure between GONRs and the polymer [22]. Consequently, GONRs with functionalized groups was studied to incorporate into polymer matrix to

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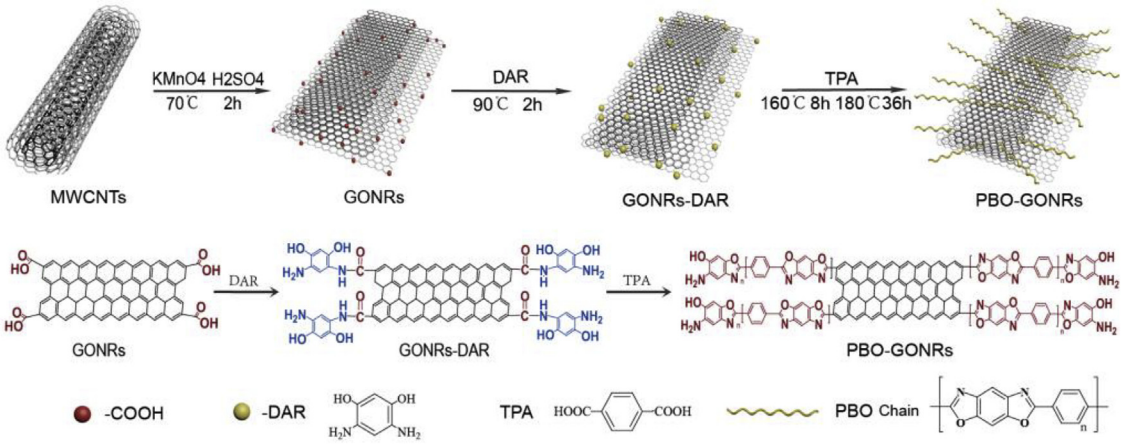

Fig. 1. (a) Reaction schematics between GONRs and PBO.

improve tensile properties and thermal properties [7–10]. However, as one of the widely used Poly(*p*-phenylene benzobisoxazole) (PBO) super strong organic polymer fiber due to its ridge molecular structure, the preparation of PBO/GONRs (PGR) composite fibers has not been reported up to now.

Hence, in this work, we report a simple and facile method to enhance the properties of PBO fibers through preparation of PGR composite fibers via one-pot in situ polycondensation in acidic media. In the present study, GONRs were first obtained by unwrapping MWCNTs side walls [6] and GONRs were then directly reacted with PBO monomer 4,6-diaminoresorcinol(DAR) and covalently grafted on PBO molecular chains. After that, another monomer terephthalic acid (TPA) was further added into above reaction system for further reaction as shown in Fig. 1. The morphology and structure of GONRs, GONRs-DAR was well demonstrated for forming the chemicals bonds between GONRs and DAR. In addition, the structure and properties of the PBO and PGR composite fibers were also investigated by the method of Wide angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), thermogravimetry (TG) and tensile testing. The tensile modulus, tensile strength, and thermal stability of PGR composite fibers were obviously increased for 32.1%, 24.2% and 10.5%, respectively compare d to original PBO fibers.

2. Experimental

2.1. Materials

4,6-diaminoresorcinol dihydrochloride (DAR·2HCl), was prepared from 1,2,3-trichlorobenzene by a modified method [23]. Terephthalic acid(TPA) purchased from Shanghai Reagents Company and the MWCNTs purchased from Nanjing XFNANO Materials Tech Co Ltd. Polyphosphoric acid(PPA), Methanesulfonic acid (MSA) and other remaining chemicals were purchased from Sigma-Aldrich Chemical Company and used as received.

2.2. Synthesis of GONRs sheet

The GONRs were prepared by the chemical oxidative longitudinal unzipping of MWCNTs in mixed acid (H_2SO_4:H_3PO_4) according to reported previously [6,24] where 5 g of $KMnO_4$ was used for each 1 g of MWCNTs. The concentration of $KMnO_4$ in H_2SO_4 was 0.5 wt%/vol as originally reported. The diameter of MWCNTs was 40 nm-60 nm (Caution: It has reported that at much higher concentrations, 7 wt%/vol $KMnO_4$ in H_2SO_4, the mixture can explode on heating). In brief, 1 g MWCNTs and 240 mL mixed acid (H_2SO_4:H_3PO_4 = 9:1) were mixed and stirred in a flask. Then, 5 g $KMnO_4$ was added to the mixture. The reaction mixture was stirred at room temperature for 1 h and then heated to 70 °C for an additional 2 h. After reaction, the reaction setup was transferred into an ice bath atmosphere. Around 750 mL deionized water and 30 mL H_2O_2 (30%) were poured slowly into the above mixture solution stirring another 2 h. The GONRs solution were then washed with a 120 mL HCl (30%) and centrifuged solution to get solid product. The obtained solid product was then washed with deionized water and ethanol many times combining with centrifuge until the pH of the product solution became about 6.

2.3. Preparation of DAR functionalized GONRs (GONRs-DAR) composite

In a four-necked 500 mL round-bottom glass flask, equipped with a high purity nitrogen inlet/outlet and a powerful mechanical stirrer. 15 g of DAR·2HCl, 90.12 g of polyphosphoric acid(PPA) (83.5 wt%) solution (50.12 g P_2O_5, 40 g H_3PO_4) and 1.5 g of $SnCl_2$ $2H_2O$ were added into flask. The mixture was continuously stirred at 90 °C until complete removal of hydrochloride gas under a high purity nitrogen atmosphere. 0.75 g (0.5 wt%, based on the amount of DAR) of GONRs were then added into above flask string at 90 °C about 8 h for reaction. After that the DAR functionalized GONRs sheet were obtained. In this work, to simplify the preparation process, the above reaction system was directly used in the following polymerization. However, to demonstrate the GONRs-DAR composite, the reaction system can terminate by the adding of deionized water into reaction system. The GONRs-DAR solid product was then obtained by filtrating the solution and dried using vacuum freeze-drying method.

2.4. Preparation of PGR polymer composite

The polymerization was continuous fabricated using above obtained the reaction solution. 12 g of TPA, and another 25.6 g of P_2O_5 were added into the reaction solution to make the P_2O_5 concentration up to 83.5 wt% and resulted in a final polymer concentration of 12 wt%. The polymerizing mixture was stirred under high purity nitrogen atmosphere at 120 °C for 8 h, 140 °C for 12 h and 160 °C for 16 h. It was then heated to 180 °C stepwise at 10 °C/h and kept at this temperature for another 36 h with constant stirring. The amount of GONRs was 0.1 0.25 0.5 0.75 and 1.0 wt% with respect to the DAR concentrations were prepared in the polymerization.

2.5. Fabrication of PBO and PGR composite fibers

The PBO and PGR composite fibers were prepared using the dry-jet wet-spinning technique. The newly prepared PBO or PGR composite dope was first transferred to the dope tank under the protection of a nitrogen atmosphere. The dope tank was then heated to 180 °C and kept this temperature about 3 h before spinning to remove the bubble