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High strength polyimide fibers with functionalized graphene

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ABSTRACT

Graphene possesses unprecedented physical and chemical properties and has been thought to be ideal filler for reinforcing fibers' mechanical properties. However, graphene is difficultly dispersed in polymer which severely restrict to prepare high-strength and high-modulus composites. In this work, we report an effective method to fabricate a kind of organ-soluble polyimide (PI)/graphene composite fiber using *in situ* polymerization. Graphene oxide (GO) is modified by 4,4′-diaminodiphenyl ether (ODA) to obtain the GO-ODA nanosheets which exhibit excellent dispersibility and compatibility with the organ-soluble PI matrix. WAXD results show that these 2D nanosheets have a significant influence on the crystallization, aggregation or assembly behaviors of the polymer chains. The PI/graphene composite fiber containing 0.8 wt% of GO-ODA presents a tensile strength of 2.5 GPa (1.6 times higher than the pure PI fiber), and tensile modulus of 126 GPa (223% raises compared with pure PI fiber). Furthermore, the incorporation of graphene significantly improves the glass transition temperature and thermal stability of the composite fibers. Thanks to the excellent hydrophobic properties of graphene, the hydrophobic behavior of the composite fibers is greatly improved. This effective approach shows a potential application in fabricating multifunctional polymer-based composite fibers.

1. Introduction

High performance fibers are unique because they are an enabling technology for so many present and future high-technology products. In recent years, significant progress has been made in high performance fibers that are produced from rigid and flexible polymers, such as Zylon, Kavlar, Dyneema, M5 and Carbon fibers [1]. The mechanical properties of the novel synthetic fibers make them competitive in most applications in light, slender, load bearing stiff advanced composite components and structures.

Among these polymeric fibers, aromatic polyimide fiber has been recognized as one of the important members due to its excellent thermal stability, mechanical properties along with their good chemical resistance, low creep and excellent radiation shielding capability [2–5]. However, the mechanical properties of as-prepared PI fibers are not adequate enough to meet the requirements of the advanced composites. To solve this problem, there are two general approaches: to structurally modify the aromatic PIs [6–8] and to fabricate PI-based nanocomposites with reinforcements [9,10]. But the increase of rigidity of polyimide backbones usually hinders their processability in common organic solvents. Polyimide nanocomposites containing various nanosheets have been extensively studied, resulting in enhanced properties of stiffness/toughness balance, heat distortion temperature, flame proofing, and/or abrasion resistance of the matrices [11–14]. Chen et al. [15] prepared a series of PI/MWNT nanofibers by electrospinning and the thermal and mechanical properties of nanofibers are significantly improved with the incorporation of MWNTs. Wu et al. [16] synthesized PI composites containing POSS units in their main chains, exhibiting a low dielectric constant, high thermal stability, good solubility, and high modulus and strength. Recently, an increasing attention has been paid to the PI/graphene nanocomposites owing to the peculiar two-dimensional structures and outstanding properties of graphene nanosheets [17–19]. It was found that the addition of modified graphene into polyimides resulted in an increased tensile strength, up to 844 MPa [20]. Luong et al. [21] reported that incorporation of 0.38 wt% ethyl isocyanate-treated graphene oxide (iGO) into PI increased the tensile strength from 122 MPa to 131 MPa and the Young's modulus from 1.8 GPa to 2.3 GPa. Huang et al. [22] achieved a 30% increase in tensile strength and a 46% raise in Young's modulus at a graphene loading 0.2 wt%, and the decomposition temperature of PI increased by 15 °C. Although PI/graphene composites have been widely reported, most of them were studied in the form of films while not fibers. Besides,

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the actual improvements of the composites were relatively lower than that have been expected [23,24]. Therefore, it is worth to research the effects of graphene on PI fibers and explore the potential applications of PI/graphene composite fibers.

It is known that there are two general methods to prepare polyimides. One common procedure is two-steps, which consists of the synthesis of polyamic acid (PAA, precursor of polyimide) and subsequent thermal imidization of PAA [25–27]. Although it is simple to prepare PI/graphene composites by utilizing PAA/graphene oxide (GO) or chemical modified GO (CMG) composites as precursors [28,29], two issues have to be addressed in the imidization process. Firstly, as the functional groups of GO are partially removed during high temperature treatment process, the interfacial interactions between PIs and graphene are not strong enough for effective load transfer [22]. Secondly, in the thermal imidization process, it is possible that amide groups of PAA may react with carboxylic acids on GO to form a line imide, resulting in a poor stability than that of cyclic imide structures. The other preparation method to prepare polyimides is one-step solution polymerization [30–32]. It can also obtain PI fibers with higher crystallinity and higher molecular weight, showing more advantages to fabricate PI-based nanocomposites. To our knowledge, there is no report about the studies on PI/graphene fiber synthesized by one-step strategy.

Based on the above considerations, in this present study, a series of organ-soluble PI/graphene composites were fabricated utilizing grafting strategy by a one-step method and then PI/graphene composite fibers were prepared by a traditional wet-spinning process. To enhance the interactions between nanosheets and polymer matrix, 4,4′-diaminodiphenyl ether (ODA) modified GO nanosheets (GO-ODA) were synthesized by treatment of the GO with excess of ODA, providing a versatile starting platform for the *in situ* fabrication of composites by grafting PI chains at the reactive sites of functional GO-ODA nanosheets. Both the tensile strength and Young's modulus of fibers are dramatically increased with low graphene loadings. Furthermore, the glass transition temperature (T_g), thermal property and hydrophobic behavior of composite fibers were also discussed in detail.

2. Experimental section

2.1. Materials

Graphite powder with an average particle size of 30 μm was obtained from Shanghai Yifan Graphite Co., Ltd. Potassium permanganate ($KMnO_4$) was purchased from Reagent NO.1 Factory of Shanghai Chemical Reagent Co., Ltd. Concentrated sulfuric acid (H_2SO_4) and hydrochloride (HCl) were purchased from Pinghu Chemical., China. Sodium nitrate ($NaNO_3$) was purchased from Shanghai Kechuang Chemicals Co., Ltd. Hydrogen peroxide (H_2O_2) was obtained from Shanghai Jinlu Chemicals Co., Ltd. 3, 3′, 4, 4′-Benzophenonetetracarboxylic dianhydride (BTDA) was obtained from Beijing Multi Technology co., Ltd., and dried in vacuo at 120 °C for 24 h prior to use. 2,2′-Bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFMB) and 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) were purchased from Changzhou Sunlight Pharmaceutical Co., Ltd. N-methyl-2-pyrrolidone (NMP) was purchased from Sinopharm Chemical Reagent Co., Ltd. and stirred in the presence of phosphorus pentoxide (P_2O_5) overnight and then distilled under reduced pressure. Other commercially available reagent grade chemicals were used without further purification.

2.2. Preparation of GO and GO-ODA

GO sheets were synthesized from nature graphite powder by modified Hummers' method [33]. Nature graphite powder (4 g), $NaNO_3$ (2 g) and concentrated H_2SO_4 (100 ml) were added into a 250 mL three-neck flask and stirred at the temperature of 0–5 °C. $KMnO_4$ (15 g) was gradually dropped, then the solution was heated to 35 °C and maintained for 12 h. Distilled water (300 ml) was slowly added into the mixture with the elevated temperature of 90 °C for 30 min. Successively, 20 ml of H_2O_2 was added. The mixture was filtered and washed with 3% HCl aqueous solution and water. The sample of GO was obtained after being dried.

To synthesize GO-ODA nanosheet, we prepared GO/NMP colloid solution by the solvent-exchange method to ensure the GO being well dispersed in NMP [34]. 0.3 g ODA was added into 100 ml GO suspension (1.0 $mg \cdot ml^{-1}$) and then stirred at 80 °C for 24 h under nitrogen atmosphere. The mixture was filtered and washed with NMP for several times to remove the excess ODA. The GO-ODA sample was obtained after being dried in vacuo at 50 °C for 24 h (as shown in Scheme 1A).

2.3. Synthesis of PI/GO-ODA and PI/GO spinning solutions

Organ-soluble PI/GO-ODA solutions with various loadings of GO-ODA were synthesized by the following procedure as shown in Scheme 2A. A representative polymerization is as follows: GO-ODA (0.087 g) was firstly dispersed in anhydrous NMP (20 mL) by sonication for 2 h. A 250 mL three-necked flask equipped with a nitrogen inlet and a mechanical stirrer was charged with distilled NMP, TFMB (3.84 g, 0.012 mol), BIA (4.03 g, 0.018 mol) and appropriate amount of GO-ODA/NMP colloid solution. After the diamines were dissolved, equimolar dianhydride BTDA (9.67 g, 0.03 mol) was added (Scheme 1B). The solution was stirred at room temperature for 3 h, and isoquinolin (*ca.* 0.2 g) was added and further stirred for 3 h at 120 °C. Then the mixture reacted at 195 °C for 10 h, and the water produced during the imidization was continuously removed with a stream of nitrogen. Thus, a spinning solution containing 0.5 wt% of GO-ODA in PI was obtained. The PI/GO-ODA solutions with 0.3 wt%, 0.8 wt% and 1 wt% of GO-ODA were prepared via the above mentioned steps. To compare the effects of GO and GO-ODA on the properties of the composite fibers, PI/GO solutions with GO particles were also prepared according to the same method.

2.4. Wet-spinning of copolyimide fibers

The above spinning solutions were filtered and degassed at 100 °C prior to spinning. The composite dopes were extruded through a spinneret (50 holes with 80 μm in diameter) into a coagulation bath. Solidified filament entered into the second and third washing bath filled with water (60 °C), and then clustered at the forth spool (Scheme 2B). The fibers were dried, and then drawn with various ratios in a furnace over 450 °C.

2.5. Characterization

ATR-FTIR spectra were recorded on a Nicolet 8700 spectroscope with the range of 4000–400 cm^{-1}. X-ray diffraction (XRD) measurements were carried out using a Rigaku D-max-2550 diffractometer with Cu K_α Radiation. Morphologies of the cross section of the fibers were observed on a scanning electron microscope (SEM) (HITACHI SU8010) at an accelerating voltage of 3.0 kV. Transmission electron microscopy (TEM) was performed with a Hitachi H-800 electron microscope operating at an accelerating voltage of 100 kV. Typical tapping-mode atomic force microscopy (AFM) measurement was taking using Multimode SPM from Digital Instrument with a Nanoscope IV controller made by Veeco Instrument Inc. Samples for AFM measurement were prepared by depositing a