



# Enhanced mechanical properties of polyimide composite fibers containing amino functionalized carbon nanotubes



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## ABSTRACT

Carbon nanotubes (CNTs) have been gained attention and interest to be as ideal reinforcement fillers due to their exceptional theoretical mechanical properties for a long time. To date, the reinforcing effect of the CNTs in most composite systems is still not satisfied. In the present study, by incorporating a novel NH<sub>2</sub>-MWCNTs/NMP suspension into the polyimide matrix *in situ* polymerization, a series of PI/NH<sub>2</sub>-MWCNTs composite fibers have been fabricated using wet-spinning technique. Detailed studies based on different spectroscopic characterizations suggested that there exist multiple interfacial interactions between NH<sub>2</sub>-MWCNTs and polyimides (PIs) including the hydrogen bonding and  $\pi$ - $\pi$  interaction. Wide-angle X-ray scattering measurements revealed the evolution of the aggregation structure of these composite fibers during heat-drawing process, and the results illustrated that the incorporated amino functionalized CNTs showed beneficial effects on the packing and orientation of PI molecular chains. Attributed to the above advantages, the resulting composite fiber containing 0.4 wt% NH<sub>2</sub>-MWCNTs presented a tensile strength of 2.41 GPa (approximately a 47% increase over neat PI fiber), and the modulus of 99 GPa (27% raises compared with neat PI fiber). Meanwhile, dimensional stability of the PI fibers also has been improved by this effective approach.

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## 1. Introduction

Aromatic polyimide fiber (PI) has been recognized as one of the most important high-performance polymeric fibers with superior performances such as excellent thermal stability, good chemical resistance, radiation shielding capability and so on [1–3]. In order to expand the application of the PI fibers, mechanical properties and other performance need to be improved. Generally, there are two approaches to improve the mechanical properties of PI fibers: to structurally modify the aromatic PIs and to fabricate PI-based composites with reinforcements. For the structure modification, such as introducing rigid heterocyclic units to the polymer backbones, several researchers have made great efforts. Sukhanova et al. fabricated a series of high performance PI fibers containing the rigid aromatic diamine 2,5-bis(4-aminophenyl)-primidine (PRM) with a tensile strength and modulus of 3.0 and 130 GPa, respectively [4]. Niu and the co-workers introduced the rigid monomer 2-(4-aminophenyl)-6-amino-4(3H)-quinazolinone (AAQ) into the PI

chains and the strength and modulus of the fibers were up to 2.8 GPa and 115 GPa, respectively [5]. Even though the mechanical properties of the PI fibers have been improved by introducing rigid heterocyclic units into the polymer chains, concomitantly, shortcomings are still followed: these monomers currently are not widely available or highly expensive. PI fiber reinforcement using a nanofiller is another promising way to improve the tensile properties as well as expand their applications [6–8]. In recent years, more and more nanomaterials with remarkable properties have been introduced into polymer matrices to modify the inadequacies of the materials to meet the stringent requirements under some special circumstances [9–12]. Among these candidates, carbon nanotubes (CNTs) have gained intensive attention as one of the most promising reinforcement nanomaterials due to their extraordinary mechanical properties, high aspect ratio and excellent thermal stability [13–15]. Introducing CNTs into polymeric fibers has been widely utilized and investigated over the past decades [16]. However, the tensile strength and modulus of these composite fibers just reached a small fraction of the theoretical value, and some polymer/CNTs systems even showed decreased tendency of mechanical properties when incorporating CNTs into the polymer matrix [17,18], which were mainly attributed to the

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dispersion difficulties and poor interaction between the polymer matrix and CNTs. Therefore, a key issue for raising the reinforcement of nanofillers includes improving both the homogeneous dispersion and interfacial interaction between the polymer and CNTs. Recently, great efforts have been focused on applying the approach of surface modification of CNTs to improve the compatibility between the matrix and the nanofillers. Hu et al. found that the incorporation of CNT-COOH into the poly (*p*-phenylene benzobisoxazole) (PBO) matrix by one-pot *in situ* polycondensation increased the tensile strength and modulus of PBO fiber from 2.2 to 2.7 GPa and from 64.8 to 89.4 GPa [19]. Sainsbury et al. functionalized MWCNTs with poly (*p*-phenylene terephthalamide) (PPTA) oligomer units, which facilitates the integration of the PPTA-MWCNTs within the PPTA matrix [20].

In this work, the asymmetric heterocyclic diamine 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) and the rigid-rod dianhydride 3,3',4,4'-biphenyltetracarboxylic (BPDA) were selected to synthesize the PI. Meanwhile, amino-functionalized MWCNTs as reinforcement fillers were introduced into PI matrix expecting enhancing the fibers' mechanical and other performances. In general, properties of polymeric fibers mainly depend on the aggregation structure and intermolecular interactions [5,21,22]. The orientation of the molecule chains as well as the formation of the interfacial interactions can be affected by the incorporated CNTs, especially when forming extra interactions or covalent bonds between polymer matrix and functional groups on the surfaces of the CNTs, thus leading to the changes of the performances of the fibers [15,17,23]. However, until now, less systematic studies have focused on investigating the interactions between CNTs and PI chains, polymer chains orientation as well as the semicrystalline structure of PI/CNTs composite fibers. Herein, we report a new effective protocol to prepare PI/CNTs composites on the basis of NH<sub>2</sub>-MWCNTs/NMP suspensions by *in situ* polymerization to improve the solubility, dispersivity and interfacial interactions of CNTs in the PI matrix. A series of PI/NH<sub>2</sub>-MWCNTs composite fibers were prepared by wet-spinning process and post heat-drawing treatment. Intricate interactions between CNTs and PI as well as the evolution of the aggregation structure of the composite fibers were investigated intensively and correlated to the mechanical and other performances of the prepared composite fibers.

## 2. Experimental section

### 2.1. Materials

MWCNTs with the CNTs' diameter of 10–20 nm and a length of 10–20 μm was supplied by Time Nano Co. Ltd, China. The amino functionalized NH<sub>2</sub>-MWCNTs and NH<sub>2</sub>-MWCNT/NMP suspensions were prepared according to the previous works [24,25]. The content of amino group (–NH<sub>2</sub>) on the surface of MWCNTs was around 0.45 wt%. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA, 99.5%) was purchased from Shijiazhuang Haili Pharmaceutical Co., Ltd. and was purified *via* sublimation under reduced pressure. 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) was supplied by Zhejiang Dragon Chemical Group Co., Ltd. *N*-methyl-2-pyrrolidone (NMP) was purchased from Adamas Chemicals and purified by distillation prior to use. Kevlar 29 and Kevlar 49 fibers was purchased from Dupont, USA. PBO fibers was supplied by the State Key Laboratory For Modification of Chemical Fibers and Polymer Materials, China.

### 2.2. Synthesis of poly(amic acid) (PAA)/NH<sub>2</sub>-MWCNTs spinning dopes

PAA/NH<sub>2</sub>-MWCNTs spinning dopes with various loadings of

NH<sub>2</sub>-MWCNTs were synthesized by the following procedure as shown in Scheme 1(A). A representative polymerization is as follows: A 250 mL three-necked flask equipped with a nitrogen inlet and a mechanical stirrer was charged with distilled NMP, BIA (11.21 g, 0.05 mol) and appropriate amount of NH<sub>2</sub>-MWCNTs/NMP suspensions. Equimolar dianhydride BPDA (14.711 g, 0.05 mol) was added as the diamine was dissolved. The solution was stirred at a low temperature (0–5 °C) for 12 h. Thus a series of spinning solutions with different NH<sub>2</sub>-MWCNTs loadings (0, 0.1, 0.2, 0.4, 0.8 wt %) were obtained and kept in a freezer until use.

### 2.3. Preparation of composite fibers

The obtained spinning solutions were degassed at room temperature prior spinning. The precursor PAA/NH<sub>2</sub>-MWCNTs composite fibers were fabricated *via* extruding the composite dopes through a spinneret (50 holes with 80 μm in diameter) into a coagulation bath (pure water), as shown in Scheme 1(B). Solidified filaments entered into the following washing bath. Then, the precursor fibers were dried under vacuum at 60 °C for 12 h, and then converted to polyimide fibers by successive heating at 100, 200 and 300 °C for 1 h at each temperature. Finally, the PI/NH<sub>2</sub>-MWCNTs composite fibers were drawn with various ratios in a furnace over 430 °C.

### 2.4. Characterization

Viscosities of the spinning solutions were characterized with a MCR 301 rheometer. Morphologies of the fibers were observed on a scanning electron microscope (SEM) (HITACHI SU8010) at an accelerating voltage of 3.0 kV. ATR-FTIR spectra were recorded on a Nicolet 8700 spectroscope with the range of 4000–400 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a PHI 5000C ESCA System using a monochromatic Al X-ray source (987.9 W, 1486.6 eV). Data analysis was carried out using CasaXPS software. Two-dimensional wide angle X-ray diffraction (WAXD) profiles were obtained at Beamline 16 B1 in the Shanghai Synchrotron Radiation Facility (SSRF). The wavelength is 0.775 nm. A CCD X-ray detector (MAR CCD 165) was employed at a distance of 168.5 mm from the sample for WAXD measurement. A typical image acquisition time was 40 s. The scattering patterns were analyzed using the software package x-Polar. Mechanical properties of the composite fibers were measured with the XQ-1 instrument, and the loading rate and gauge length are 10 mm/min and 15 mm, respectively. One specimen was measured at least ten times and the average value was used as the representative. Thermal stability of the fibers was analyzed using a Netzsch 209 F3 under nitrogen flow. Thermal dynamic mechanical behavior of the composite fibers was carried out on a thermomechanical analyzer (TA, Q800) from 50 to 550 °C at a heating rate of 3 °C/min. Thermal dimensional stability of the composites was also tested on Q800 under a tension force of 8 MPa.

## 3. Results and discussion

Fig. 1 shows the dependence of viscosities of the PAA/NH<sub>2</sub>-MWCNTs spinning solutions with various CNTs mass fractions on the shear rates. Clearly, at relatively low shear rate, an increase in nanotube loadings from 0 to 0.4 wt% leads to a continuous increase of the viscosity  $\eta_a$ , ranging from 100 Pa s to 400 Pa s, which is due to the effect of NH<sub>2</sub>-MWCNTs. Increasing the CNTs loading further to 0.8 wt% results in a decrease in the shear viscosity, attributing to the obstacle effect of NH<sub>2</sub>-MWCNTs on the molecule weights of PAAs. Actually, the increased viscosities endow the spinning dopes with better spinnability, which has been observed in the spinning

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