Structures and properties of polyimide/polyacrylonitrile blend fibers during stabilization process

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ABSTRACT

The polyimide (PI)/polyacrylonitrile (PAN) blend fibers were successfully prepared through a wet-spinning method, derived from the blend of poly (amic acid) (PAA) and PAN precursors in dimethyl sulfoxide (DMSO) solvent. Herein, the effects of thermal treated time and PAN weight ratios on the structures and properties of the PI/PAN blend fibers were systematically explored. The increased thermal treated time favored the imidization of PAA and cyclization of PAN. As a consequence, the optimum mechanical properties of the PI/PAN blend fibers were obtained at a thermal treated time of 10 min with the tensile strength of 1.15 GPa and initial modulus of 50.87 GPa. On the other hand, the combination of PI and PAN facilitated the imidization process of PAA and the formation of ladder structures of PAN, while the optimum mechanical performances were achieved when the PAN weight ratio was 23 wt%. In addition, the PI and PAN macromolecules exhibited good compatibility in the blend fibers with the glass transition temperature around 300 °C.

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1. Introduction

Aromatic polyimide (PI) fibers are in the class of high-performance polymeric fibers due to the specific rigid heterocyclic structures in the polymer backbone [1—3]. These features promise PI fibers with outstanding mechanical performances, remarkable thermal as well as dielectric properties and excellent chemical and irradiation resistance [4—6]. Currently, a widely developed and practiced two-step technique is mainly adopted in preparing PI fibers, in which poly (amic acid) (PAA) fibers are obtained by spinning PAA solution into coagulation bath and then converted into corresponding PI fibers through thermal or chemical imidization [7,8]. Owing to the accumulative progresses, a number of advances have been made for PI fibers to be large-scale produced and utilized in widespread fields, especially in high-temperature resistance areas [9—11]. Recently, much efforts have been paid to improve the comprehensive performances of the PI fibers by incorporating functional groups into the polymer backbone

[12—14]. Meanwhile, in order to reduce the cost without sacrificing the inherent excellent performances of the PI fibers, the blend of polyimide with other polymers is expected to be an efficient approach to yield high-performance blend fibers.

Polyacrylonitrile (PAN), the most suitable precursor to produce high-performance carbon fibers (CFs), has deserved much attentions due to the high carbon yield and low cost [15,16]. During the *pre*-oxidative stabilization process for CFs production, the PAN fibers are heated in the air atmosphere around 300 °C to form thermally stable ladder polymers [17,18]. The conversion in this step is complicated since different chemical reactions take place during the stabilization process. Also, the stabilization process is a speed-limiting step, which occupies large amount of time and takes a decisive effect in preparing high-performance CFs [19—21]. In this regard, reduce the stabilization time without sacrificing the mechanical properties of the PAN fibers (tensile strength of 320 MPa after *pre*-oxidation) has arisen to be a challenging task at present [22].

So far, attempts have been made to prepare PI/PAN blend fibers via the wet-spinning method [23,24]. It is acknowledged that the cyclization of PAA to PI possesses an endothermic feature, which can be promoted by the released heat with respect to the cyclization of nitrile groups. Therefore, this time-consuming stabilization

step could be accelerated. Meanwhile, the high molecular orientation of PI will give rise to regular molecular arrangement of the PI/PAN blend fibers, resulting in the excellent mechanical as well as thermal properties of the resultant fibers [25,26]. On the other hand, the PI/PAN blend fibers have the potential to produce high-performance CFs, deriving from the high carbon yield and simple procedure of PI fibers for carbonization and graphitization as reported by Zhang et al. [27].

In the present work, the PI/PAN blend fibers were prepared by first mixing 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA)/p-phenylenediamine (p-PDA)/4,4′-oxydianiline (ODA) PAA solution and PAN solution to form a homogeneous PAA/PAN blend solution in dimethyl sulfoxide (DMSO) solvent, and then was spun into the coagulation bath via a typical two-step wet-spinning method. It is well known that the stabilization process constitutes an important intermediate during the cyclization of PAN fibers to form conjugated ladder structures. Herein, the effects of thermal treated time and PAN weight ratios on the structures and properties of the resultant PI/PAN blend fibers were systematically investigated to serve as a general rule in fabricating high-performance polymeric fibers. The results showed that the PI/PAN blend fibers exhibited superior mechanical as well as thermal properties as compared with those of pure PI and PAN fibers, which were in agreement with our expectations.

2. Experimental

2.1. Materials

The monomer BPDA was purchased from Shi Jiazhuang Hai Li Chemical Company and purified by sublimation. The monomers p-PDA and ODA were obtained from Shangyu Li Xing Chemical Company and purified by recrystallization. The PAN powder with the average molecular weight of 1,50,000 g/mol was obtained from Japan KANEKA Co. Ltd. and used without further treatment. The solvent DMSO (analytical pure) was purchased from Tianjin Fu Chen Chemicals Reagent Factory and utilized after distillation. The deionized water used in the experiment was prepared by the Laboratory Water Purification System.

2.2. Preparation of the PI/PAN blend fibers

The PI/PAN blend fibers were prepared via a wet-spinning method based on the following procedures. First, the precursor PAA spinning solutions were synthesized by mixing equimolar amounts of dianhydrides and diamines in DMSO solvent under a dried atmosphere, while the molar ratio of two diamines p-PDA/ODA was 7/3. After stirring at 25 °C for 5 h, a viscous PAA solution with 15 wt% solid content was obtained. Meanwhile, the PAN powder was dissolved in DMSO solvent by stirring at 25 °C for 5 h to get a viscous PAN solution with 15 wt% solid content. Accordingly, the PAN and PAA solution were mixed and stirred at 25 °C for another 3 h to obtain a viscous PAA/PAN blend solution.

The PAA/PAN blend solution was filtrated and degassed prior to use, and then was extruded into a H_2O coagulation bath through a spinneret (100 holes, 70 μm in diameter) to get as-spun PAA/PAN blend fibers. After washed by deionized water to remove the residual DMSO solvent in the fibers, the PAA/PAN blend fibers were then dried in the oven at the temperature range from 80 to 150 °C. Subsequently, the PAA/PAN blend fibers were converted to corresponding PI/PAN fibers by successive heating at 200, 230, 260 and 280 °C in ambient atmosphere through a series of high temperature tube with concomitant drawing on the spinning rollers.

2.3. Characterization

Fourier transform infrared (FT-IR) measurement was carried out on Nexus 670 made by Nicolet Company with scanning wavenumber ranging from 4000 to 400 cm^{-1}. Generally, the band at 1358 cm^{-1} (C—N—C stretching) is selected for quantifying the imidization degree (ID) of the PI fibers, and the aromatic band at 1511 cm^{-1} (C—C stretching of the p-substituted benzene backbone) is selected as the internal standard. Thus, the ID can be calculated using the equation:

$$ID(\%) = \frac{(D_{1358}/D_{1511})_p}{(D_{1358}/D_{1511})_c} \times 100\% \tag{1}$$

where D is the area of the absorption band, and subscript p and c represent precursor fibers and the fully cured PI fibers, respectively [28]. On the other hand, the relative cyclization index (RCI) of PAN fibers during stabilization process can be measured by the equation:

$$RCI = \frac{I_{C=N}}{I_{C=N} + I_{C\equiv N}} \tag{2}$$

where $I_{C=N}$ represents the intensity of the C=N absorption band, and $I_{C\equiv N}$ represents the intensity of the C≡N absorption band [29].

The mechanical properties of the PI/PAN blend fibers were measured using an YG001A-1 instrument with a gauge length and extension speed of 20 mm and 10 mm min^{-1}, respectively. For each type of fibers, at least 15 monofilaments were tested and the average value was used as the representative.

Two-dimensional wide angle X-ray diffraction (2D WAXD) was performed on a Bruker D8 Discover diffractometer equipped with GADDS as a 2D detector. X-ray diffraction measurements were taken from transmission mode at room temperature using Ni-filtered Cu Kα (λ = 0.154 nm) radiation operated at 40 kV and 40 mA. The degree of molecular orientation can be calculated by integrating the corresponding intensity of azimuthal scans along the isolated and preferred crystalline plane [30–32]. The degree of molecular orientation of the fibers is calculated based on the Hermans equation:

$$f = \left(3 < \cos^2 \phi > - 1\right)\Big/2 \tag{3}$$

where f is the degree of molecular orientation along the preferred direction and ϕ represents the angle between the fiber axis and c-axis crystal unit cell. The numerical values of the mean-square cosines in the equation above are determined by corrected intensity distribution $I(\phi)$ diffracted from the crystalline plane by Gaussian fitting following the equation:

$$< \cos^2 \phi > = \frac{\int_0^{\pi/2} I(\phi)\sin \phi \cos^2 \phi d\phi}{\int_0^{\pi/2} I(\phi)\sin \phi d\phi} \tag{4}$$

The surface and cross-section fractured morphologies of the PI/PAN blend fibers were recorded on a Hitachi S4700 scanning electron microscope (SEM) operating at 20 kV. The fibers were embedded in epoxy resin and fractured in liquid nitrogen for cross-section morphologies measurements. Also, the samples were coated with Pt before observation.

Differential scanning calorimetry (DSC) was carried out on a DSC Q20 system. Samples weighing about 5.0 mg were heated from 50 to 400 °C under nitrogen atmosphere with the heating rate of 10 °C min^{-1}.