

Effects of Using Polyacrylonitrile on the Thermal, Morphological and Mechanical Properties of Polyimide/Polyacrylonitrile Blend Fibers

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Abstract: High-performance polyimide/polyacrylonitrile (PI/PAN) blend fibers were prepared through wet-spinning of the polymer blends of polyamide acid (PAA) and PAN solutions followed by a thermal treatment in air. During the heat treatment process, PAA was imidized into its final heteroaromatic PI form with the concomitant evolution of PAN into its ladder-like preoxidized form, thus yielding PI/PAN blend fibers with desirable properties. The structure evolution was traced by fourier transform infrared radiation spectrometer, differential scanning calorimetry and thermogravimetry, implying that the PAA moiety in the blend fibers played a role as initiator for the cyclization of PAN. The final PI/PAN blend fibers exhibited a single glass-transition peak at 326 °C and a smooth surface without any pores. Moreover, the PI/PAN blend fibers possessed the tensile strength of 1.06 GPa and modulus of 59.9 GPa.

Keywords: Polyimide, Polyacrylonitrile, Blend fibers, Preparation, Characterization

Introduction

Aromatic PI fibers have been considered as promising materials for the use in automobile and aerospace industries, production of heat protective clothes and high-performance composites due to their outstanding physical and chemical properties [1-5]. Currently, two major techniques including one-step method and two-step method are mainly used to prepare PI fibers [6-8]. The two-step method is developed by first spinning of polyamide acid (PAA) solutions, which are synthesized in low toxic solvent, into PAA fibers and then being subjected by chemical or thermal imidization to convert PAA into the final PI fibers [9,10]. As well known, wet and dry-jet spinning methods have been broadly used for fabricating PI fibers. In the wet-spinning process, water or aqueous solutions are often used as coagulating agents. The PAA fibers passed directly into the non-solvent bath where fiber coagulation and solvent extraction take place at the same time, following by heat-drawing treatment to form PI fibers. However, the processability and high cost of PI fibers are challenging tasks for PI fibers prepared by two-step wet-spinning method so far.

Polyacrylonitrile (PAN) is one of the most important fiber-forming polymers and has been broadly used because of its strength, high abrasion resistance, low price, good insect resistance and other advantages [11-15]. The wet-spinning method can be also used for preparing PAN fibers, since PAN is soluble in polar solvents such as dimethylacetamide (DMAc), dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) [16]. It is well known that the thermal stabilization or pre-oxidization process usually performing in atmosphere

at the temperature range from 200 to 400 °C can change chemical structure of the fiber and cause them to become thermally stable [17-21]. Chemical reactions are involved in this process, resulting in the formation of the conjugated ladder structure to enable the fibers to undergo processing at higher temperatures [22]. However, the mechanical properties of PAN fibers display a continual decline with stabilization. This phenomenon is attributed to two aspects, the first is the decrease of cohesive energy between molecular chains induced by chemical reactions from $-C\equiv N$ group to the conjugated ladder structure within the fiber; the second is the decrease in the lateral and orientational order during thermal stabilization [23,24].

In recent years, much attention has been paid to the preparation of high performance fibers based on polymer blends. The judicious selection of the precursors combined with the optimized fabrication processes (i.e., spinning, and stabilization) could be one of the ways to get high performance blend fibers [16]. The PI fibers exhibit excellent flame resistance with high limiting oxygen index (LOI) values of 60, but currently are too expensive for most high flame resistance applications. The oxidized PAN fibers also possess high LOI values of 40-60. Thus, the PAN component has been focused on the modification of PIs to maintain their superior flame resistance and to reduce the high cost of pure PIs. These unique properties enable the PI/PAN blend fibers to be one of the most promising materials using in high heat and flame resistance areas [25]. Therefore, aimed at preparing high performance fibers with high thermal stability, excellent mechanical properties and outstanding flame resistance from polymer blends, and inspired by the fact that both PI and PAN fibers can be fabricated using the same polar solvent spinning method, the PI/PAN blend fibers were prepared via the wet-spinning process followed by a thermal treatment in

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air. During the thermal treatment, PAA and PAN are supposed to be subjected to the imidization and pre-oxidization, respectively. Herein, we focus on the structural evolution, thermal and mechanical properties of the PI/PAN blend fibers during heat treatment process. This investigation may serve as the initial stage of exploring novel high performance fibers from polymer blends.

Experimental

Materials

The monomers 3,3',4,4'-biphenyldianhydride (BPDA) and *p*-phenylenediamine (*p*-PDA) were purchased from Shanghai Pharmarketech Co. Ltd., and purified prior to use. Polyacrylonitrile (PAN) powder (viscosity average molecular weight ~150000 g/mol) was obtained from Japan KANEKA Co. Ltd., and purified before use. Dimethyl sulfoxide (DMSO) (analytical pure) was purchased from Xilong Chemical Co. Ltd., and used after distillation.

Preparation of PI/PAN Blend Fibers

The PI/PAN blend fibers were fabricated through the wet spinning method according to the following procedures. First, the BPDA/*p*-PDA PAA solution for wet spinning was prepared by dissolving the diamine, *p*-PDA, in DMSO followed by gradually adding equimolar amount of BPDA. After stirring at 25 °C for 5 h, a viscous solution with 20 wt % solid content was obtained. Simultaneously, a PAN solution (20 wt %) was prepared by dissolving the PAN powders in DMSO and stirring at 25 °C for 5 h. The PAA/PAN blend solutions were obtained by mixing the PAA and PAN solutions with a weight ratio of 4/1 and stirring at 25 °C for 3 h. The intrinsic viscosity of resultant PAA/PAN blend solution was measured to be 2.25 dl·g⁻¹ at 35 °C, which is a suitable precursor solution for spinning.

The PAA/PAN blend solution for the wet-spinning was degassed under vacuum at 25 °C to remove the air bubbles prior to use. The PAA/PAN precursor fibers were produced by extruding the viscous PAA/PAN blend solution through the spinneret (100 holes, 75 μm in diameter) under a high-pressure nitrogen atmosphere into a H₂O coagulation bath and were then dried in the oven with a temperature of 80 °C. Subsequently, the dried fibers were delivered into ovens in the temperature range of 120-250 °C in air for 30 min with concomitant drawing on the spinning rollers. After the initial imidization of PAA and cyclization of PAN, the PI/PAN blend fibers were finally obtained by further drawing at 300 °C and 370 °C. To make comparisons, the pure PI and PAN fibers were prepared under the same spinning condition.

Characterization

Intrinsic viscosity of the PAA/PAN was measured at 35 °C using a SCHOTT 52510 Ubbelohde viscometer with capillary inner diameter of 0.58 mm. The PAA/PAN blend solution in

DMSO with concentrations of 0.5, 1.0, 1.5 and 2.0 mg·mL⁻¹ were measured and the intrinsic viscosity was determined by extrapolating the concentration of PAA/PAN solution to zero. Thermogravimetric analysis (TGA) measurements were carried out on a TA instrument TGA Q50 system. Samples weighing about 5.0 mg were heated from 50 to 800 °C in dynamic nitrogen and air environment at a heating rate of 10 °C·min⁻¹. Fourier transform infrared (FTIR) spectra were obtained at a resolution of 4 cm⁻¹ on Nexus 670 instrument made by Nicolet Company. The samples were prepared by pulverizing the fibers in a KBr matrix. Differential scanning calorimetry (DSC) was performed on a TA instrument DSC Q20 system. Samples weighing about 5.0 mg were heated from 50 to 450 °C in nitrogen environment at a heating rate of 10 °C·min⁻¹. Thermal dynamic mechanical behavior of the prepared fibers were measured using a dynamic mechanical analysis (DMA) system of Q800 (TA instrument) in tension mode to obtain storage and loss moduli. The loss factor (tanδ) was then calculated through the ratio of these two moduli. The frequency was 1 Hz, and the heating rate was 5 °C min⁻¹ from 50 to 500 °C. Single fiber tensile testing was performed on an YG001A-1 instrument at an extension rate of 10 mm min⁻¹. The length of the fiber samples was set to 20 mm. For each type of fiber, at least 20 monofilaments were tested and the average values were used as the representative. The morphologies of the surface and fractured surfaces for the prepared fibers were recorded on a Hitachi S-4700 scanning electron microscope (SEM) operating at 20 kV.

Results and Discussion

Structure Evolution of the PI/PAN Blend Fibers

TGA measurements were performed under the nitrogen and air atmospheres to investigate the thermal degradation of PAA, PAN and PAA/PAN fibers and to determine the preparation conditions for PI/PAN blend fibers, and the resulting TGA curves are shown in Figure 1. It is observed that the mass losses of the pure PAA fibers mainly occur in temperature ranges of 150-250 °C and 500-700 °C under both nitrogen and air atmosphere, respectively, representing the imidization and the chemical decomposition. The pure PAN fibers in nitrogen atmosphere undergo a main mass loss in the temperature range of 200-450 °C due to the cyclization and thermal degradation. On the other hand, the mass changes of the pure PAN fibers occurred in air atmosphere mainly occur around 709 °C, indicating that the PAN fibers are stabilized in air due to reaction with oxygen by forming ladder structure to enable them to withstand high temperature during pyrolysis process [26,27]. The thermal behavior of the PAA/PAN blend fibers under nitrogen atmosphere shows a combination of pure PAA and PAN. Notably, the PAA/PAN blend fibers in air exhibits two-step mass loss in temperature ranges of 150-300 °C and 500-

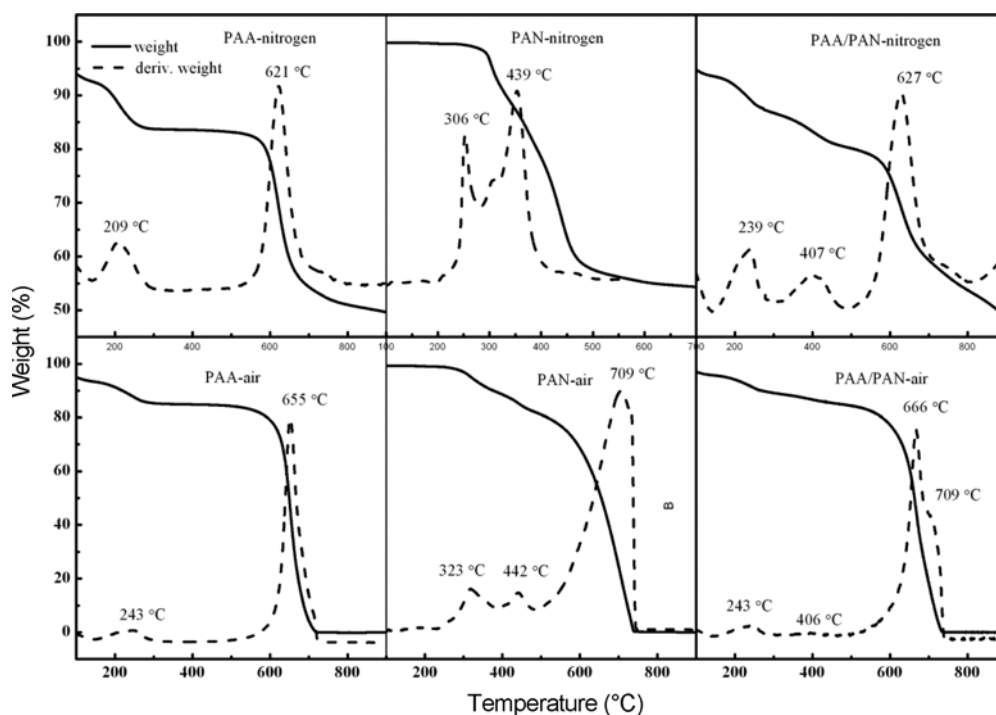


Figure 1. TGA of the pure PAA, PAN and PAA/PAN blend fibers at a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen and air atmosphere.

800 °C. About 8 % mass loss in the first stage is attributed to the imidization of PAA and cyclization of PAN during stabilization. Compared with pure PAN, there is few mass loss in the vicinity of 406 °C in the case of the PAA/PAN blend fibers, suggesting that PAA has a positive effect on promoting the oxidative stabilization process of PAN, which may be associated with additional cross-linking reaction. The major mass losses around 666 °C and 709 °C are attributed to the thermal pyrolysis processes of the PI molecular and ladder PAN structure, respectively. The result also indicates that the PI/PAN blend fibers possess rather high thermal stabilities and are in the class of high-temperature synthetic fibers after the imidization and cyclization processes, during which the original polymer structure is transformed to partially cyclized ladder structure to sustain high temperature treatment. Moreover, according to the thermal behaviors of the PAA/PAN blend fibers from the TGA results, the blend fibers were further thermally treated from 80 to 370 °C in an air atmosphere to investigate the structural evolution.

The FTIR spectroscopy provides a substantial quantity of information about the chemical structure variations during heating process. Figure 2 displays the FTIR spectra of pure PAA and PAN and PAA/PAN blend fibers at different heating temperatures. In Figure 2(a), four characteristic absorption bands of PI, i.e., 1772 cm^{-1} (asymmetric stretching vibration of the C=O), 1714 cm^{-1} (symmetric stretching vibration of the C=O), 1352 cm^{-1} (the C-N stretching vibration in the imide ring) and 734 cm^{-1} (imide ring vibration) appeared after the PAA fibers were thermally treated at

temperatures above 200 °C, revealing that cyclic imide rings were successfully formed. In Figure 2(b), the intensity of the band at 1624 cm^{-1} (the vibration of $>\text{C}=\text{N}-$ group) get much stronger accompanied by a gradual decrease in intensity of the absorbance at 2244 cm^{-1} ($-\text{C}\equiv\text{N}$ stretching vibration) with increasing temperatures, implying the gradual conversion of $-\text{C}\equiv\text{N}$ to the $>\text{C}=\text{N}-$ groups. No absorbance at 2244 cm^{-1} is observed at 200 °C, which implies that the cyclization degree of the PAN has reached a relatively high value and is no longer sensitive to the thermal treatment temperatures. In Figure 2(c), the gradual appearance of characteristic peaks of PI and the disappearance of $-\text{C}\equiv\text{N}$ groups manifests the enhanced imidization of PAA and cyclization of PAN, respectively. Nevertheless, compared to pure PAN fibers, the absorbance at 2244 cm^{-1} of the PAA/PAN blend fibers still exists at 250 °C, indicating that the PAA moiety influences the preoxidation of PAN. Additionally, the DSC analyses were performed to investigate the endothermic and exothermic reactions of the blend fibers during the heat treatment process.

Figure 3 shows the DSC curves the pure PAA, PAN, PAA/PAN blend fibers with different heating temperatures in nitrogen. In Figure 3(a), the pure PAA fibers exhibit a broad endothermic peak at 212 °C due to the thermal imidization. And no endothermic peak is observed after the pure PAA fibers are treated at temperatures above 200 °C, suggesting the formation of PI structure. This result is also in agreement with the FTIR results. In Figure 3(b), a relatively sharp narrow peak resulting from cyclization reaction is observed

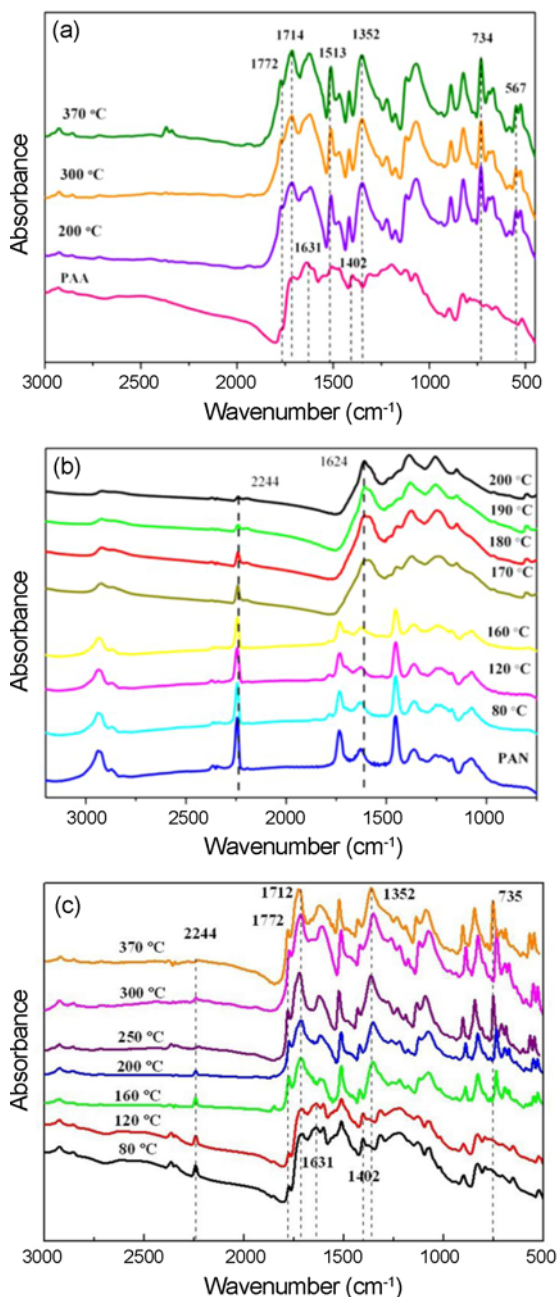


Figure 2. FTIR spectra of the prepared fibers at different heating temperature; (a) pure PAA fibers, (b) pure PAN fibers, and (c) PAA/PAN blend fibers.

in the untreated pure PAN fibers, and the exothermic peak becomes much broader and shifts towards a higher temperature for PAN fibers treated with increasing temperatures due to the gradual conversion from $-C\equiv N$ to $>C=N-$ groups. The exothermic peak disappears in the case of the PAN fibers treated at 200 °C in air, which is due to the preoxidation of the PAN fibers during heat treatment. For the PAA/PAN blend fibers, as illustrated in Figure 3(c), the addition of PAN elevates the endothermic peak of PAA to a higher

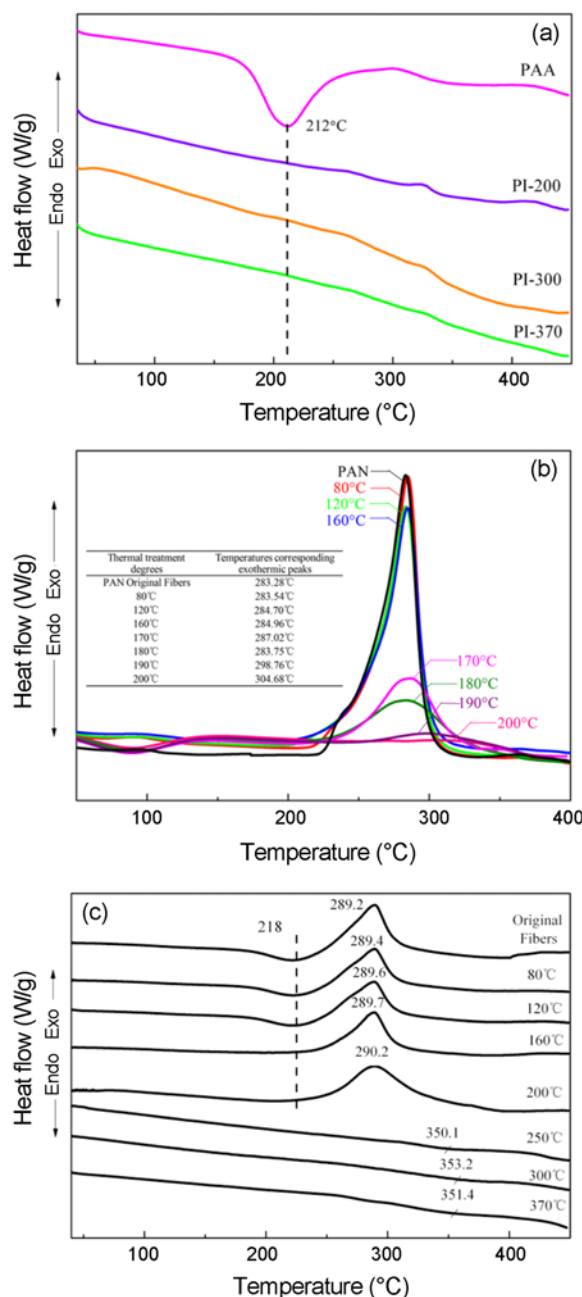


Figure 3. DSC curves of the prepared fibers at different heating temperature; (a) PAA fibers, (b) PAN fibers, and (c) PAA/PAN blend fibers.

temperature (218 °C). It can be concluded that the imidization temperature of PAA moiety has been improved slightly from 212 °C to 218 °C, indicating that there might be some interactions between PAA and PAN. Meanwhile, the exothermic peaks of PAN are much broader and still exist in the blend fibers treated at 200 °C, demonstrating that the PAA moiety is useful to alleviate the abrupt exothermic reaction of PAN during the preoxidation process.

There are two kinds of chemical reactions involved in the

heating process in air for the PAA/PAN blend fibers, which are the imidization of PAA and the preoxidation of PAN. Moreover, it has been clearly recognized that the cyclization of PAN homopolymer can be initiated through a radical mechanism, so some comonomers, such as itaconic acid, has been copolymerized in order to slow the highly exothermic cyclization and to avoid some extent fusion and breaking of the fibers [28]. Based on the TGA, FTIR and DSC results, the PAA moiety in the blend fibers plays a role as initiator for the cyclization of PAN and has a positive effect on slowing the exothermic reaction, which will reduce the defects in the resultant fibers. Therefore, the PI/PAN fibers were prepared by initial heating from 80 to 250 °C followed by further thermal treatment 300 °C and 370 °C.

DMA Measurements of the PI/PAN Fibers

DMA is a sensitive means to detect the phase transformation behavior of polymers compared with DSC analyses, which not only characterizes the glass-transition of polymers (α transition) but also reveals the microcosmic movement by detecting the secondary transition (β transition). Figure 4 shows the DMA thermograms for the PI/PAN blend fibers with different heating temperatures. Two series of peaks are identified in the curves, in which the higher ones are α relaxations corresponding to the glass transition temperature (T_g), and the other ones are β relaxations representing sub-glass transition of the fibers. In our previous research, for the pure PI fibers, the T_g increases with increasing the thermal treatment temperature, illustrating that with increasing temperature, the completely amorphous portion of the PI reduces and the molecular packing becomes increasingly dense to limit the molecular chain mobility due to improved imidization structures [29,30]. For the PI/PAN blend fibers, the glass transition temperatures ($T_{g,s}$) of PI are continually increased with the thermal treatment temperatures, and reached 326 °C when the blend fibers were treated to 370 °C, which is suggested to be due to the continually improved imidization structures in the PI component. The β relaxations

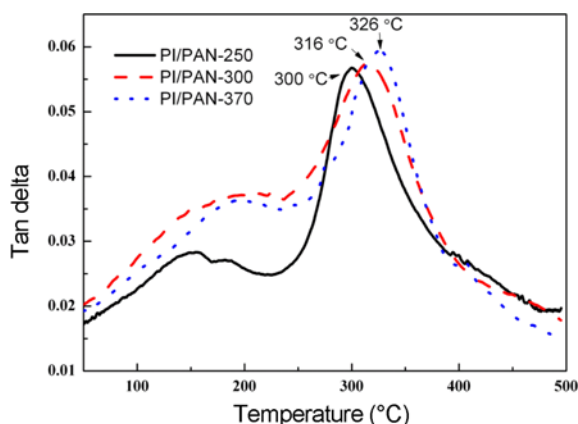


Figure 4. DMA curves of the PI/PAN blend fibers in nitrogen.

shift to higher temperatures with increasing treating temperature. It has been reported that the β transition happens as a result of the rotation of benzene rings and the cooperative motion within a small localized scale [31,32]. It suggests that the higher temperature of the corresponding β transition peak, the more difficult for benzene rings to rotate [33,34]. Accordingly, the introduction of PAN ingredient can limit the mobility of benzene rings in the blend fibers due to the formation of ladder structure in PAN with increasing the treating temperature and therefore results in an increase of the β relaxation temperatures.

Mechanical Properties of PI/PAN Blend Fibers

The mechanical properties of the pure PI, pure PAN and PI/PAN blend fibers with different heat treatment temperatures are illustrated in Figure 5. The tensile strength and modulus of the pure PI fibers increased with an increase of temperature. However, the elongation was reduced to a low value, indicating a degradation of the PAA chains at 200 °C [29,35]. Thermal treatments result in a significant improvement in the mechanical properties of the pure PI fibers, which is attributed to the gradual enhancement of the imidization degree as observed in FTIR spectra. The tensile strength and modulus of the pure PI fibers reach 1.09 GPa and 64.7 GPa, respectively, at a temperature of 370 °C. For the pure PAN fibers, the tensile strength and modulus decrease with the increase of temperature in the pre-oxidizing process due to the decrease of cohesive energy between molecular chains and the decline in the lateral and orientational order during thermal stabilization. It is notable that the tensile strength and modulus of the PI/PAN blend fibers increase with increasing temperature and variation tendency of the mechanical properties is similar to those of pure PI fibers, implying that the imidization of PI moiety plays a dominant role on the structural evolution of the blend fibers. The final PI/PAN blend fibers exhibit the tensile strength of 1.06 GPa and

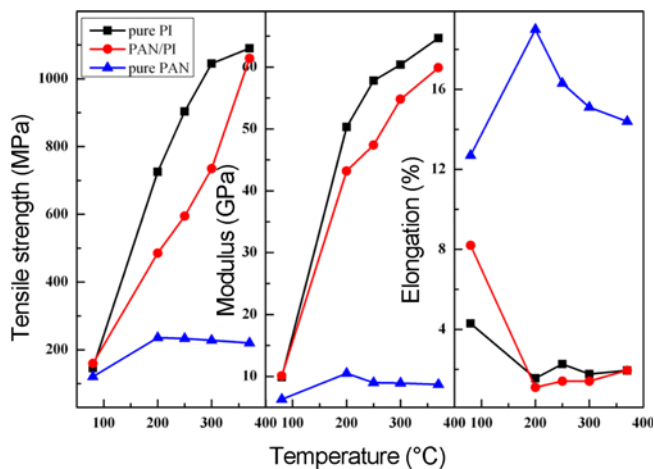


Figure 5. Mechanical properties of the pure PI, pure PAN and PI/PAN blend fibers with different heating temperatures.

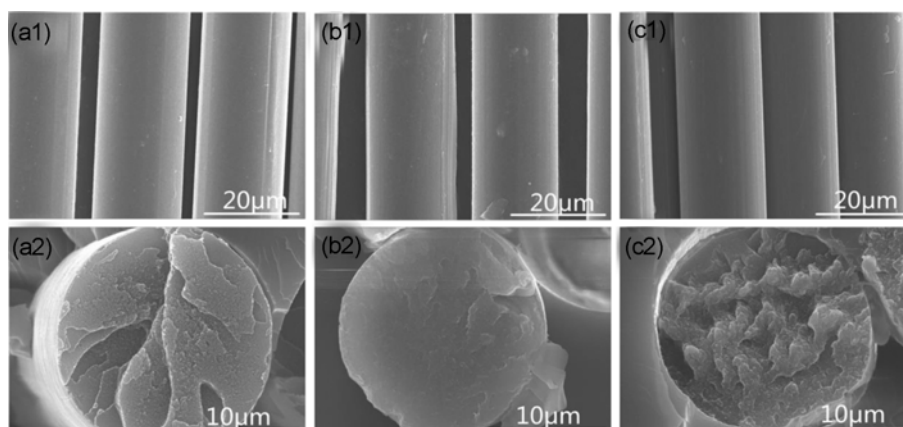


Figure 6. SEM morphologies of the pure PI, PAN and PI/PAN blend fibers; (a1, a2) pure PI fibers, (b1, b2) pure PAN fibers, and (c1, c2) PI/PAN blend fibers.

modulus of 59.9 GPa at 370 °C, which is slightly lower than that of pure PI fibers due to the brittleness of the PAN structure.

Morphologies of PI/PAN Fibers

The morphologies of the pure PI, PAN and PI/PAN blend fibers are shown in Figure 6. As for the morphologies of the PI/PAN blend fibers, they possess smooth surface without any pores or cavities and the mean diameters of fibers are about 20 μm . For the visualization of the internal morphologies, the pure PI fibers show better toughness than PAN ones, which is ascribed to poor mechanical properties of pure PAN fibers. The PI/PAN fibers show a flake-like structure on the cross-sections. During the wet-spinning, the coagulation of fibers is a dual diffusion process, and the coagulating rate depends on the precursors, the temperature and concentration of the coagulating bath [36]. The PI/PAN blend fibers exhibit less smooth cross-sections than the pure PI and PAN fibers, indicating that the coagulating rate of PAA and PAN moieties are different during the coagulating process. The fact that the PI/PAN blend fibers do not have any defects implies the completed imidization of PI and cyclization of PAN during the thermal treatment.

Conclusion

High-performance PI/PAN blend fibers were prepared through the wet-spinning of the polymer blends of PAA (BPDA/PDA) and PAN solutions in DMSO to obtain PAA/PAN precursor fibers followed by the thermal treatment in air. The structural evolution and properties of the blend fibers were evaluated by various analytic techniques. During the heat treatment process, the precursor fibers cyclimidized the PAA into its final heteroaromatic PI form with the concomitant evolution of PAN into its ladder-like form. The PAA moiety in the blend fibers plays a role as initiator for the cyclization of PAN and has a positive effect on slowing

the exothermic reaction, which will reduce the defects in the resultant fibers. The final PI/PAN blend fibers have a single glass transition at 326 °C and a smooth surface without any pores as well as the tensile strength of 1.06 GPa and modulus of 59.9 GPa.

Acknowledgments

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