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Releasing silica-confined macromolecular crystallization to enhance mechanical properties of polyimide/silica hybrid fibers

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ABSTRACT

Polyimide (PI)/silica hybrid fibers containing 1% silica were prepared by the sol–gel method. Under tension-free thermal treatment at 300 °C, PI fibers and PI/silica hybrid fibers possess 0.98 GPa and 1.38 GPa respectively. However, it is found that the silica-reinforced effect is almost disappeared after the temperature of tension-free thermal treatment increasing to 420 °C. Wide angel X-ray diffraction (WAXD) patterns indicated that, by 420 °C tension-free treatment, PI fibers are reinforced due to crystallization of PI; PI/silica hybrid fibers are still amorphous since dispersed silica inhibits the crystallization of PI, which counteracts the silica reinforced effect. Through a hot-drawing process at 420 °C, PI fibers cannot obtain additional reinforcement, while tensile strength of hybrid fibers increases from 1.83 GPa to 2.34 GPa for crystallization. Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) tests revealed that the dispersed silica transforms into larger particles after hot-drawing, so the confinement of macromolecular crystallization is released for further reinforcing. As a result, the advantages of silica reinforcing in amorphous domain and macromolecules crystallizing are combined together, resulting in excellent mechanical properties of fibers.

1. Introduction

Polyimide (PI) fibers play a critical role in high-performance fibers production since the 1960s due to their excellent thermal stability, chemical resistance, radiation resistance and low dielectric constant. These advantages of PI fibers are derived from their high bond energy, strong intermolecular interaction and conjugated polymer molecules, which leads to potential applications in microelectronics, atomic energy, and astronautics industry [1]. However, a general weakness of PI fibers is lack of satisfactory mechanical strength compared with other high-performance fibers [2].

Incorporating inorganic components into polymers is an effective strategy to enhance mechanical properties [3]. However, inorganic components are generally poorly dispersed into the polymer matrix driven by their high surface energy. A simple method to overcome this disadvantage has been proposed to reinforcing polymers, that is, hybridizing organic and inorganic components by the sol–gel method in situ [4–6]. Different from other hybridizing methods, the sol–gel method generates nanoscale domain size and homogeneous phase, which obtains excellent mechanical properties of the polymer [4]. In preparation of the sol–gel organic/inorganic composites, silica is the most used inorganic components because of its availability and cost, outstanding mechanical properties and thermal resistance [7]. Silica has been successfully incorporated in PI matrix to improve the mechanical properties [8–10]. To obtain better mechanical properties of PI, thermal imidization at a high temperature is always needed. However, after PI imidizes completely in PI/silica hybrid materials, carboxyl and amide vanish. The diminished interactions between silica and PI thus weaken the silica-reinforced effect on PI. Hence, the essential problem of preparing PI/silica hybrid materials of desirable mechanical strength is to enhance the compatibility between silica and PI after imidization. To solve this problem, monomers containing benzimidazole were introduced into PI/silica hybrid films to enhance hydrogen bonding interactions [11,12]. After imidization, benzimidazole in PI can still interact strongly with silica through hydrogen bonds, so organic/inorganic compatibility and the silica-reinforced effect can be maintained. Unfortunately the intense interactions between silica and PI inhibit the crystallization of PI macromolecules, hindering further reinforcing of PI hybrid materials. The confinement of crystallization was also

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reported in other polymers [13–15]. It remains challenging to release the silica-confined PI macromolecular crystallization for further improving mechanical properties and drives us to look for alternative solutions.

In this paper, polyimide/silica hybrid fibers with 1% silica were prepared via wet spinning method. It is found that by tension-free thermal treatment at a temperature beyond glass transition temperature, PI fibers can crystallize while PI/silica hybrid fibers are always amorphous, because crystallization of PI is confined by dispersed silica in PI/silica hybrid fibers. Reinforcement and crystallization confinement of silica counteract with each other, hindering further reinforcing of fibers. The dispersed silica transforms into larger particles after hot-drawing at a temperature beyond glass transition temperature, so the confinement of macromolecular crystallization is released for further reinforcing. By combining reinforcing effect of silica and PI macromolecular crystallization together, mechanical properties of fibers are enhanced further significantly.

2. Experimental

2.1. Materials

N-methyl-2-pyrrolidone (NMP) was obtained from Puyang MYJ Technology Co. Ltd., and was distilled under reduced pressure before use. 2-(4-aminophenyl)-5-aminobenzimidazole (PABZ), and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) were obtained from Changzhou Sunlight Medical Raw Material Co. Ltd. BPDA was dried at 200 °C in an oven for more than 10 h. The structures of monomers are shown in Fig. 1. Tetraethoxysilane (TEOS) was obtained from Shantou Xilong Chemical Company. Oxalic acid was obtained from Chengdu Kelong Chemical Company.

2.2. Synthesis of polyamide acid (PAA) hybrid solution

The PAA solution was prepared by stirring equimolar amounts of dianhydride and diamine in NMP at room temperature under a nitrogen atmosphere for 50 h, and the PAA solid content was 12%. Oxalic acid was added into distilled water to keep PH value at 2. The subacid water and TEOS were added into a one-neck round flask at molar ratio of 4:1. Then NMP was added into the one-neck round flask as cosolvent, making the mass fraction of TEOS become 40%. The mixed TEOS solution was stirred for 2.5 h at 40 °C until it hydrolyzed completely and became homogeneous. Afterwards, hydrolyzed TEOS solution was added into the PAA solution. The mixture was stirred at room temperature for 5 h to obtain excellent compatibility, forming PAA/silica hybrid solution.

2.3. Preparation of PI/silica hybrid fibers

PAA/silica hybrid solution was moved into deaeration kettle and deaerated under reduced pressure for 24 h. PAA/silica hybrid fibers were prepared via wet-spinning. Hybrid solution was extruded through a spinneret (50 holes, 80 μm diameter) into the first coagulation bath (Ethylene glycol). The as-spun PAA hybrid fibers were drawn 2.5 times in the second coagulation bath (Ethanol/water). After washing in water, the PAA/silica hybrid fibers were collected onto the winding machine. The winded PAA/silica hybrid fibers were dried under reduced pressure at 60 °C for 5 h, and the silica content in dried PAA/silica hybrid fibers was 1%. The pretreatment was followed by three thermal treatments:

(1) The dried PAA/silica hybrid fibers imidized with heating rate of 6–8 °C/min in oxygen-free environment. The end-point treatment temperature was 300 °C, and the fibers were kept at 300 °C for 30 min.
(2) The (1) procedure was completed first. The fibers were treated under tension-free thermal treatment at 420 °C. The tension-free thermal treatment started from room temperature to 420 °C with heating rate of 6–8 °C/min in oxygen-free environment, and the end-point temperature was 420 °C and was kept for 10 min.
(3) The (1) procedure was completed first. Then, the fibers went through a hot-drawing process at 420 °C with drawing ratio of 1.5.

The PI fibers without silica were prepared as respective controls. The preparation of control PI fibers was similar to that of PI/silica fibers except that hydrolyzed TEOS solution was not added into the PAA solution.

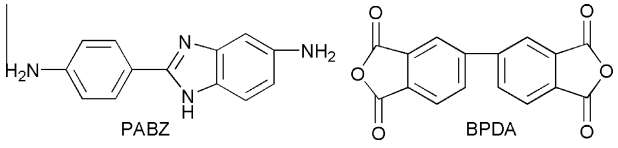

Fig. 1. Monomers used to prepare PI and PI/silica fibers.

2.4. Characterization

Mechanical properties of fibers were determined with a Shenzhen Kaiqiangli Testing Instrument using a tensile velocity at 5 mm/min. The fixture span of fiber tests was set to 10 mm. Wide angel X-ray diffraction (WAXD) patterns of fibers were measured with a Philips X'Pert PRO MPD. Flourier transformed infrared spectroscopy (FTIR) spectra of fibers were obtained with a Nicolet Magna 650 spectroscope. Scanning Electron Microscope (SEM) measurement was carried out with a JEOL JSM-5900LV SEM. Differential Scanning Calorimetry (DSC) measurement was carried out with a TA Instrument DSC Q200 V24.2 Build 107 at a heating rate of 10 °C/min. The dispersion of silica was measured with a FEI Tecnai G2 F20 S-TWIN Transmission Electron Microscope (TEM), and the samples were embedded in epoxy resin and cut into 100 nm thick slices with a Leica EMUC6 ultramicrotome before measurement. Small angle X-ray scattering (SAXS) measurements were carried out using a NanoSTAR-U (BRUKER AXS INC.) with Cu Kα radiation (λ = 0.154 nm). The generator was operated at 40 kV and 650 μA. Two-dimensional SAXS patterns were obtained using a HI-STAR detector, and the sample to detector distances were LSD = 1074 mm.

3. Results and discussion

Table 1 summarizes the mechanical properties of PI fibers and PI/silica hybrid fibers. By incorporating only 1% silica into polyimide matrix, the hybrid fibers under tension-free thermal treatment at 300 °C possess a tensile strength 40% higher than pure PI fibers (1.38 GPa and 0.98 GPa, respectively). Compared with films, the hybrid fibers developed in our study exhibit much stronger

Table 1
Mechanical properties of PI fibers and PI/silica hybrid fibers.

Components	Treatment temperature (°C)	Ratio of hot-drawing	Tensile strength (GPa)
PI	300	–	0.98
PI/silica	300	–	1.38
PI	420	–	1.80
PI/silica	420	–	1.83
PI	420	1.5	1.78
PI/silica	420	1.5	2.34