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Tensile modulus enhancement and mechanism of polyimide fibers by post-thermal treatment induced microvoid evolution

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ABSTRACT

The correlation between mechanical property and the microstructure of two-step wet spinning polyimide (PI) fibers after thermal annealing was investigated. *In-situ* wide-angle X-ray diffraction (WAXD) and *ex-situ* small angle X-ray scattering (SAXS) methods were utilized to study the liquid crystal-like structure orientation and microvoids structure (the length and the orientation angle of microvoids) for PI fibers during annealing process. The effects of annealing temperature and time on the microstructure were systematically studied. The results reveal that the liquid crystal-like structure and the orientation degree keep nearly the same after annealing. Both of the molecular chain relaxation and the evolution of aligned microvoids are attributed to the change in tensile modulus. In low pre-drawing fiber, a slight decrease in microvoid length and an obvious rise in microvoid orientation angle lead to improved tensile modulus after annealing. In highly pre-drawn fiber, the tensile modulus decreases first due to de-orientation of polymer chains and then increase owing to disordering microvoids with decreasing size. Our work demonstrates the relationship between microvoids and mechanical properties in annealed PI fibers which provides a new avenue to access high performance PI fiber by facile annealing method and a deep insight into the structure and properties of high performance PI fibers.

1. Introduction

High-performance polymeric fibers have received tremendous attention for their excellent thermal stability and high mechanical properties in the past decades. The structures and properties of these fibers, such as Kevlar fibers, poly(*p*-phenylenebenzobisoxazole) (PBO) fibers and poly(p-phenylenebenzobisthiazole) (PBT) fibers have been widely investigated by researchers [1–7]. Among these high-performance fibers, polyimide (PI) fibers are highly attractive not only for their stunning fiber-wise properties, but also for their

Abbreviations: PI, polyimide; WAXD, wide-angle X-ray diffraction; SAXS, small angle X-ray scattering; BPDA, 3,3′,4,4′-biphenyldianhydride; *p*-PDA, *p*-phenylenediamine; BIA, 2-(4-aminophenyl)-5-aminobenzimidazole; ODA, 4,4′-oxidianiline

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advances in chemical resistance, electrical performance and excellent radiation shielding capability [8,9]. Nowadays, high performance PI fibers are highly desired to satisfy high-tech application, such as protecting suits, aerospace and electrics [1,10–12].

In the effort to prepare high performance PI fibers, both chemical and physical approaches has been explored [13–17]. Regarding chemical method, an array of novel monomers are introduced to synthesized PI. Cheng et al. fabricated organo-soluble and optical transparent PI by using 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and different aromatic diamines [14]. Qiu et al. reported a kind of PI copolymer by incorporating diamine containing N-phenyl-1,2,4-triazole moiety. This new PI shown better water absorption depression and proton conductivity while the high thermal stability and the good mechanical properties were retained. To enhance the mechanical properties, the rigid aromatic heterocyclic monomer units have been widely utilized, which was proved to effectively increase the rigidity of PI backbones and create additional intermolecular association effect [8,12,14,18–20]. In addition, some physical means, such as pre-drawing and annealing, can be utilized to tune the structure and properties of PI. Liu et al. reported a hydrogen-bonding containing PI fibers and films which shows tunable tensile stress by regulating the annealing temperature [20]. Commonly, the thermal annealing is expected to have an influence on the crystallization and molecular chains orientation degree under heat and tension which would affect the mechanical properties of fibers [15,21].

The polyimide fibers with co-polymerized aromatic heterocyclic units have been fabricated by the two-step method to get rid of the poor fibers processibility in conventional one-step method [13,14,22,23]. In this case, precursor polyamic acid (PAA) was spinned into PAA fibers followed by thermal imidization or chemical imidization process. However, this method suffers from low draw ratio of PAA fibers during the wet-spinning process as well as the release of solvents and the volatile products during the imidization. These disadvantages lead to relatively poor mechanical properties and the formation of microvoids for original fibers [18,24–27]. Pre-drawing was utilized to effectively improve the tensile modulus of such copolyimide fibers. However, much higher draw ratio is difficult which may also compromise the mechanical properties of obtained fiber. As discussed previously, the thermal annealing would affect the microstructure and properties of fibers. To access high performance fibers by physical method, it is of great significance to understand how the crystallization and microvoids structures evolve during annealing. And what is the relationship between the microstructure and mechanical properties in high performance fibers.

In this work, we focus on the correlation between microstructural evolution and mechanical property of microvoid containing PI fibers under thermal annealing conditioning. The liquid crystal-like structural evolution and the microvoid structural evolution during annealing process were analyzed by *in-situ* wide-angle X-ray diffraction (WAXD) and *ex-situ* small-angle X-ray scattering (SAXS). Mechanical property and relaxation of PI fiber were tested by dynamic mechanical analysis (DMA). The effects of annealing temperature and time on the microstructure were systematically studied. This system provides an opportunity to study the role of microvoids in high performance PI fibers. It was found that the evolution of molecular orientation and microvoid structure played critical roles in the mechanical properties. Based on our results, a model was proposed to illustrate the evolution of microvoids of PI fibers with different pre-draw ratios under annealing.

2. Experimental

2.1. Materials

The PI fibers were synthesized from 3,3′,4,4′-biphenyldianhydride (BPDA), *p*-phenylenediamine (*p*-PDA), 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) and 4,4′-oxidianiline (ODA) with the mole ratio of *p*-PDA, BIA and ODA of 8:1:1. The PI fibers were fabricated by the wet-spinning method: first, the BPDA/*p*-PDA/BIA/ODA copoly(amic acid) (co-PAA) solution was prepared; then, the co-PAA solution was degassed for the preparation of co-PAA precursor fibers; finally, the co-PAA precursor fibers were thermal imidized into PI fibers with draw ratios of 1 and 3 (named as PI-1 and PI-3, respectively) [21]. The chemical structure of PI fibers is shown in Fig. 1.

2.2. Preparation of annealed PI fibers

The annealed PI fibers were prepared by fixing the PI filaments on the homemade aluminum sample holders and put in the oven of DMA 800 (TA Instruments) for the thermal treatments with a preload force of 0.01 N to keep the fibers unbend. The annealing process was carried out at 360 °C, 385 °C or 435 °C for 15 min and 435 °C for 5 min, 15 min and 25 min (as listed in Table 1).

2.3. Characterization

Dynamic mechanical analysis (DMA) and the preparation of annealed PI fibers were carried out on the DMA 800 (TA

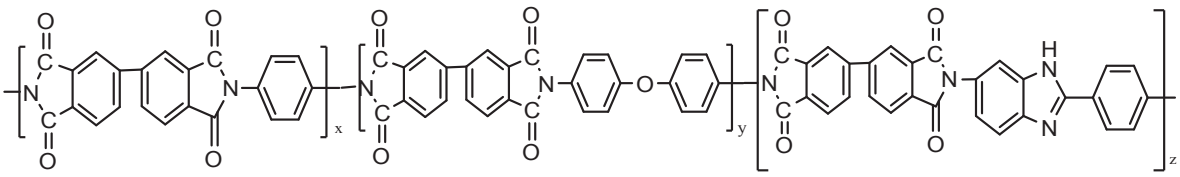

Fig. 1. The chemical structure of PI fibers.