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Enhanced mechanical and hydrophobic properties of polyimide fibers containing benzimidazole and benzoxazole units

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ABSTRACT

A series of rigid-rod co-polyimides (co-PI) containing benzimidazole and benzoxazole moieties were synthesized by the reaction of 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) and 5-amino-2-(4-aminobenzene)benzoxazole (BOA) with 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA). The corresponding co-PI fibers with various diamine ratios were prepared by the two-step wet-spinning process. The small chemical structure difference between benzimidazole and benzoxazole moieties leads to unexpected great changes on the aggregation structures and properties of the obtained fibers. The two-dimensional wide-angle X-ray diffraction (WAXD) spectra imply that the co-PI fibers containing more than 70% molar ratio of BIA show better-defined ordered crystal structures, while for those samples with more BOA contents, a new ordered lateral packing occurs. Meanwhile, the equatorial scattering streaks in the small-angle X-ray scattering (SAXS) patterns for the co-PI fibers suggest the presence of microvoids, whose sizes were evaluated by means of Guinier and Ruland's method. The optimum tensile strength and modulus of co-PI fibers are as high as 1.74 and 74.4 GPa, respectively, at the BIA/BOA molar ratio of 7/3. Besides, the co-PI fibers exhibit excellent thermal and thermo-oxidative stabilities due to the rigid molecular chains. The introduction of BOA units in the polymer backbones have apparently improved the hydrophobic properties of PI fibers.

1. Introduction

High-performance polymeric fibers are of great interest to researchers due to their high strength-to-weight ratio, ease of processing and availability of structural variations to control both mechanical and physical properties. In response to the need of high strength polymeric fibers for various engineering applications, scientists have long been active in researches in the area of aromatic polymer fibers with rigid heterocyclic units [1–3]. The *p*-configured poly(*p*-phenylenebenzobis-oxazole) (PBO) [4], poly(*p*-phenylene. benzobisthiazole) (PBT) [5], poly(*p*-phenylene benzobiaimidazole) (PBI) [6] and polypyridobisimidazole (PIPD, M5) [7] fibers have been successfully developed and show high tensile strength, high modulus and excellent thermo-oxidative stabilities (see Fig. 1).

Aromatic polyimide (PI) and co-polyimide (co-PI) fibers have been well-known as a class of high-performance polymers possessing valuable properties, of which in particular, they exhibit excellent thermal stability and good chemical resistance as well as outstanding dielectric properties [8,9]. These combined properties make them competitive in most applications: in light, slender, load bearing stiff advanced composite components and structures [10]. However, the properties of polyimide fibers

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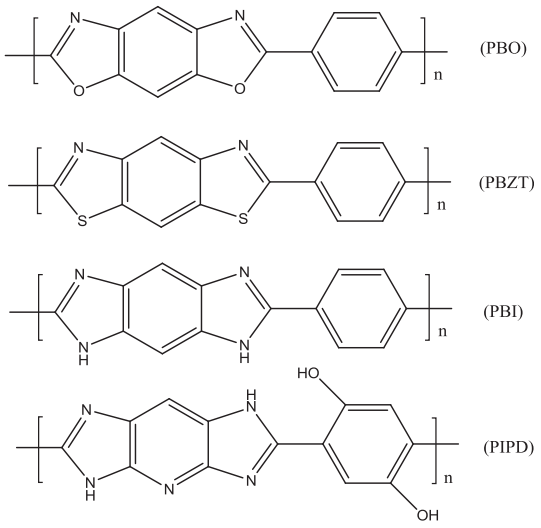

Fig. 1. Chemical structures of several typical aromatic polymers.

are in need of further improvement when employed in severer environments. For instance, the requirements of polyimide fibers for more advanced composites with high reliability in radome application include high strength, high modulus, excellent hydrophobicity and dimensional stability along with high adhesion to the resin [11]. To improve the mechanical properties of polymeric fibers, one attempted approach is structural modification, such as introducing the rigid heterocyclic units to the polymer backbone that leads to increased rigidity of the molecular chains [12–14]. Among them, the heterocyclic diamine 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) is a versatile monomer with an asymmetry structure feature, it can introduce strong inter- and intra-molecular hydrogen-bonding interaction that may strengthen the mechanical properties of resulting materials [12,15,16]. It has been successfully introduced into rigid-rod, *para*-substituted, wholly aromatic polyamide fibers (armid-fiber, Armos) in order to improve mechanical properties of the Kevlar [17]. Moreover, the benzimidazole moiety with both proton donor (—NH—) and proton acceptor (=N) hydrogen bonding sites would exhibit additional hydrogen bonding interactions with sulfonyl and carbonyl groups in the resin materials, and in turn enhance the adhesive properties of the polyimide fibers. However, the benzimidazole unit has its weakness, that is, high affinity for water, which may cause package cracking and reduce the dimensional stability when the fibers are produced into the radomes or the spacesuits [7]. Therefore, in order to produce a kind of polyimide fiber with good comprehensive performance, other components are also needed to incorporate into the polymer chains. With an analogous chemical structure, the heterocyclic benzoxadazole moiety also shows unique properties. As a kind of high performance polymer fibers containing benzoxazole units, Zylon® fiber (PBO) possesses very high tensile strength (~5.8 GPa) and modulus (~270 GPa) and excellent thermal stability as well as good environmental resistance [18,19], moreover, the heat treated Zylon® HM fiber almost shows zero moisture sensitivity [1]. Zhuang et al. [20] has introduced the benzoxadazole unities into the polyimide backbones to improve the mechanical and thermal properties of the polyimide films. They illustrated that the enhanced performance of the films was attributed to the improved regularity of the interchain packing. Based on the above analysis, we can conclude that the incorporation of benzimidazole moieties into the polyimide chains is expected to enhance both the intermolecular forces of polyimide chains, and the introduction of benzoxazole units is possible to enhance the mechanical and thermal properties, as well as decrease the water absorption of the PI fibers. In addition, Upilex-S, a typical high-performance commercialized polyimide derived from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and p-phenylenediamine (PDA), exhibits superior thermal, chemical and physical properties due to the stiff and linear chain structure, high molecular orientation and ordered structures caused by strong interchain interactions. Cheng et al. [21] have prepared a type of polyimide fiber based on BPDA and 2,2′-dimethyl-4,4′-diaminobiphenyl (DMB), showing a tensile strength of 3.3 GPa with a tensile modulus of ~140 GPa. Besides, Liu et al. [16] also have fabricated homo- and copolyimide fibers based on BPDA and various diamines, and the corresponding fibers showed excellent thermal stabilities and mechanical properties. Thus, what will happen if we introduce all the three moieties into the backbones of polyimide fibers?

With the purpose of obtaining high-performance PI fibers, in the present work, polyimide fibers containing benzimidazole and benzoxazole units were developed via a two-step wet spinning technology by copolymerization of 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) with two novel diamine monomers, 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) and 5-amino-2-(4-aminobenzene)benzoxazole (BOA). In comparison, the homo-BPDA/BIA and homo-BPDA/BOA polyimide fibers also have been produced. The effects of the incorporated BIA and BOA moieties on the aggregation structures and properties of the PI fibers are systematically investigated.

2. Experimental

2.1. Materials

3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA) was obtained from Shijiazhuang Haili Pharmaceutical Co., Ltd. and dried in vacuum at 120 °C for 24 h prior to use. 2-(4-Aminophenyl)-5-aminobenzimidazole (BIA) and 5-amino-2-(4-aminobenzene)benzoxazole (BOA) were purchased from Changzhou Sunlight Pharmaceutical Co., Ltd. *N*,*N*-dimethylacetamide (DMAc) with the water containing <100 ppm was obtained from Shanghai Jinshan Jingwei Chemical Co., Ltd. DMAc was purified by distillation under reduced pressure over calcium hydride.

2.2. Preparation of co-polyimide fibers

The chemical structures of the BPDA/(BIA/BOA) co-poly(amic acid) (co-PAA) and co-PIs prepared in the present work are illustrated in Fig. 2. The co-PI fibers were