



Superior comprehensive performance of a rigid-rod poly(hydroxy-p-phenylenebenzobisoxazole) fiber

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ABSTRACT

The novel poly(hydroxy-p-phenylenebenzobisoxazole) (HPBO) was synthesized by different polymerization routes, including hydroxy-orderly distributed polymer (*ord*-HPBO) and hydroxy-randomly distributed polymer (*ran*-HPBO). Surface elemental composition, thermal stability, intrinsic viscosity, UV resistance, surface morphology, mechanical and interfacial properties of HPBO fiber were investigated. ATR-FTIR and EDS spectrums identify the formation of mono-hydroxyl modified polymer. Excellent thermal stability (up to 600 °C), mechanical properties (tensile strength of 4.32 GPa, modulus of 169.7 GPa) and rheological spinnability of *ran*-HPBO-AS via HD self-polymerization route were obtained. Meanwhile, the SEM after UV irradiation indicated that the photostability of HPBO is better than PBO. The interfacial shear strength (IFSS) between HPBO-AS fiber and epoxy resin is 21.7 MPa, 87.1% higher than that of PBO-AS fiber. Comparing different HPBO synthesis routes, the self-polymerization of HD salt route is believed to be a feasible route for industrial production and the *ran*-HPBO is expected to become a new generation of high-performance fiber.

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1. Introduction

Poly(p-phenylenebenzobisoxazole) (PBO) is a rigid-rod heterocyclic polymer, which has gain extensive attentions for its excellent thermal stability, flame resistance, remarkable mechanical strength, high modulus and low density [1–3]. PBO fiber was commercialized with the trade name Zylon® by Toyobo Co., Japan in 1998. PBO (Zylon®) is currently the strongest commercialized organic fiber with tensile strength of 5.8 GPa, tensile modulus of 270 GPa, LOI of 68 and decomposition temperature of 650 °C [3–7]. Owing to its outstanding properties, PBO can be used as advanced composite material and has a great potential application in many fields such as aerospace, military and general industry [8–10]. However, due to chemically inert and the lack of polar functional groups in its polymer repeat units, the interfacial adhesion of PBO fibers to the matrix resin is very poor, which seriously restricted the whole performance and application in the field of fiber/resin composites [5,8,11–15]. Different methods for surface treatment have been proposed to improve the interfacial adhesion between PBO fiber and epoxy resin, including chemical treatment [16,17],

plasma treatment [18], coupling reagent treatment [19], and so on. However, most technologies would lead to the damage of the fiber and the decline of the original mechanical properties. Meanwhile, the photodegradation of PBO fibres under UV exposure is very serious, which has prompted the rapid development of the study of UV-ageing resistance [4,20–22]. Although many researches have focused on the avoiding light treatment technologies such as fiber surface coating [14,23], formation of crosslinking bonds in the chemical structure [24,25], usage of organic and inorganic UV absorbers [4,26], it will cause gradual loss of fiber's softness and lightweight. Therefore, it is critical to find a novel and efficient method to improve PBO fiber interfacial adhesion, photostability effectively while maintaining the original superior properties.

In recent years, most of the chemical modification studies were done via the introduction of binary hydroxyl polar groups into the main chains of PBO to provide a hydrogen bond interaction. A series of modified PBO fibers (Fig. 1) such as dihydroxy poly(p-phenylenebenzobisoxazole) (DHPBO) [27–29], poly(-pyridobisimidazole) (PIPD or M5) [30–32] and Poly{1,4-(2,5-dihydroxy)-phenylene-2,6-benzo-[4,5-b:4',5'-e]bis-imidazole} (PDBI) [33,34] all which containing binary hydroxyl groups in polymer chains, were prepared by co-polymerization of 2,5-dihydroxyterephthalic acid (2,5-DHTA) with 4,6-diaminoresorcinol dihydrochloride (DARH), 2,3,5,6-

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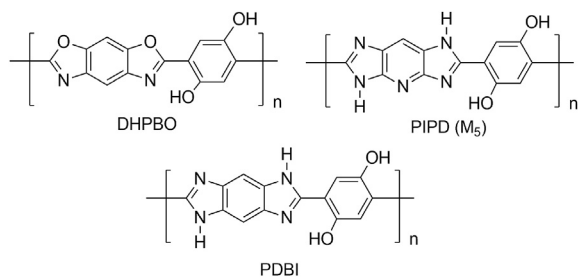


Fig. 1. The molecular structure of dihydroxy-modified PBO fibers.

tetraminopyridine trihydrochloride (TAP·3HCl) and 1,2,4,5-tetraaminobenzene tetrahydrochloride (TAB·4HCl) respectively. The compressive strength of PIPD (M5) (including PDBI) is nearly four times more than that of PBO fiber because of the hydrogen bond network structure in its molecular chains formed by the polar groups –OH and skeleton groups –NH– [32]. The interfacial adhesion and photostability of these fibers are superior to PBO. However, the heat resistance of these fibers is much lower than that of PBO fiber (at least 100 °C above), the price of PIPD is 1.8 times to PBO, the tensile strength and the LOI (<50) are all lower than that of the PBO fiber. These factors seriously restrict the application of these high-performance fibers.

To further enhance the interfacial adhesion and photostability of poly(p-phenylenebenzobisoxazole) (PBO) fiber while maintaining its superior thermal stability and mechanical property, PBO was modified with hydroxy terephthalic acid (HTA) instead of terephthalic acid (TA). Herein, we reported the designing and synthesis of mono-hydroxyl modified PBO—poly(hydroxy-p-phenylenebenzobisoxazole) (HPBO) via different polymerization routes. The effects of hydroxyl polar group on the surface properties of PBO fiber were investigated. Interfacial shearing strength (IFSS) test, tensile property test, thermal stability test, FTIR spectra, energy-dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) had been used for characterization.

2. Experimental section

2.1. Materials

HABA 99.0%, HTA 99.5%, HD of 4,6-diaminoresorcinol (DAR) and HTA were own products. DARH 99.8% was purchased from Zhejiang Dragon Chemical Co. Ltd., China. The PBO-AS fibers (Zylon, AS) were supplied by Toyobo Ltd., Japan. Phosphorus pentoxide (P₂O₅) and 85% poly phosphoric acid (PPA) were industrial products.

2.2. Measurements

FTIR spectra (IR) of the polymers and thermo-stabilized fibers were recorded on a Thermo Nicolet iS10 FTIR spectrometer (Nicolet, USA) in attenuated total reflectance (ATR) mode, with spectra recorded between 4000 and 650 cm⁻¹. A KBr pellet technique was used and 32 scans were collected at a resolution of 4 cm⁻¹.

¹H NMR spectra of the samples were obtained on a Bruker AVANCE 400 instrument (Bruker Co., Germany) with dimethyl sulfoxide-d₆ (DMSO-d₆) as solvent and tetramethylsilane (TMS) as an internal standard.

Thermal properties of the polymers were studied by a HTG-3 thermal analyzer (Beijing permanent scientific instrument factory, China). About 10 ± 0.5 mg of samples was placed in an aluminium oxide pan, and heated from room temperature up to 1000 °C with a heating rate of 15 °C/min under air and nitrogen atmospheres.

Intrinsic viscosities [η] of the synthesized polymer were measured in methane sulfonic acid (MSA) at 30 ± 0.1 °C using a 0.8–0.9 mm modified Ubbelohde capillary viscometer. Molecular weight was calculated from the intrinsic viscosities of the corresponding solutions using the following Mark-Houwink-Sakurada equation.

$$[\eta] = 2.77 \times 10^{-7} Mw^{1.8} \quad (1)$$

Single fiber tensile strength was tested by a semiautomatic, Electric strength tester (YG020, Ningbo Textile Instrument Co., Ltd, China) with a 200 mm clip distance and a 20 mm/min test speed. The interfacial shear strength (IFSS) between fibers and resin were measured by a single fiber pull out test under the room temperature with a cross head rate of 1 mm/min to calculate the interface shear strength (IFSS) of the PBO-AS and ran-HPBO-AS fibers. The samples were prepared by the same method of literature [35]. Single fiber tensile property test was carried out with YG(B)003A model Electronic Single Fiber Strength Tester (Wenzhou Darong Textile Instrument Co., Ltd, China). The final value of each sample is the average one after 50–60 measurements. The calculation was carried out according to equation (2):

$$\tau = \frac{F}{\pi dL} \quad (2)$$

Where F is the value of maximum pull-out force (N), d is the average diameter of the fiber (m) and L is the embedded length of fiber sample in resin (m).

SEM images of the fiber samples were collected using a field emission scanning electron microscope (Hitachi Co., TM3030Plus, Japan) at an accelerating voltage of 15 kV. Their surface chemical compositions were analyzed using energy-dispersive spectroscopy (EDS, FEI Nova Nano SEM 450, USA).

2.3. Preparation of HPBO single fibers

Due to the asymmetric mono-hydroxyl position in the molecule, HPBO can be subdivided into two molecular structures including hydroxy-ordered distributed polymer (*ord*-HPBO) and hydroxy-randomly distributed polymer (*ran*-HPBO) (Fig. 2).

In this study *ord*-HPBO and *ran*-HPBO were synthesized by homo-polymerization of AB type monomer 2-hydroxyl-4-(5-amino-6-hydroxy benzoxazole-2-yl)benzoic acid (HABA) [36], self-polymerization of composite monomer (HD) and co-polymerization with 4,6-diaminoresorcinol dihydrochloride (DARH) and hydroxy terephthalic acid (HTA).

2.3.1. Preparation of *ord*-HPBO single fiber (Scheme 1)

81.60 g of PPA (85.0 wt% of P₂O₅) and 12.33 g of HABA (purity 99.21%, 0.0429 mol) were added into the reactor (Fig. 3) with 13.13 wt% monomer concentration. The mixture was stirred at 110 °C for 1.5 h and 125 °C for 40 min in nitrogen atmosphere, gradually heated to 150 °C in 1 h to present a liquid crystalline state. The reaction continued at 160 °C for 20 min and 180 °C for 20 min. The liquid crystalline solution of the ordered polymer was obtained (11.48 wt% of *ord*-HPBO).

The single fiber was manually drew from above liquid

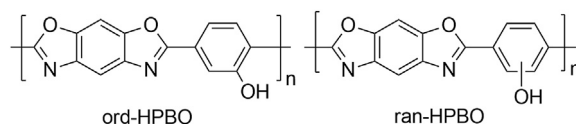


Fig. 2. Molecular structure of HPBO's ordered and random polymers.

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