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ORIGINAL PAPER

Synthesis and characterization of a rigid-rod dihydroxy poly(*p*-phenylene benzobisoxazole) fiber with excellent surface and axial compression properties

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Abstract A series of dihydroxy poly(*p*-phenylene benzobisoxazole) (DHPBO) were prepared by introducing binary hydroxyl polar groups into poly(*p*-phenylene benzoxazole) PBO macromolecular chains and the effects of hydroxyl polar groups on surface wettability, interfacial adhesion and axial compression property of PBO fiber were investigated. Contact angle measurement showed that the wetting process both for water and for ethanol on DHPBO fibers were obviously shorter than that on PBO fibers, implying DHPBO fibers have a higher surface free energy. Meanwhile, single fiber pull-out test showed that DHPBO fibers had higher interfacial shear strength than that of PBO fibers. Scanning electron microscope proved that there was more resin remained on the surface of DHPBO fibers than on PBO fibers after pull-out test. Furthermore, axial compression bending test showed that the introduction of binary hydroxyl groups into macromolecular chains apparently improved the equivalent bending modulus of DHPBO fibers.

Keywords PBO fiber · DHPBO fiber · Contact angle ·
Interfacial shear strength (IFSS) · Axial compression properties

Introduction

Owing to its outstanding mechanical and thermal properties, poly(*p*-phenylene benzoxazole) (PBO) fibers can be used as reinforcement materials in advanced composites and have great potential applications in the fields of aerospace, military industry and general industry [1–10]. However, due to its smooth surface and chemical inactive characteristic, PBO fiber has poor interfacial adhesion ability with

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matrix resin, which greatly limits its application. To improve surface free energy of PBO fibers, various surface modification techniques have been proposed recently [11–15].

On the other hand, it is well known that PBO fiber possesses excellent tensile strength and tensile modulus. However, the use of PBO fibers in structural application has been highly restricted by their poor compressive performance [16]. Dang et al. [17, 18] added –OH to PBO, poly(*p*-phenylenebenzobisthiazole) (PBZT) and polybenzimidazoles (PBI), and thus obtained fibers with extremely high modulus/high strength fibers. Poly {2,6-diimidazo[4,5-b:4′5′-e]pyridinylene-1,4(2,5-dihydroxy)phenylene} (PIPD), a rigid-rod polymeric fiber with the highest compressive strength found in polymeric materials so far [19, 20], is thought to have a bidirectional network of hydrogen bonds in its chemical structure [21–23]. We propose the introduction of hydrogen bonds to polymers may help to improve the compressive strength [24].

In this work, through introducing binary hydroxyl polar groups into PBO macromolecular chains, we obtained DHPBO fibers with excellent surface wettability, improved interfacial adhesion ability and axial compressive strength. The effects of hydroxyl groups on surface properties and compressive properties of DHPBO fiber were investigated. Contact angle measurement, single fiber pull-out test, scanning electron microscopy (SEM), and fiber micro-compression test have been used for characterization.

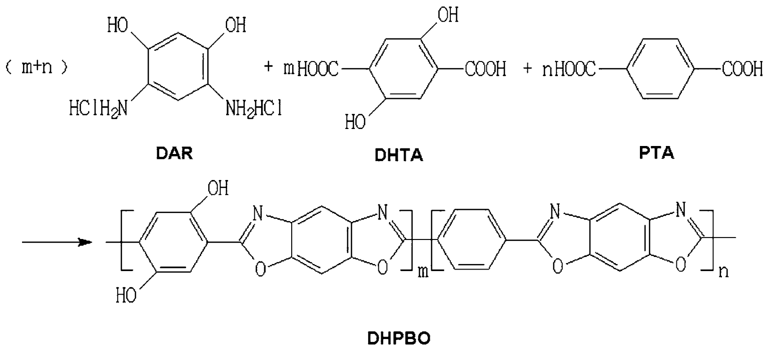
Experimental

Polymer synthesis and fiber spinning

PBO was prepared by copolymerization from 4,6-diamino resorcinol dihydrochloride (DAR) and pure terephthalic acid (PTA) in polyphosphoric acid (PPA) according to the Wolfe's method [25].A series of DHPBO polymers were obtained by the same method with certain amount PTA replaced by 2,5-dihydroxyterephthalic acid (DHTA) (synthesized in our laboratory) [DAR mol%: (DHTA mol% + PTA mol%) = 1:1] as shown in Scheme 1. DHPBO polymers with DHTA mole percentage of 5, 10, 20 and 50% (DHPBO-5%, DHPBO-10%, DHPBO-20%, DHPBO-50%) were spun into fibers through a spinneret with a hole size of 0.30 mm via dry-jet wet-spinning process. The coagulation bath system was PPA/H_2O. The coagulation bath concentration is 10 wt% and bath temperature is 25 °C. The intrinsic viscosity of the obtained DHPBO polymers is in the range of 21.9–28.3 dL/g.

Characterization

Fourier transform infrared (FTIR) spectrum (Niolet 20sx B) was used to characterize the chemical structures of the as-spun PBO and DHPBO fibers. Thermogravimetric analysis (TGA) (Netzsch STA449C) was used to measure the thermal stability of these fibers. The surface wettability of fibers was analyzed by an



Scheme 1 Preparation of DHPBO from DAR, DHTA and PTA

OCA40 Micro dynamic contact angle analysis system. Both the contact angles for water (θ_{water}) and for ethanol ($\theta_{\mathrm{ethanol}}$) and the variation of the contact angle with time ($d\theta/dt$) had been recorded. Surface free energy of those fibers were calculated from the contact angle results. The interfacial shear strength (IFSS) between fibers and resin were measured by pulling out fibers embedded in epoxy resin [A618(E-51)] matrix [22]. After single fiber pull-out test, SEM was used to characterize the surface morphology of the pulled-out PBO and DHPBO fibers. Single fiber tensile property test was carried out at room temperature with tensile testing equipment XQ-1 Tensilon (made by Donghua University, the testing accuracy of this equipment is 1%). For each sample, 50–60 specimens were tested to get an average value. Standard deviations of all tensile measurements are below 10%.

Axial compression bending test was carried out on a fiber compression bending apparatus developed by Textile Materials and Technology Lab in our university [21]. The testing process is as following: a miniature loading apparatus was used to compress the fiber axially while the compressive load being directly detected and recorded. The equivalent compression bending modulus could then be calculated based on the compressive load, the diameter of fiber and the length of fiber.

Results and discussion

FTIR analysis of DHPBO fibers

We carefully compared the FTIR spectrum of PBO and DHPBO-50% fibers. Research shows that the FTIR spectrum of DHPBO-50% fibers has an extra peak located at 3,116 cm^{-1}, which should be owing to stretching vibrations of O–H groups involved in the hydrogen-bonding interaction. This indicates that due to the introduction of DHTA, intermolecular hydrogen-bonds are formed in DHPBO fibers. It should be noted that, as suggested by studies on M5 fibers [24], hydrogen-bonds may enhance the compressive strength of fibers.

Table 1 Thermal properties of PBO and DHPBO polymer

Sample	DC[a] (mol %)	T_d (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	W[b] (wt %)
PBO	0	689.0	598.7	679.7	64.1
DHPBO-5%	5	662.0	408.3	612.3	55.9
DHPBO-10%	10	667.1	529.0	655.0	62.9
DHPBO-20%	20	641.7	214.6	556.6	55.3
DHPBO-50%	50	611.8	98.3	191.3	58.7

[a] Mole content of DHTA in DHPBO polymers

[b] Residual weight percentage at 800 °C

Thermal stability of the DHPBO fibers

Thermogravimetry measurements prove that DHPBO fibers have excellent thermal stability. With the incorporation of binary hydroxyl polar groups, their thermal degradation temperatures (T_d) are just slightly lower than that of PBO fibers, but still above 610 °C in nitrogen (Table 1). The temperatures at which the weight loss is 5 or 10 wt% ($T_{5\%}$ and $T_{10\%}$) of those samples are also listed in Table 1. It is interesting that, the $T_{5\%}$ and $T_{10\%}$ of the DHPBO samples first remarkably increase then decrease with the increasing content of DHTA. That can be understood by following: The introduction of DHTA will enhance intermolecular actions, at the same time, it will lower the polymerization degree. The former factor plays a dominant role when DHTA content is low, while the later factor becomes more and more obvious with the increase of DHTA content.

Surface wettability and surface free energy

Table 2 shows the contact angles for water (θ_{water}) and for ethanol ($\theta_{\mathrm{ethanol}}$) on PBO and DHPBO fibers. With the increase of DHTA content, both θ_{water} and $\theta_{\mathrm{ethanol}}$ gradually decrease, implying the influence of hydroxyl groups on the wettability of these polymers. Figure 1a and b showed the wetting process of water on PBO fibers and DHPBO-50% fibers. The wetting process of water on PBO fibers lasted 1,300 ms, while the wetting process on DHPBO-50% fiber lasted only 650 ms.

Table 2 Surface properties of PBO and DHPBO fibers

Samples	Contact angle (to water)	Contact angle (to ethanol)	σ (mJ/m^2)	σ_d (mJ/m^2)	σ_p (mJ/m^2)
PBO	71.4	37.2	35.51	10.76	24.75
DHPBO-5%	66.0	38.2	39.12	10.42	28.70
DHPBO-10%	61.2	32.6	42.44	11.13	31.31
DHPBO-20%	59.8	27.8	43.42	15.40	31.67
DHPBO-50%	50.7	27.4	49.97	11.58	38.39

IFSS of DHPBO fibers/epoxy resin

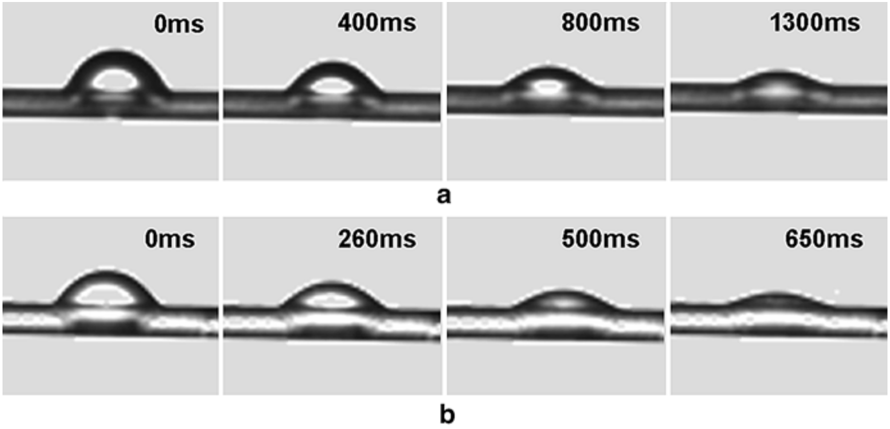


Fig. 1 Wetting process of water on **a** PBO fibers and **b** DHPBO-50% fibers

These results prove the wettability of DHPBO fibers are greatly improved by introducing of double hydroxyl polar groups into macromolecular chains.

Based on contact angle results, the surface free energy of those fibers were calculated according to harmonic mean approximation model [26, 27]. Both the total surface free energy (σ) and its dispersive (σ_d) and polar (σ_p) components are shown in Table 2. The σ and σ_p of DHPBO fibers increase with the increasing of DHTA, which proves the introduction of polar hydroxyl groups enhances the polarity of DHPBO fiber surface and results in increase of surface free energy. That will lead to increase in the interfacial adherence ability of the fibers.

IFSS is an important factor in evaluating the stress transfer ability between matrix and fibers in a composite. Better interfacial adherence ability will result in a larger IFSS value. As shown in Table 3, the IFSS of each DHPBO fiber/epoxy resin is apparently higher than that of PBO fiber. When the mole content of DHTA is 10%, DHPBO fibers have the best IFSS value. SEM images shown in Fig. 2 give more direct evidence. As can be seen, there was more resin remaining on the surface of DHPBO fibers than on PBO fibers after pull-out test. These results exhibit that the surface adhesion ability of PBO fibers had been greatly improved by incorporation of DHTA.

Mechanical properties of the DHPBO fibers

Table 4 shows tensile property parameters of DHPBO and PBO fibers. With the addition of DHTA, DHPBO fibers still exhibit good tensile properties, with no

Table 3 IFSS of the PBO and DHPBO fiber/epoxy resin

Samples	PBO	DHPBO-5%	DHPBO-10%	DHPBO-20%	DHPBO-50%
IFSS (MPa)	9.80	16.83	18.87	17.43	18.29
Increment relative PBO fiber (%)	–	71.73	92.55	77.85	86.65

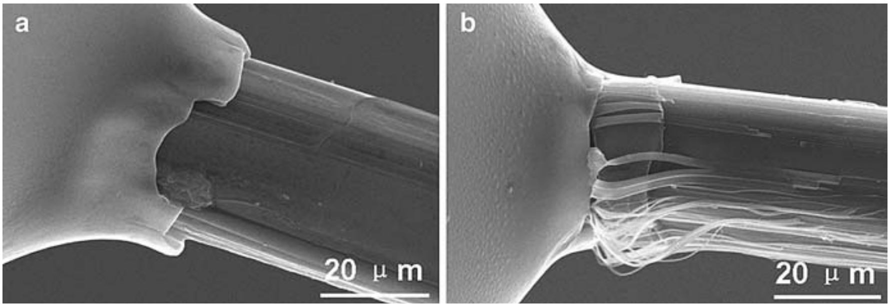


Fig. 2 Typical SEM images of pull-out **a** PBO fiber and **b** DHPBO fiber

Table 4 Tensile properties of DHPBO and PBO fibers

Samples	Tensile strength (cN/dtex)/(GPa)	Tensile modulus (cN/dtex)/(GPa)	Elongation at break (%)
PBO[a]	37.00/5.80	1150.00/180.00	3.50
PBO[b]	35.37/5.52	1105.05/172.39	3.60
DHPBO-5%	33.56/5.24	1100.05/171.61	3.30
DHPBO-10%	32.40/5.05	919.75/143.48	3.27
DHPBO-20%	28.53/4.45	680.95/106.23	3.35

[a] Commerical PBO (AS)

[b] Lab-produced PBO (AS)

remarkable decline compared with that of PBO fibers. However, too high DHTA loading will result in obvious decline in tensile property.

Axial compressive properties

Compared with PBO, DHPBO fibers showed improved axial compressive properties. Figure 3a and b are two typical SEM images of the kink bands on PBO and DHPBO fiber surface induced by axial compression. Under same compression load, the kink band on PBO fiber surface is very clear, while the surface of DHPBO fiber still remains smooth and uniform. Table 5 shows the axial compression bending

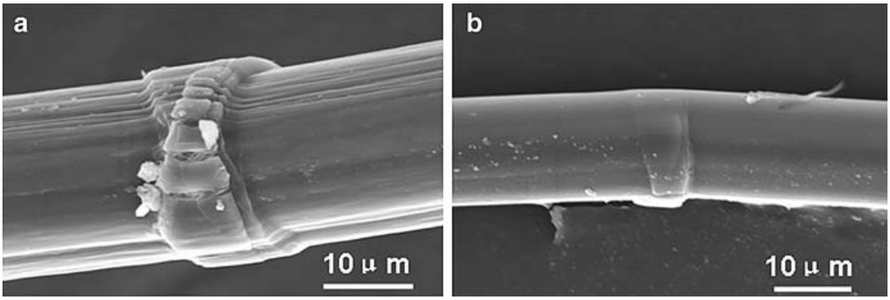


Fig. 3 SEM images of kink band induced by axial compression bending on **a** PBO fiber and **b** DHPBO-10% fiber under same axial compression load

Table 5 Compression bending parameters of single fiber

Samples	Mean diameter (μm)	Equivalent bending modulus (GPa)
PBO	26.02	15.36
DHPBO-5%	17.10	17.50
DHPBO-10%	16.80	19.37
DHPBO-20%	18.60	21.88
DHPBO-50%	39.60	22.52

characteristics of PBO and DHPBO fibers. DHPBO fibers have larger equivalent bending modulus compared with that of PBO fibers, which is consistent with the results of SEM observation. Furthermore, the equivalent bending modulus of DHPBO fibers show increasing trend with increasing DHTA content. As shown in Table 5, when the mole content of DHTA is 50%, the DHPBO fibers showed the highest equivalent bending modulus.

The formation of intermolecular hydrogen-bonds in DHPBO fibers resulted from the incorporation of DHTA is believed to be the main origin of the phenomena mentioned above. The emergence of kink bands and cracks can be ascribed to the lack of strong lateral support between polymer chains in PBO fibers, which will also result in a low compressive strength (0.2–0.3 GPa) [28].

Conclusions

In this work, PBO fibers were modified by incorporating binary hydroxyl polar groups into macromolecular chains. The effects of hydroxyl polar groups on the surface properties and axial compressive properties of PBO fibers were investigated. Compared with PBO, DHPBO fibers have smaller contact angle and shorter wetting process both for water and ethanol, indicating a higher surface free energy. Single fiber pull-out test show that DHPBO fibers have obviously larger IFSS values than that of PBO fiber, which indicates a stronger interaction between DHPBO fiber and resin matrix. DHPBO fibers show larger equivalent bending modulus compared with that of PBO under same axial compressive load, which can be ascribed to the formation of intermolecular hydrogen-bonds in DHPBO fibers. When the mole content of DHTA is 10%, balancing various properties, the DHPBO fibers have the best comprehensive properties. Our results prove that introducing hydroxyl polar groups into macromolecular chains is an effective way to improve the surface wettability, interfacial adhesion and axial compression properties of polymer fibers.

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