

Effect of Hydrogen Bonding on the Compressive Strength of Dihydroxypoly(*p*-phenylenebenzobisoxazole) Fibers

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ABSTRACT By the introduction of binary hydroxyl groups into poly(*p*-phenylenebenzobisoxazole) (PBO) macromolecular chains, a series of dihydroxypoly(*p*-phenylenebenzobisoxazole) (DHPBO) chains were prepared, and the effect of the hydroxyl groups on the axial compression property of DHPBO fibers was investigated. The variable-temperature Fourier transform infrared spectrum proved the existence of hydrogen bonds in DHPBO chains. Furthermore, the axial compression bending test showed that the introduction of hydroxyl groups into macromolecular chains apparently improved the compression resistance property of DHPBO fibers. Finally, a proposed arrangement of the hydrogen bonding in DHPBO fibers is presented.

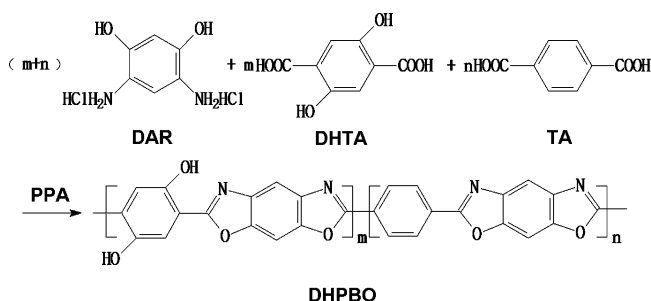
KEYWORDS: dihydroxypoly(*p*-phenylenebenzobisoxazole) fibers • hydroxyl groups • hydrogen bonds • compressive strength

1. INTRODUCTION

Poly(*p*-phenylenebenzobisoxazole) (PBO) fibers are well-known to possess the highest tensile modulus and tensile strength among all commercial synthetic polymer fibers, which can be used as reinforcement in advanced composites and have great potential applications in the fields of aerospace, military, and general industry (1–4). However, the use of PBO fibers in structural applications has been highly restricted by their poor compressive strength (0.2–0.4 GPa) (5). Poly(pyridobisimidazole) (PIPD), a rigid-rod polymeric fiber with the highest compressive strength among all of the polymeric materials to date (1.7 GPa) (6), is thought to have a bidirectional network of hydrogen bonds in its molecular chains formed by the hydroxyl groups on the phenyl ring (7–10). Inspired by the chemical structure of PIPD, we proposed that the introduction of hydroxyl groups into the macromolecular chains of a PBO polymer may be an effective method to improving the compression resistance property of the PBO fiber. The preliminary results showed that this method has excellent surface modification efficiency compared with post-treatment methods (11) and endowed fibers with excellent axial compressive strength (12). At the same time, it does not damage the mechanical properties of the PBO fibers (13).

In this paper, by the introduction hydroxyl polar groups into PBO macromolecular chains, we obtained dihydroxypoly(*p*-phenylenebenzobisoxazole) (DHPBO) fibers. The hydrogen bonds and the compressive property of the DHPBO

Scheme 1. Synthesis of DHPBO from DAR, DHTA, and TA



fiber were studied systematically by the Fourier transform infrared (FTIR) spectrum and a single-fiber compression bending apparatus, respectively. An proposed arrangement of the hydrogen bonds in DHPBO fibers was also presented.

2. EXPERIMENTAL SECTION

2.1. Preparation of the PBO and DHPBO Fibers. PBO was prepared by copolymerization from 4,6-diamino resorcinol dihydrochloride (DAR) (synthesized in our laboratory) and terephthalic acid (TA; Hyosung Company) in poly(phosphoric acid) (PPA) according to Wolfe's method (14). DHPBO was obtained by the same method except that a certain amount of TA was replaced by 2,5-dihydroxyterephthalic acid (DHTA; synthesized in our laboratory), as shown in Scheme 1. Polymerizations were carried out with a polymer concentration of 13 wt % and a P_2O_5 concentration of 84 wt %. DHPBO polymers with DHTA mole percentages of 5%, 10%, 20%, and 50% (DHPBO-5%, DHPBO-10%, DHPBO-20%, and DHPBO-50%) were prepared (DAR mol % : DHTA mol % + TA mol % = 1:1). The obtained DHPBO/PPA dope was directly spun into fibers via a dry-jet wet-spinning process (13). The fiber spinning was carried out at 185 °C through an 18-hole spinneret (the hole size is 0.30 mm). The coagulation bath contained 10% PPA/water solutions and was maintained at room temperature. An

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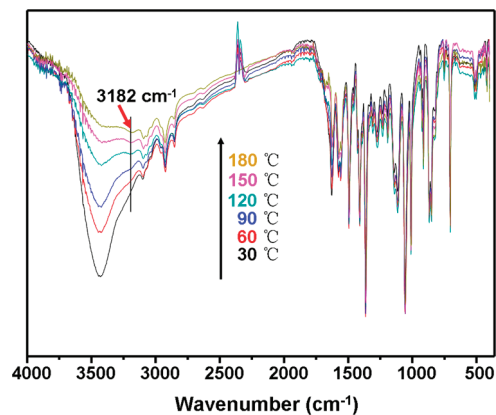


FIGURE 1. FTIR spectrum of the DHPBO-10% fibers at various temperatures.

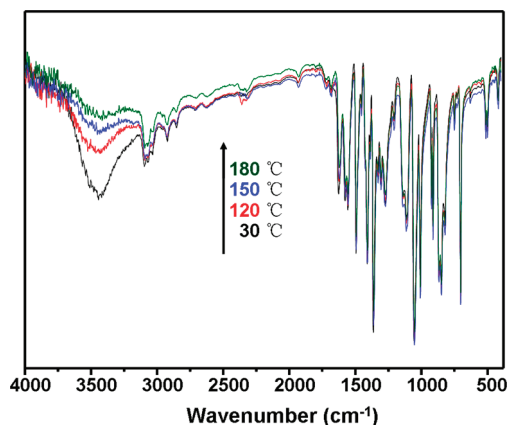


FIGURE 2. FTIR spectrum of the PBO fibers at various temperatures.

air gap of 30–50 cm was applied in the front of the coagulation bath. Fibers were spun at a speed of 110 m/min, then completely washed in running water, and dried at 100 °C in a vacuum. The intrinsic viscosity of the obtained DHPBO polymers is in the range of 21.9–28.3 dL/g.

2.2. Characterization. A variable-temperature FTIR spectrum (Niolet 20sx B) was used to characterize the change of the chemical structures of the as-spun PBO and DHPBO fibers during a heating process from 30 to 180 °C.

An axial compression bending test was carried out on a fiber compression bending apparatus developed by Textile Materials and Technology Lab in our university. The testing process is as follows: a miniature loading apparatus was used to compress the fiber axially, while the compressive load was directly detected and recorded. The equivalent compression bending modulus can be calculated by following equation (15):

$$P_{cr} = (0.99E_B K_B) \frac{D^4}{L^2} \quad (1)$$

where P_{cr} , E_B , K_B , D , and L are the compressive critical load, equivalent compression bending modulus, shape factor, diameter of the fiber, and length of the fiber, respectively. P_{cr} can be calculated automatically by the fiber compression bending apparatus.

3. RESULTS AND DISCUSSION

3.1. Variable-Temperature FTIR Spectra of the PBO and DHPBO Fibers.

The FTIR spectra of PBO

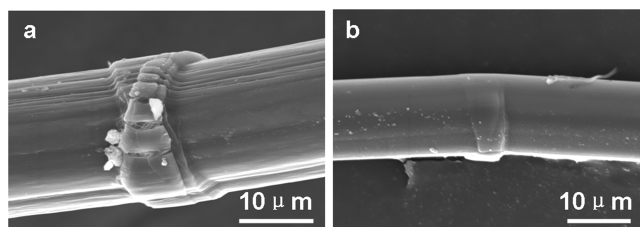


FIGURE 3. SEM images of a kink band induced by axial compression bending on (a) a PBO fiber and (b) a DHPBO-10% fiber under the same axial compression load.

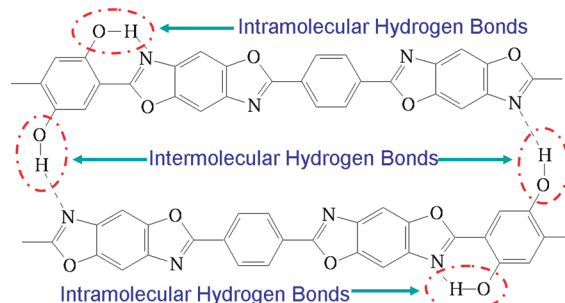


FIGURE 4. Proposed arrangement of the hydrogen bonds in DHPBO.

Table 1. Compression Bending Parameters of a Single Fiber

sample	mean diameter (μm)	equivalent compression 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

and DHPBO-10% fibers at various temperatures were compared. When the temperature was increased from 30 to 180 °C, the spectral peak related to the stretching vibrations near 3430 cm^{-1} of the DHPBO-10% fibers decreases gradually. Meanwhile, the FTIR spectrum of the DHPBO-10% fibers has an extra peak located at 3182 cm^{-1} , which should be ascribed to the stretching vibrations of OH groups involved in the intramolecular and intermolecular hydrogen bonds. Compared with the intermolecular hydrogen bonds, the intramolecular hydrogen bonds are more stable, with no change with temperature increases, whereas the intermolecular hydrogen bonds may be weakened gradually during the heating process. In contrast, the FTIR spectrum of the PBO fibers did not show new absorption spectra during the heating process except that the FTIR bands near 3430 cm^{-1} also gradually decreased.

This clearly proves the formation of hydrogen bonds in the DHPBO fibers due to the introduction of DHTA. It should be noted that, as proposed by studies on M5 fibers (16–18), hydrogen bonds may enhance the compressive strength of the fibers.

3.2. Axial Compressive Properties. Compared with PBO, DHPBO fibers showed improved axial compressive properties. Figure 3 gives two typical scanning electron

microscopy (SEM) images of the kink bands on the PBO and DHPBO-10% fiber surface induced by axial compression. Under the same compression load, the kink band on the PBO fiber surface is very clear, while the surface of the DHPBO-10% fiber still remains smooth and uniform. Table 1 shows the axial compression bending characteristics of the PBO and DHPBO fibers. DHPBO fibers have larger equivalent compression bending moduli compared with those of PBO fibers, which is consistent with the results of SEM observation. Furthermore, the equivalent compression bending moduli of DHPBO fibers show an increasing trend with increasing DHTA content. As shown in Table 1, when the mole content of DHTA is 50 mol %, the DHPBO fibers showed the highest equivalent compression bending modulus.

The formation of hydrogen bonds in DHPBO fibers resulting 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 (0.2–0.4 GPa) (5).

3.3. Proposed Arrangement of the Hydrogen Bonds in DHPBO. Based on the analysis of the FTIR spectra of DHPBO fibers at various temperatures, the formation of intermolecular hydrogen bonds via hydroxyl groups on adjacent chains is conceivable. Figure 4 illustrates the proposed relative positioning of the neighboring chains and the consequent hydrogen-bond formation in DHPBO fibers. DHPBO has hydroxyl groups along its macromolecular chains, which lead to the formation of both intramolecular and intermolecular hydrogen bonds. In contrast, there are only weak intermolecular links between neighboring chains in PBO fibers. The hydrogen bond, which is the strongest intermolecular force and is very stable, can control the aggregation structure of macromolecules at the molecular level. That is the reason why DHPBO fibers exhibit higher compressive strength than PBO fibers.

4. CONCLUSIONS

By incorporating double hydroxyl polar groups in PBO macromolecular chains, we synthesized DHPBO polymers and obtained their fibers through dry-jet wet-spinning techniques. On that basis, we investigated the effect of hydroxyl

groups on the compressive properties of DHPBO fibers. FTIR spectra proved that, by the introduction of DHTA into the polymerization system, hydrogen bonding formed in DHPBO fibers. DHPBO fibers have better compressive properties than PBO fibers. Our results indicate that the introduction of hydroxyl polar groups into macromolecular chains is an effective way of improving the axial compression properties of polymer fibers, which is important for their applications.

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