Carbohydrate Polymers 78 (2009) 364–366

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Short communication

A rigid-rod dihydroxy poly(*p*-phenylene benzobisoxazole) fiber with improved compressive strength

Tao Zhang, Junhong Jin, Shenglin Yang, Guang Li *, Jianming Jiang

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 201620, China

ARTICLE INFO

Article history:
Received 16 March 2009
Received in revised form 26 March 2009
Accepted 30 March 2009
Available online 8 April 2009

Keywords:
Poly(*p*-phenylene benzobisoxazole) fiber
Hydroxyl groups
Composite materials
Elastic loop test
Compressive strength

ABSTRACT

A series of dihydroxy poly(*p*-phenylene benzobisoxazole) (DHPBO) were prepared by introducing binary hydroxyl groups, that is 2,5-dihydroxyterephthalic acid (DHTA) into poly(*p*-phenylene benzoxazole) (PBO) macromolecular chains and then DHPBO fibers were prepared by dry-jet wet-spinning method. As indicated by Fourier transform infrared spectrum (FTIR), hydroxyl groups were incorporated into DHPBO polymer chains successfully and intermolecular hydrogen-bonds had been formed. The effects of hydroxyl groups on the compressive property of PBO fibers were investigated by elastic loop test method. The test results showed that the compressive strength of DHPBO fibers with 10 mol% DHTA content were obviously higher than that of PBO fibers.

1. Introduction

Poly (*p*-phenylene benzobisoxazole) (PBO) fibers are known to possess the highest tensile modulus and strength among all commercial synthetic polymer fibers. PBO can be used as reinforcement in advanced composites and has a great potential application in the fields of aerospace, military and general industry (Bourbigot, Flambard, & Duquesne, 2001; Chae & Kumar, 2006). However, the use of PBO fibers in structural application has been highly restricted by their poor compressive performance (Leal, Deitzel, & Gillespie, 2007). To improve the compressive property of PBO fiber is of great importance for the application of PBO fiber in advanced composites.

Several methods have been used to estimate single-fiber compressive strength (Furuyama, Higuchi, & Kubomura, 1993). Different from other compressive test methods, elastic loop test use a single filament without use of matrix. It can measure the compressive properties of fibers, which are free from the influence of matrix. Dobb, Johnson, and Saville (1981) studied the compression deformation of Kevlar fibers by elastic loop test and proposed a mechanism describing the mode of deformation based on the initial formation of kink bands. van der Zwaag and Kampschoer (1987) studied the formation of kink band in aramid fibers. They measured the kink band formation in single aramid filaments as a function of the applied compressive strain. Allen (1983) studied the bending and compressive behaviors of poly(*p*-phenylene benzobisthiazole) (PBZT) and poly(*p*-phenylene terephathalamide) (PPTA) fibers by elastica loop test. Nonlinear behaviour is a typical phenomenon not only for high-modulus fibers, but also for new super-high strength T-800 fibers, as which was showed by Jones and Johnson (1971). Subsequently, Bazhenov and Kozey (1991) using loop test method studied the compressive strength of carbon fibers.

In this work, poly(*p*-phenylene benzobisoxazole) (DHPBO), a modified PBO polymer containing double hydroxyl groups in the main chains, was synthesized by copolymerization from 4,6-diamino resorcinol dihydrochloride (DAR) and terephthalic acid (TA), with certain amount of TA replaced by 2,5-dihydroxyterephthalic acid (DHTA) in polyphosphoric acid (PPA). The compressive property of DHPBO fiber was investigated by elastic loop test.

2. Experiment

2.1. Preparation of DHPBO fibers

Dihydroxy poly(*p*-phenylene benzobisoxazole) (DHPBO) polymer was synthesized by the polycondensation of DAR, TA, and DHTA in PPA according to the Wolfe's method (Wolfe, 1988), as shown in Fig. 1.

Polymerizations were carried out with polymer concentration of 13 wt% and final P_2O_5 concentration of 84 wt%. DHPBO polymers with DHTA content of 5 mol%, 10 mol%, and 20 mol% (DHPBO-5%, DHPBO-10%, DHPBO-20%) were prepared. The obtained DHPBO/PPA dopes were directly spun into fibers via dry-jet wet-spinning process (Wolfe, 1988; Zhang et al., 2009). Fiber spinning was car-

* Corresponding author. Tel./fax: +86 021 67792830.
E-mail address: lig@dhu.edu.cn (G. Li).

0144-8617/$ - see front matter Crown Copyright © 2009 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2009.03.043

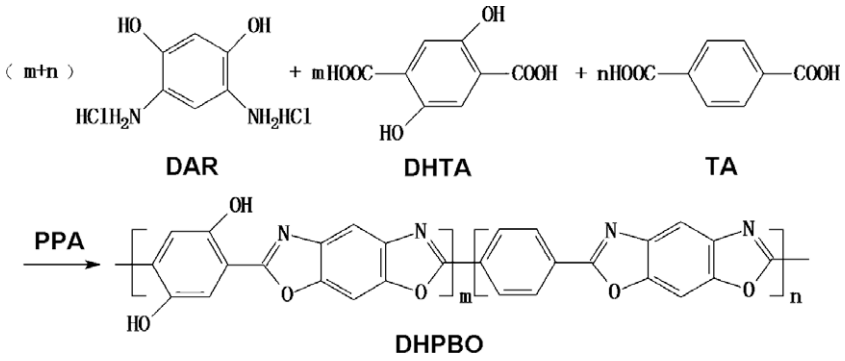

Fig. 1. Synthesis of DHPBO from DAR, DHTA and TA.

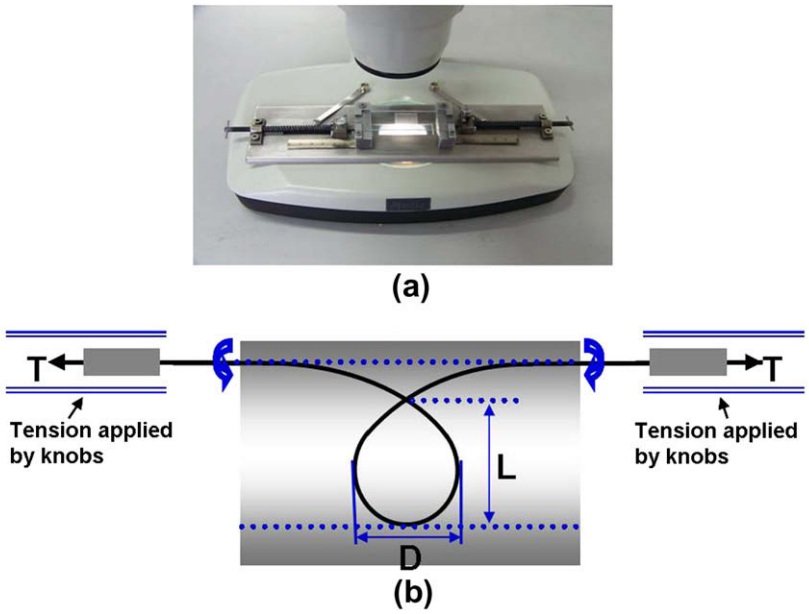

Fig. 2. Illustration for single-fiber compressive test using elastic loop method. (a) Apparatus used for the elastic loop test under optical microscope. (b) Schematic of the apparatus for the elastic loop test.

ried out at 185 °C through a 18 holes spinneret (hole size 0.30 mm). An air gap of 30–50 cm was applied above the coagulation bath, which contained 10% PPA/water solutions and was maintained at room temperature. Fibers were spun at a speed of 110 m/min, then completely washed in running water, and dried at 100 °C in vacuum.

2.2. Characterization

The chemical structure of PBO and DHPBO fibers were characterized by FTIR Spectrum. The compressive strength of fibers was measured by elastic loop method.

Elastic loop test was illustrated in Fig. 2. A filament loop was placed in light oil between two glass slides (Furuyama et al., 1993). The loop was successively deformed by pulling on both ends of the filament, with its longitudinal and transverse dimensions being measured by optical microscope (Bazhenov & Kozey, 1991). Theoretically (Sinclair, 1950), the fiber compressive strength (σ_f) can be calculated from

$$\sigma_f = 1.43 d_f E_f / L_c \quad (1)$$

where d_f is fiber diameter, E_f is fiber elastic modulus, L_c is the longitudinal size of the loop at which the longitudinal/transverse size ratio, L/D, falls below 1.34. The fiber elastic modulus under compression was assumed to be equal to its tensile modulus (Bazhenov & Kozey, 1991). The test results were averaged after examining twenty samples.

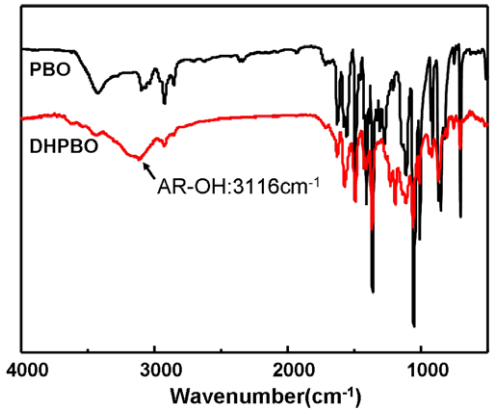

Fig. 3. FTIR spectra of PBO and DHPBO-10% fibers.

Table 1
Compressive strength of PBO and DHPBO fibers.

Fiber	Diameter (μm)	E^a (GPa)	$L_c{}^b$ (μm)	Compressive strength from loop test (GPa)	Tensile strength (GPa)
PBO	65.00	166.0	–	0.43	5.23
DHPBO-5%	17.10	171.6	5821.6 ± 10	0.72	5.24
DHPBO-10%	16.80	143.5	4604.6 ± 10	0.75	5.05
DHPBO-20%	18.60	106.2	6718.4 ± 10	0.42	4.45

[a] Fiber tensile modulus.
[b] L_c is the longitudinal size of the loop at which the longitudinal/transverse size ratio falls below 1.34.

3. Results and discussion

3.1. FTIR analysis of fibers

Fig. 3 shows the FTIR spectrum of PBO and DHPBO-10% fibers, with the contribution of H_2O having been subtracted. Due to the similar chemical structures of DHPBO and PBO fibers, these two FTIR spectrums are very similar to each other. Despite their similarity, as indicated by the arrow, the spectrum of DHPBO fiber has an extra peak located at 3116 cm^{-1}, which is attributed to stretching vibrations of O–H groups involved in the hydrogen-bonding interaction. This indicates the formation of intermolecular hydrogen-bonds in DHPBO fibers resulted from the introduction of DHTA. It should be noted that, as suggested by studies on M5 fibers (So, 2000), the formation of hydrogen-bonds may enhance the compressive strength of fibers.

3.2. Fiber compressive strength

The results of compressive strength testing are listed in Table 1. The compressive strength of PBO fiber tested by Fidan and Palazotto (1993) using the same method was 0.43 GPa. The compressive strength of DHPBO-10% fibers was measured to be 0.75 GPa, which is 62% higher than that of PBO fiber. While for DHPBO-20% fiber, the compressive strength decreases to the level of PBO fiber. The formation of intermolecular hydrogen-bonds in DHPBO fibers is believed to be the main origin of compressive strength improvement. It should be noted that the molecular weight and mechanical property of DHPBO fiber decreases when the DHTA content is more than 10 mol%, which will have a negative influence on the compressive strength.

4. Conclusions

By introducing hydroxyl groups into PBO macromolecular chains, DHPBO fiber with high tensile and compressive strength was produced. The elastic loop test results indicated the incorporation of hydroxyl groups was an effective way to improve the compressive strength of PBO fiber, which could be improved around 62% to 0.7 GPa. Similar to the mechanism suggested by studies on M5 fibers, the formation of intermolecular hydrogen-bonds is considered to the main origin of the compressive strength improvement.

Acknowledgment

The authors would like to thank the National Natural Science Foundation of China (50673017) and the Program of Introducing Talents of Discipline to Universities (111-2-04) for financial support.

References

Allen, S. R. (1983). Mechanical and morphological correlations in poly(*p*-Phenylenebenzobibthiazole) fibers. *Ph.D dissertation*, University of Massachusetts.
Bazhenov, S. L., & Kozey, V. V. (1991). Compression fracture of unidirectional carbon fibre-reinforced plastics. *Journal of Material Science, 26*, 6764–6776.
Bourbigot, S., Flambard, X., & Duquesne, S. (2001). Thermal degradation of poly(*p*-phenylenebenzobisoxazole) and poly(*p*-phenylenediamine terephthalamide) fibres. *Polymer International, 50*, 157–164.
Chae, H. G., & Kumar, S. (2006). Rigid-rod polymeric fibers. *Journal of Applied Polymer Science, 100*, 791–802.
Dobb, M. G., Johnson, D. J., & Saville, B. P. (1981). Compressional behaviour of Kevlar fibres. *Polymer, 22*, 960–965.
Fidan, S., & Palazotto, A. (1993). Compressive properties of high-performance polymeric fibers. *Composites Science and Technology, 49*, 291–297.
Furuyama, M., Higuchi, M., & Kubomura, K. J. (1993). Compressive properties of single-filament carbon fibres. *Journal of Material Science, 28*, 1611–1616.
Jones, W. R., & Johnson, J. W. (1971). Intrinsic strength and non-hookean behaviour of carbon fibres. *Carbon, 9*, 645–650.
Leal, A. A., Deitzel, J. M., & Gillespie, J. W. (2007). Assessment of compressive properties of high performance organic fibers. *Composites Science and Technology, 67*, 2786–2794.
Sinclair, D. (1950). A bending method for measurement of the tensile strength and Young's modulus of glass fibers. *Journal of Applied Physics, 21*, 380–399.
So, Y. H. (2000). Rigid-rod polymers with enhanced lateral interactions. *Progress of Polymer Science, 25*, 137–157.
van der Zwaag, S., & Kampschoer, G. (1987). Compressive failure in the high modulus polymeric fibers. In *Proceedings of the 2nd International Meeting on Polymer Science and Technology*. London: Elsevier Applied Science.
Wolfe, J. F. (1988). *Encyclopedia of polymer science and technology* (2nd ed.). New York: John Wiley and Sons.
Zhang, T., Hu, D. A., Jin, J. H., Yang, S. L., Li, G., & Jiang, J. M. (2009). Improvement of surface wettability and interfacial adhesion ability of poly(*p*-phenylene benzobisoxazole) (PBO) fiber by incorporation of 2,5-dihydroxyterephthalic acid (DHTA). *European Polymer Journal, 45*, 302–307.