Note

Significant Enhancement in Compressive Strength of Poly(p-phenylenebenzobisoxazole) Fibers by Incorporation of Carbon Nanofibers

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Abstract: Poly(p-phenylenebenzobisoxazole) (PBO) composite fibers containing small amounts (~2 wt.%) of carbon nanofibers (CNFs) were successfully prepared by *in-situ* polymerization and dry-jet wet spinning. Polarized optical microscopy images displayed a lyotropic liquid-crystalline phase in the as-polymerized dopes. Solution viscosity measurements revealed that the molecular weights of the composite fibers were in the range from 1.81×10^4 gmol^{-1} to 2.2×10^4 gmol^{-1}. Field emission scanning electron microscopy images of the composite fibers etched by UV irradiation showed that CNFs embedded in the PBO matrix were individually dispersed, and well oriented along the fiber direction. Tensile tests indicated that the tensile moduli of the PBO/CNF composite fibers were higher than those of the pristine PBO fibers, whereas the tensile strengths were lower or similar to those of the pristine PBO fibers. The elastic loop test was carried out to measure the compressive strength of the fibers. The compressive strength of the pristine PBO fiber was 0.3 GPa, whereas that of a PBO composite fiber containing 1.0 wt.% CNF increased to 0.92 GPa, which is about twice the compressive strength of Zylon (0.43 GPa). Moreover, a heat-treated PBO composite fiber containing 2.0 wt.% CNFs exhibited the high compressive strength of 1.17 GPa, which is the second highest value among all reported values for organic polymers.

Keywords: Poly(p-phenylenebenzobisoxazole) (PBO), Carbon nanofiber, Composite fiber, Compressive strength

Introduction

Poly(p-phenylenebenzobisoxazole) (PBO) is a heterocyclic aromatic polymer, which exhibits a lyotropic liquid-crystalline phase [1-3]. PBO fibers, spun from a liquid-crystalline state, have high crystallinity and high orientation of rigid-rod molecules, which provides excellent tensile properties, such as modulus of 270 GPa and strength of 5.8 GPa [1,4]. On the other hand, the compressive properties of PBO fibers are poor due to weak intermolecular interactions. Particularly, the compressive strength of PBO fibers (0.43 GPa) is lower than 10 % of its tensile strength [1,5], which severely limits their application. Many attempts have been made to improve the compressive strength of PBO fibers, such as introducing intermolecular hydrogen bonds [6], crosslinking by radiation [7] or multifunctional monomers [8], and incorporation of carbon nanotubes [9]. Zhang *et al*. [6] prepared dihydroxy poly(p-phenylene benzobisoxazole) fiber containing hydroxyl groups on a PBO backbone, and this material presented a higher compressive strength (0.75 GPa) than that of a PBO fiber. Akzo Nobel developed a new polymer, poly{2,6-diimidazo[4,5-b:4'5'-e]pyridinylene-1,4(2,5-dihydroxy)phenylene} (PIPD) [10,11], in order to solve the issue of weak compressive strength of rigid-rod polymers such as PBO. This polymer has a bidirectional network of intermolecular and intramolecular hydrogen bonds, resulting in the highest compressive strength (1.7 GPa) ever reported for polymers [10]. Kumar *et al*. [9] prepared PBO/single wall carbon nanotube (SWCNT) composite fibers by *in-situ* polymerization and dry-jet wet spinning. The tensile and compressive strengths of the PBO/SWCNT composite fiber containing 10 wt.% SWCNTs were about 50 % and 40 % higher than those of pristine PBO fibers, respectively.

The use of carbon nanofibers (CNFs) as fillers in polymeric composite fibers is known to improve the compressive strength of the composite. CNFs act as a barrier against kink propagation and delay compressive failure [12,13]. Uchida *et al*. [14] prepared a poly(p-phenylene benzobisthiazole) (PBZT) composite fiber filled with 10 wt.% CNFs. Even though the tensile modulus and tensile strength of the composite fiber were lower than those of the pristine PBZT fiber due to impurities in the CNFs, the compressive strength was enhanced to ~400 MPa. It was also reported that the incorporation of CNFs improved the compressive strength of flexible polymeric fibers such as polypropyrene [15] and poly(ethylene terephthalate) [13]. However, to the best of our knowledge, the preparation of PBO/CNF composite fibers has not yet been reported.

In this study, PBO composite fibers containing ~2.0 wt.% CNF were prepared by *in-situ* polymerization and dry-jet wet spinning, in order to enhance the compressive strength of PBO fibers. Tensile and compressive properties of the composite fibers were investigated using tensile test and

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loop test, respectively.

Experimental

Materials

Synthesis of PBO was carried out using 4,6-diaminoresocinol dihydrochloride (DAR·2HCl, Zhejiang Dragon Chemical Co.) and terephthalic acid (TPA, Kolon industries) as monomers, and a mixture of polyphosphoric acid (PPA, Sinopharm Chemical Reagent Co.) and phosphorus pentoxide (P_2O_5, Sinopharm Chemical Reagent Co.) as solvent. Tin(II) chloride ($SnCl_2$, Sigma Aldrich) was used to prevent the oxidation of PBO. The average diameter and length of the CNFs (Sigma Aldrich), used to prepare the PBO/CNF composites, were about 100 nm and 20-200 μm, respectively. Methanesulfonic acid (Sigma Aldrich) was used as solvent for the PBO and PBO/CNF composite viscosity measurements. Phosphoric acid (PA, Daejung Chemicals & Metals Co.) was used in the preparation of the aqueous coagulation non-solvent. All materials and chemicals were used as received, except for TPA. Given the low solubility of TPA in the polymerization solvent, it is important to obtain small TPA particles. Small-sized TPA particles were prepared by using a re-precipitation method: TPA (100 g) was dissolved in dimethyl sulfoxide (500 g), and then distilled water was slowly added. The precipitated TPA was collected by filtering, and dried in a vacuum oven. The average size of the TPA particles was about 10 μm.

Preparation of the PBO/CNF Composite Fibers

The process for *in-situ* polymerization, and subsequent spinning of PBO and PBO/CNF composites was similar to one previously reported [8,16,17]. Firstly, DAR·2HCl (40 mmol), TPA (40 mmol), $SnCl_2$ (0.14 g), and PPA (37 g) were transferred into a three-necked round flask equipped with a mechanical stirrer, and purged with N_2. The solution was initially maintained at 60 °C for 4 h, and then heated to 80 °C for another 4 h for dehydrochlorination. Afterwards, P_2O_5 (20 g) was added to the reaction mixture in order to maintain the PBO content in PPA at 14 wt.%, which is an appropriate condition for spinning. CNFs were added to this reaction mixture, and the content was adjusted to 0, 0.5, 1, and 2 wt.% based on the PBO weight. Secondly, the polymerization was carried out at 110 °C for 7 h, and then at 150 °C for 6 h. Finally, the reaction mixture was maintained at 190 °C for 12 h for cyclization. The PBO and PBO/CNF composite fibers were fabricated by dry-jet wet spinning. When the polymerization was completed, the solutions were transferred into a spinning cylinder preset at 140 °C. The polymer dopes were spun into a coagulation bath through a round spinneret nozzle with a 0.2 mm diameter by applying pressure. The extruded fibers passed through two coagulation baths, sequentially connected. The first was a vertical bath containing an aqueous solution of 5 wt.% PA, while the

second was a horizontal bath containing pure water. The details for the spinning conditions were identical to those reported (Table 2 of reference 17). The solidified fibers were wound on spools, washed with distilled water, and dried in a vacuum oven. PBO/CNF composite fibers are referred to as PBO/CNFc, where c denotes the CNF content between 0.5 and 2 wt.%. Heat-treatment was conducted on the PBO/CNF2 composite fiber at 500 °C for 1 min under tension in a furnace (Nobertherm GmbH, R 100/75012-9320). The heat-treated fibers are referred to as HT-PBO/CNF2.

Characterization

A polarized optical microscope (POM, Jenapol-d, Carl Zeiss Inc.) equipped with a heating-stage was used to analyze the as-polymerized dopes at 140 °C. Measurements of the solution viscosities were carried out at 30 °C using an Ubbelohde viscometer. In order to observe the CNF embedded in the PBO matrix, field emission scanning electron microscopy (FE-SEM, JSM-6500F, JEOL) was conducted on the PBO/CNF composite fibers after UV irradiation during 16 h with an UV irradiation device (SMCM-M1K1, SeiMyung Co.). Tensile tests were performed using a universal testing machine (UTM, Instron series 4467) with a cross-head speed of 5 mmmin^{-1} and a specimen length of 25 mm. Fiber diameter was measured using a optical microscope. The elastic loop test [5,18-20] was carried out in order to measure the compressive strength of the fibers. The device used for the loop test was homemade, and is illustrated in Figure 1. The loop test was conducted as follows: firstly, a single fiber loop was made and placed between two glass slides; a camera recorded the gradual reduction in loop size on pulling both loop ends; the longitudinal and transverse dimensions (L and D, respectively) of the loop were measured during the pulling process. The L/D ratio remained almost constant before failure. When the compressive failure occurred via kink band formation, the L/D ratio began to increase with decreasing L. The L_c could be defined as the longitudinal dimension along which the L/D ratio began to increase. The compressive strength (σ_f) was calculated using equation (1) [18,19],

$$\sigma_f = 1.43 d_f E_f / L_c \tag{1}$$

where d_f is the fiber diameter, and E_f is the fiber modulus. The measurements of both tensile and loop tests were
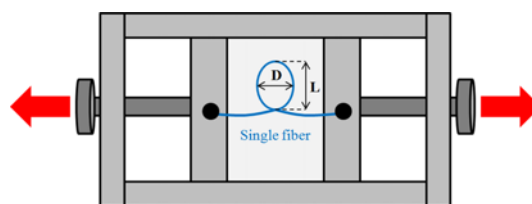

Figure 1. Homemade loop test device for measuring the compressive strength of fibers.

performed 10 to 20 times for each sample, in order to obtain an average value and standard deviation of the mechanical properties.

Results and Discussion

POM Image and Molecular Weight

Figure 2 shows the POM images for the as-polymerized PBO and PBO/CNF2 composite dopes at 140 °C. A liquid-crystalline phase was well developed for all dopes. Intrinsic viscosities for PBO, PBO/CNF0.5, PBO/CNF1, and PBO/CNF2 were 12.8, 16.5, 18.4 and 16.6 d/g^{-1}, which correspond to viscosity average molecular weights of 1.81×10^4, 2.09×10^4, 2.2×10^4, and 2.09×10^4 gmol^{-1}, respectively, according to the Mark-Houwink equation [21]. Both results (development of a liquid-crystalline phase and high molecular weight) confirm that PBO was successfully polymerized, regardless of the presence of CNF. Figure 3 shows photos of the PBO and PBO/CNF composite fibers wound on spools. The pristine PBO fiber has a golden color, whereas the PBO/CNF composite fibers exhibit a dark-blue color, associated with the presence of CNF dispersed in the PBO matrix.

Identification of CNF Embedded in PBO Matrix

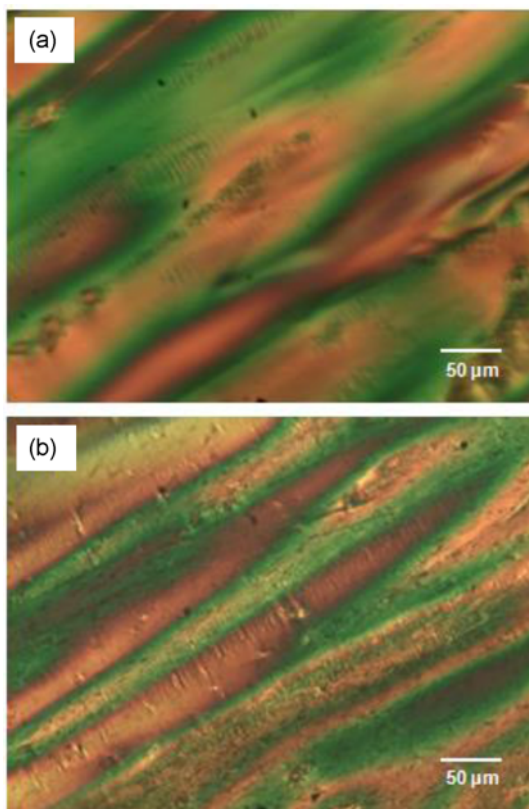When the PBO/CNF composite fibers were UV-irradiated,

Figure 3. Photos of (a) PBO, (b) PBO/CNF0.5, (c) PBO/CNF1, and (d) PBO/CNF2 composite fibers wound on spools.

Figure 2. Polarized optical micrographs for the as-polymerized dopes at 140 °C; (a) PBO and (b) PBO/CNF2.
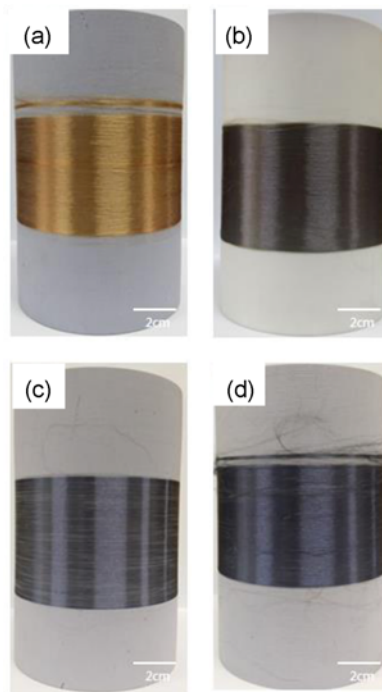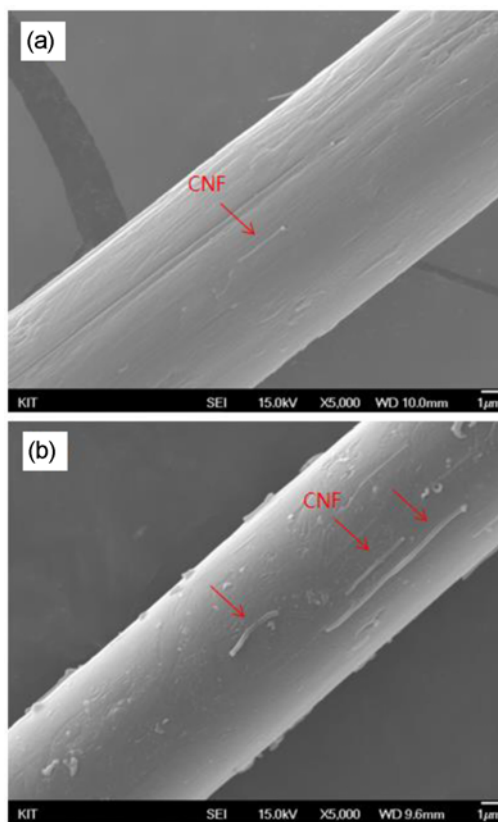

Figure 4. FE-SEM images of (a) PBO/CNF1 and (b) PBO/CNF2 composite fibers after UV irradiation during 16 h.

the fiber diameter decreased with increasing UV irradiation time, due to the continuous degradation and detachment of surface molecules, as previously reported [17]. Hence, portions of CNFs buried in the PBO matrix emerged to the fiber surface after UV irradiation during 16 h (Figure 4). Emerged CNFs were individually present without aggregation, which meant that CNFs were well dispersed in the PBO matrix. It was also observed that CNFs were relatively well oriented along the fiber direction, despite a slight flexure.

Tensile Properties of the PBO/CNF Composite Fibers

Figure 5 shows representative stress-strain curves for the PBO fibers. The stress-strain correlations were almost linear until failure without yielding, which might be due to the high crystallinity and degree of orientation of the rigid PBO molecules. Three PBO/CNF composite fibers also exhibited a tensile behavior similar to that of the PBO fiber alone. The average values for tensile strength and tensile modulus are listed in Table 1. Tensile moduli of the composite fibers were higher than those of the pristine PBO fibers, suggesting a reinforcement effect of the CNF. The modulus of PBO/CNF2 was somewhat lower than that of PBO/CNF1, which
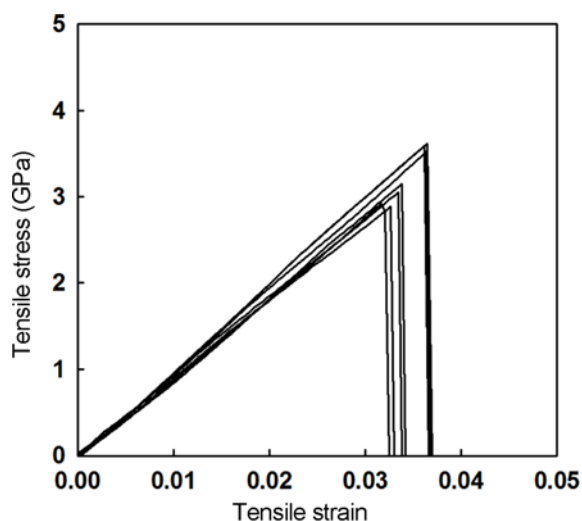
might be caused by the lower molecular weight of the PBO polymer matrix. On the other hand, the tensile strengths of the composite fibers were lower or similar to those of pristine PBO fibers. In general, failure occurred at the weakest part of the sample. It was considered that ~2 wt.% of CNFs was not enough quantity to cover the weak parts of the sample. It was previously reported that incorporation of 5 or 10 wt.% of SWCNT in PBO/SWCNT composite fibers was effective in increasing the tensile strength [9]. The tensile modulus of the heat-treated PBO/CNF2 fibers increased from 120 (without heat-treatment) to 172 GPa. This modulus increment was due to the improvement in both crystal orientation and perfection during heat-treatment. Meanwhile, heat-treatment was not effective in enhancing the tensile strength, as previously reported [1,2,22].

Compressive Strength of the PBO/CNF Composite Fibers

Figure 6 shows representative plots of L/D versus L for the PBO and PBO/CNF composite fibers obtained by the elastic loop test. As L decreased, L/D values for all fibers were almost constant before failure. It was clearly seen that L_c (the onset point where the L/D value increases sharply) decreased with increasing CNF content in the fiber. A smaller L_c value means that the compressive failure via kink band formation occurs for smaller loops and indicates a higher compressive strength. Fiber diameter, L_c, and compressive strength of the PBO and PBO/CNF composite fibers are listed in Table 2. The compressive strengths of the fibers were calculated by equation (1), using the tensile modulus values from Table 1. The compressive strength of the pristine PBO fiber was 0.3 GPa, whereas that of PBO/CNF1 increased to 0.92 GPa. This increment originates from both higher modulus and lower L_c values, with the latter
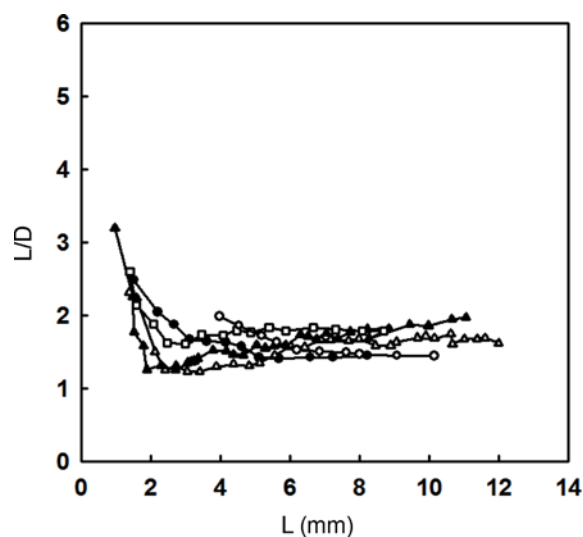
Figure 5. Representative strain-stress curves for several PBO fibers.

Table 1. Tensile modulus and tensile strength for PBO and PBO/CNF composite fibers

Fiber	Tensile modulus (GPa)	Tensile strength (GPa)
PBO	100±3	3.5±0.3
PBO/CNF0.5	107±17	2.7±0.6
PBO/CNF1	127±15	3.6±0.5
PBO/CNF2	120±15	3.2±0.4
HT-PBO/CNF2	172±6	3.0±0.6

Figure 6. Representative plots of L/D versus L for PBO (○), PBO/CNF0.5 (●), PBO/CNF1 (△), PBO/CNF2 (▲), and HT-PBO/CNF2 (□) composite fibers obtained by the loop test.

Table 2. Fiber diameter, L_c, and compressive strength for PBO and PBO/CNF composite fibers

Fiber	Fiber diameter (μm)	L_c^{a} (mm)	Compressive strength (GPa)
PBO	12.5±1.5	5.8±0.5	0.30±0.03
PBO/CNF0.5	13.7±1.3	4.4±0.6	0.48±0.11
PBO/CNF1	14.7±2.0	2.9±0.4	0.92±0.15
PBO/CNF2	13.6±2.1	2.6±0.3	0.90±0.09
HT-PBO/CNF2	12.4±1.8	2.6±0.6	1.17±0.13

[a]Longitudinal dimension of the loop, at which the L/D ratio began to increase.

being the main factor. This value of 0.92 GPa is about twice the compressive strength (0.43 GPa) of Zylon (trade name for the PBO fiber) produced by Toyobo [19,23,24], and higher than that of as-spun PIPD (0.7 GPa) [10,11]. The compressive strength of PBO/CNF2 was comparable to that of PBO/CNF1, which was attributed to a slight decrease of both modulus and L_c. Heat-treatment improved the compressive strength of PBO/CNF2 to 1.17 GPa, which is the second highest value compared to that of heat-treated PIPD (1.7 GPa) [10,11] among all reported values for organic polymers. The L_c value for HT-PBO/CNF2 was identical to that of PBO/CNF2 without heat-treatment. Hence, the high compressive strength of HT-PBO/CNF2 fiber originated from the modulus increment induced by the heat-treatment.

Conclusion

PBO/CNF composite fibers were prepared by *in-situ* polymerization and dry-jet wet spinning. A liquid-crystalline phase was well developed in the as-polymerized dopes. CNFs embedded in the PBO matrix were well dispersed and oriented along the fiber direction. Tensile moduli of the PBO/CNF composite fibers were higher than those of the pristine PBO fibers. The compressive strength of the pristine PBO fiber was 0.3 GPa, whereas that of PBO/CNF1 increased to 0.92 GPa. Moreover, HT-PBO/CNF2 exhibited a compressive strength of 1.17 GPa, which is the second highest value among all reported values for organic polymers. Hence, the incorporation of CNF in PBO fibers is a very effective technique to enhance the compressive strength.

Acknowledgement

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