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Preparation of Polybenzoxazole Nanofibers by a Downsizing Process

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Poly(*p*-phenylene benzobisoxazole) (PBO) nanofibers were prepared from commercially available PBO fiber by a simple downsizing process for the first time. Partial alkaline hydrolysis of the oxazole ring brought ionic functional groups on the fiber surface, enabling the disintegration of the PBO fiber into nanofibers with the help of electrostatic repulsive force. The obtained nanofibers, whose average diameter was 24 nm, were characterized by SEM, FT-IR, ζ-potential analyzer, XRD, and TGA. They dispersed homogeneously in water due to the surface charges. Filtration allowed a PBO nanofiber sheet to be easily prepared from the homogeneous dispersion in water.

1. Introduction

Since nanofibers are extremely thin and have very high surface-to-volume ratios, their properties are different from those of microfibers.[1,2] The preparation of nanofibers is an important subject due to their unique dimensional, optical, and mechanical characteristics. Poly(*p*-phenylene benzobisoxazole) (PBO) is a rigid polymer having an oxazoline heterocyclic ring in the repeating unit (Fig. 1). PBO fiber is obtained by a wet-spinning process from the polymer solution dissolved in sulfuric acid.[3] The PBO solution forms liquid crystal due to the orientational ordering of the rigid polymer. PBO fiber has the highest strength, Young's modulus, impact resistance, and thermal stability among the so-called super fibers.[4] This high performance is attributable to PBO's 100% paracrystalline structure with rigid molecular chains oriented along the fiber axis caused by the process of spinning lyotropic liquid crystal. If nanofibers from PBO are developed, they will offer useful applications as a novel high-performance material, such as reinforcement filler for fiber-reinforced plastics. The electrospinning process is a well-known way to artificially produce nanofibers from a wide range of polymer solutions.[5] However, it is difficult to electrospin PBO because it is not soluble in common solvents. Thus, PBO nanofibers must be prepared from the precursor of PBO, which is soluble in organic solvent, thus enabling electrospinning and thermal conversion from the precursor.[6,7] In another approach, PBO nanofibers were prepared by cooling crystallization from a 0.1 wt% of dilute PBO solution in sulfuric acid.[8] Thus, all the previously reported PBO nanofibers were prepared from PBO solution by a bottom-up process. Recently, Yang *et al*. and our group reported the preparation of aramid (poly(*p*-phenylene terephthalamide) nanofibers by a top-down approach.[9,10]

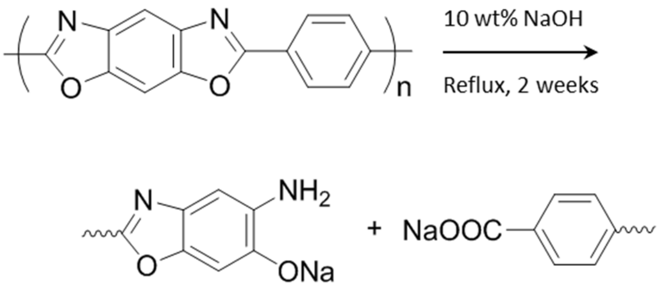

Fig. 1. Chemical structure of poly(*p*-phenylene benzobisoxazole) and the alkaline hydrolysis.

Since commercial aramid fiber consists of paracrystallite, it was disintegrated into nanofibers by a downsizing process. Although aramid fiber is also a sort of super fiber, PBO fiber is superior in performance and cost. Here, inspired by the previous works, we studied the facile mechanical disintegration of commercially available PBO fiber into nanofibers for the first time. Since PBO fiber also consists of paracrystals, PBO fiber may be converted into nanofibers by the downsizing approach.

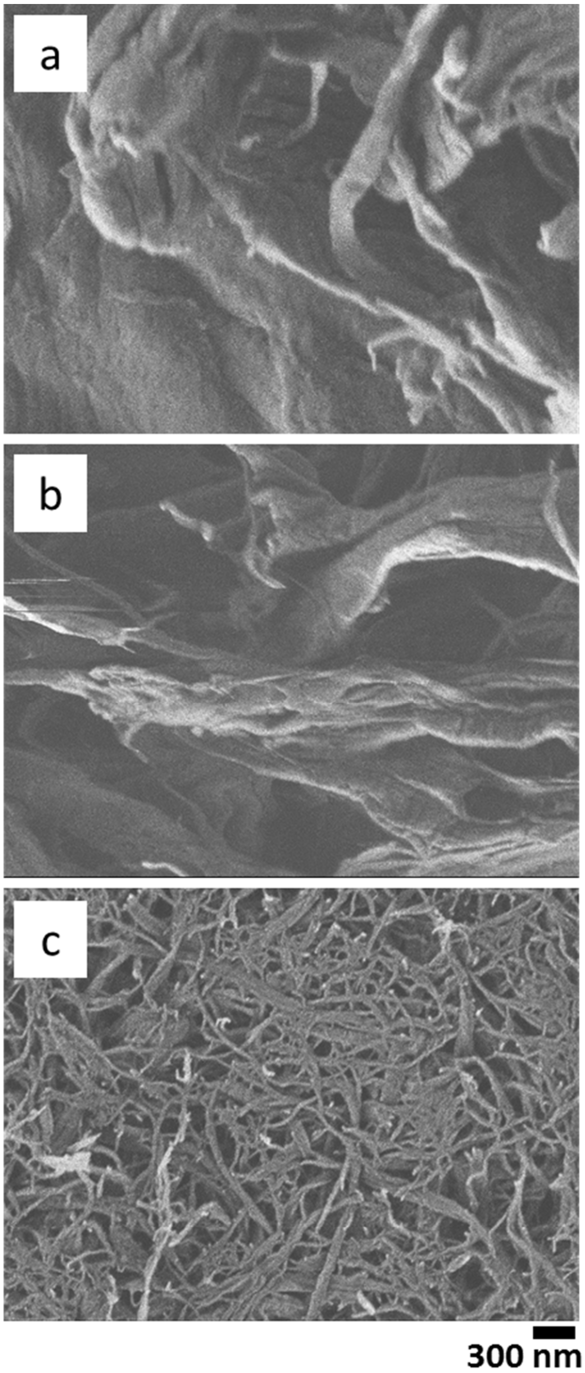

Figure 2. FE-SEM images (a) poly(*p*-phenylene benzobisoxazole), (b) after mechanical treatment, and (c) after hydrolysis treatment followed by mechanical treatment.

2. Results and discussion

Figure 2a shows an SEM image of PBO fibers, which are known to be made up of aggregates of microcrystals. To disintegrate the aggregate, the PBO fibers were treated with a high-pressure atomization system with 1 wt% concentration in water. After 30 cycles of mechanical treatments, the PBO fibers were not disintegrated at all even though the system applied a super high-pressure water-jet of 200 MPa (Fig. 2b). This is due to strong interactions between PBO microcrystals *via* hydrogen bond interaction and π-π aromatic stacking interaction. To increase disintegration efficiency, PBO fiber was treated with 10 wt% NaOH under reflux for 2 weeks before mechanical treatment. The yield of PBO fiber was 74%. After mechanical treatments, the sample was dispersed homogeneously in water and was stable for more than 1 month, although PBO is a hydrophobic polymer (Fig. 3a). The dispersion has yellow color due to the conjugate system of PBO. The SEM image of the water dispersion shows that the PBO fiber was successfully disintegrated into nanofibers by the mechanical treatment (Fig.

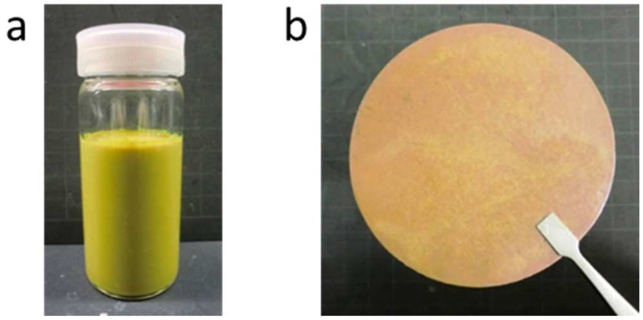

Figure 3. (a) poly(*p*-phenylene benzobisoxazole) nanofibers dispersed in water with 1.0 wt%, and (b) the sheet prepared by filtration.

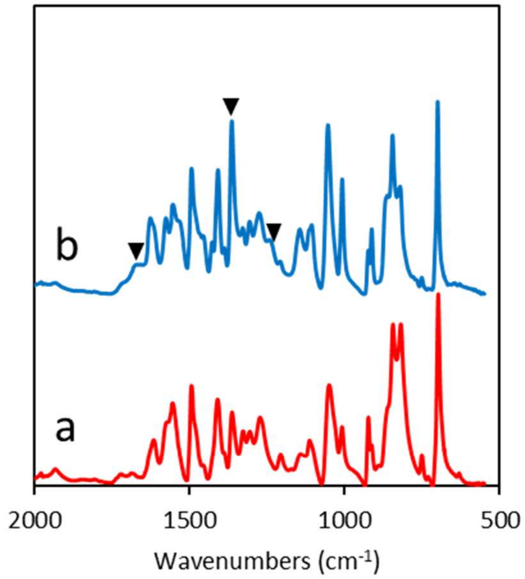

Figure 4. FT-IR spectra of (a) poly(p-phenylene benzobisoxazole), and (b) the nanofibers obtained by alkaline hydrolysis and mechanical treatments.

2c). The widths of the nanofibers were distributed across a range of 10-100 nm with an average width of 24 nm. The nanofibers were much thinner than conventional PBO fibers prepared by the bottom-up approach.[6-8] The PBO nanofibers were highly uniform over an extensive area (Fig. S1). Alkaline hydrolysis time strongly affected the structure of PBO fibers (Fig. S2). When the time was shorter than 2 weeks, broader fibers were observed. On the other hand, when the time was 3 weeks, aspect ratio of PBO fibers became decreased due to the excessive alkaline hydrolysis.

Table 1. ζ-Potential of poly(*p*-phenylene benzobisoxazole) nanofiber

pH	3.1	6.8	9.1
ζ-potential (mV)	56.6	-19.2	-32.1

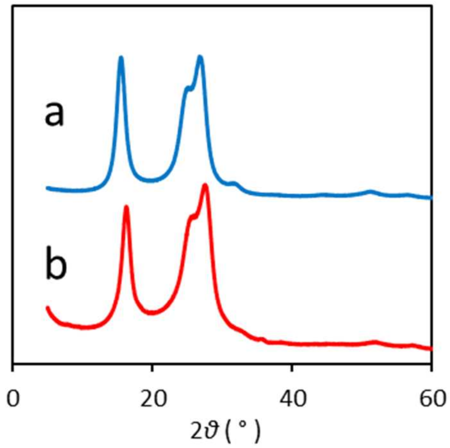

Figure 5. XRD profiles of (a) poly(*p*-phenylene benzobisoxazole), and (b) the nanofibers obtained by alkaline hydrolysis and mechanical treatments.

To learn the alkaline treatment's effect on the chemical structure, FT-IR spectra of PBO nanofibers were collected (Fig. 4). After the alkaline treatment, a C=O stretching vibration band corresponding to carboxylic acid and a C-N stretching vibration band corresponding to the primary amine appeared at 1685 cm^{-1} and 1237 cm^{-1}, respectively, as small shoulder peaks. Moreover, phenolic O-H bending vibration bands were observed at 1237 cm^{-1} and 1365 cm^{-1}. Those changes indicate that partial alkaline hydrolysis of PBO occurred in the oxazole ring and converted PBO into carboxyl, amino, and phenolic hydroxyl groups (Fig. 1). These ionically charged functional groups on the PBO fiber surface enabled the disintegration of microcrystalline aggregate into nanofibers and homogeneous dispersion in water due to the electrostatic repulsive force. To estimate the surface charge of the thus-obtained PBO nanofibers, ζ-potentials in water at pH 3.1 – 9.1 were measured (Table 1). The nanofibers had a high cationic charge of +56.6 mV in water at pH 3.1 due to the protonation of amino groups (-NH3$^+$). On the other hand, the nanofibers had an anionic charge of -32.1 mV at pH 9.1 due to the anionization of carboxylic acid (-COO$^-$) and phenolic hydroxyl groups (Ph-O$^-$), and the potential decreased as the pH decreased to 6.8. Thus, again the disintegration of PBO fibers and stable dispersion in water can be achieved by the downsizing process by applying electrostatic repulsion between the PBO microcrystals with highly cationic or anionic surface charges. Although conventional PBO fiber precipitates immediately in water, the nanofiber can disperse homogeneously (Fig. 3a). Hence, the nanofiber was easy to handle and shape into the desired forms by a drying process such as filtration or freeze drying (Fig. 3b). This characteristic will expand the application of PBO as a novel material with extremely efficient mechanical properties. The crystalline

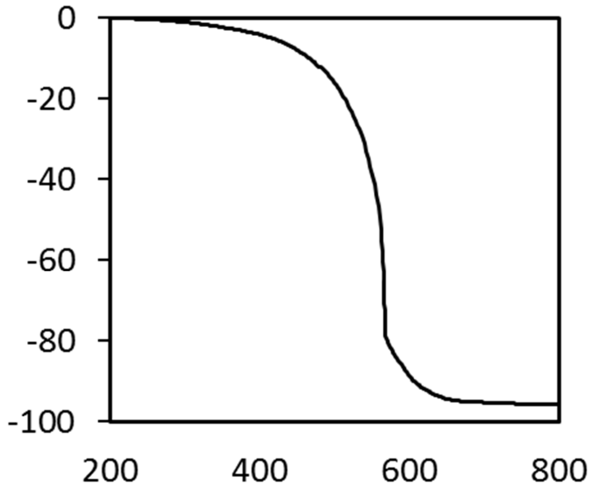

Figure 6. TGA thermogram of poly(*p*-phenylene benzobisoxazole) nanofiber.

structure of PBO nanofibers was studied by XRD patterns (Fig. 5). The diffraction pattern of PBO nanofibers coincided closely with that of the original PBO fibers. The diffraction peaks of the nanofibers observed at 2θ = 16.4°, 26.0°, and 27.8° corresponded to 200, 010, and -210 planes, respectively.[11] They were typical crystal patterns of PBO fiber. The orientational degrees of crystal of PBO fiber and the nanofiber estimated from the half-width of the (200) peak were 97.9% and 97.5%, respectively.[12] Thus, partial alkaline hydrolysis occurred on the PBO fiber surface, and the original crystalline structure was maintained. PBO nanofiber exhibited high thermal resistance (Fig. 6). TGA thermograms revealed that the degradation started from approximately 400 °C and that the 50% weight loss temperature was 561 °C.

3. Experimental

To prepare the nanofibers, PBO fibers chopped to 1 mm length were obtained from Toyobo (brand name: Zylon) and were treated with 10 wt% NaOH for 2 weeks under reflux for partial hydrolysis of oxazole rings. After washing with distilled water, the obtained sample was dispersed in water at 1 wt% and was passed through 30 cycles of a high-pressure waterjet atomization treatment (Star Burst Mini, HJP-25001S, Sugino Machine). The atomization system was equipped with a ball-collision chamber. The slurry was ejected from a small nozzle with a diameter of 100 μm under high pressure of 200 MPa.

Infrared spectra of the samples were recorded with an FT-IR spectrophotometer (Spectrum 65, Perkin-Elmer Japan) equipped with an ATR attachment. For field emission scanning electron microscopic (FE-SEM) observation, the sample was coated with platinum by an ion sputter coater and observed by FE-SEM (JSM-6700F; JEOL) operating at 2.0 kV. X-ray diffraction profiles of the nanofibers were obtained with Ni-filtered CuK_α from an X-ray generator (Ultima IV, Rigaku) operating at 40 kV and 30 mA. ζ-Potentials were measured at 25 °C using a laser-Doppler electrophoresis-type apparatus (ELSZ-1000ZS; Otsuka Electronics). The consistency of nanofibers in water was set to 0.1 wt%, and the pH was changed from 3.1 to 9.1. Thermogravimetric analysis was carried out using a Thermo Plus Evo II (Rigaku). Samples were placed in an open platinum pan. Temperature programs were conducted at a heating rate of 10 °C min^{-1} in argon gas.

4. Conclusions

This study revealed that partial alkaline hydrolysis before mechanical treatment enabled PBO fiber to disintegrate into nanofibers. This is the first report of the facile production of PBO nanofibers by a top-down process. Nanofibers with the highest performance in physical properties and improved formability will expand novel applications of the super fibers.

Acknowledgement

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