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Poly(p-phenylene benzobisoxazole) (PBO) has excellent thermal stability and mechanical properties because of its rod-like rigid structure. Preparing nanofibers of PBO using ordinary methods is difficult (e.g., electrospinning) because PBO is not soluble in organic solvents. Herein, we report the preparation of PBO nanofibers with an average diameter of approximately 50 nm via crystallization from a dilute solution in sulfuric acid. In addition, a PBO nanofiber mat was prepared that exhibited extremely high thermal stability and high thermal diffusivity, etc.

Keywords: rigid polymer, crystallization, nanofiber, nanofiber mat

1. Introduction

Poly(p-phenylene benzobisoxazole) (PBO) (Fig. 1) is a rigid polymer in which the molecular chains are unable to fold. PBO fibers have excellent properties, including high strength, a high elastic modulus, and high thermal stability [1-5].

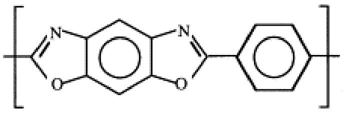

Fig.1. Chemical structure of Poly(p-phenylene benzobis oxazole) (PBO).

On the other hand, nanofibers with diameters of 100 nm or less and aspect ratios of 100 or higher are expected to be applied in various fields, including high-efficiency filters, organic electronics, electromagnetic shield materials, compact batteries, and synthetic blood vessels, and have thus attracted significant attention as useful materials in recent years [6–10]. Methods for the preparation of nanofibers include conjugated melt spinning, melt-blowing, and electrospinning, with the lattermost being the most versatile. However, these methods require not only specialized equipment but also a high voltage. Furthermore, using ordinary nanofiber preparation methods for a rigid polymer such as PBO is difficult because it is insoluble in organic solvents and soluble only in concentrated sulfuric acid and the like.

We previously reported that single crystals with different forms are obtained by crystallizing PBO from dilute solutions in concentrated sulfuric acid [11]. Herein, we describe the preparation of PBO nanofibers using the rapid cooling crystallization (self-assembly) of PBO from such a dilute solution. The properties of a PBO nanofiber mat prepared using the obtained PBO nanofibers were also investigated.

2. Experimental Methods

2.1 Preparation of PBO Nanofibers

PBO with an intrinsic viscosity of 10.7 dl/g and a weight-average molecular weight of 16,600 was used [12]. An aqueous solution of 94.5 wt% sulfuric acid and 0.1 wt% PBO was added to an eggplant flask and heated to 120 °C to dissolve the PBO. Subsequently, PBO nanofibers were

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prepared by rapidly cooling the solution to 0 °C. The obtained nanofibers were then rinsed.

2.2 Characterization of the PBO Nanofibers

Scanning electron microscopy (SEM) observations were performed via a JSM 6320F (JEOL Ltd.). Transmission electron microscopy (TEM) observations were performed at an acceleration voltage of 200 kV via a JEM2000EX II (JEOL Ltd.). Specific surface area measurements were performed under a nitrogen gas flow of 25 ml/min after degassing for 15 minutes at 150 °C via a GEMINI2370 (Shimadzu Corporation).

2.3 Preparation of the PBO Nanofiber Mat

PBO nanofibers dispersed in water were precipitated via filtration under reduced pressure. The PBO nanofiber mat was prepared by performing decompression pressing of the PBO nanofiber precipitate via a vacuum heating press.

2.4 Evaluation of the PBO Nanofiber Mat

Tensile tests were performed at a velocity of 4 mm/min using an SV-201NA (IMADA-SS Corporation). Thermogravimetric analyses were performed from room temperature to 900 °C at a heating rate of 10 °C/min under a nitrogen gas flow using a Thermo Plus TG8120 (Rigaku Corporation.) A RHEOVIBRON (DDV-01FP-AO, ORENTEC) was used for the viscoelastic modulus measurements and a Thermowave Analyzer TA-LT (BETHEL) was used for the thermal diffusivity measurements.

3. Results and Discussion

The diameter and length of the obtained PBO nanofibers (Fig. 2) were 53 ± 22 nm and 6.7 ± 1.1 μm, respectively. Electron diffraction images revealed that the molecular chains of the PBO were oriented in the longitudinal direction of the nanofibers, and that the nanofibers were highly crystalline. In addition, the specific surface area of the PBO nanofibers was 88.4 g/m^2, which is a large specific surface area. From these results, it was concluded that a method for the preparation of high crystallinity PBO nanofibers was developed that required neither high voltage nor special equipment (Table 1).

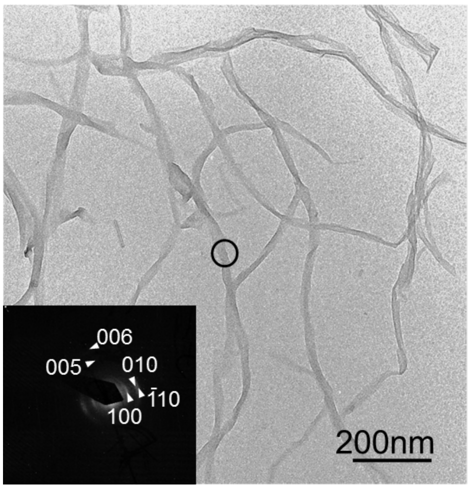

Fig. 2. TEM photo of PBO nanofibers and a selected -area electron diffraction image of the circled area.

Table1. Size and specific surface area of the PBO nanofibers.

Diameter	53 ± 22 nm
Length	6.7 ± 1.1 μm
Specific surface area	88.4 g/m^2

A PBO nanofiber mat was then prepared using the obtained PBO nanofibers (Fig. 3). Because PBO fibers exhibit excellent properties, including high strength, high elasticity, and high heat stability [1-3] as described above, the PBO nanofiber mat was also expected to exhibit excellent properties. In particular, since the thermal diffusivity of PBO fibers is high [4, 5], it is expected that the thermal diffusivity of the PBO nanofiber mat is also high.

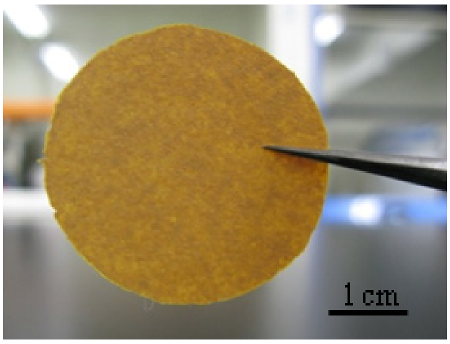

Fig. 3. Photo of the PBO nanofiber mat.

The apparent density of the prepared PBO nanofiber mat was 1.10 ± 0.07 g/cm^3. The porosity calculated using a PBO fiber density of 1.54 g/cm^3 [13] was found to be 28.7 ± 4.2%. In addition, the PBO nanofiber mat was determined to have a high specific surface area of 42.6 g/m^2, and numerous meso pores were observed in its structure.

A tensile test was then performed on the PBO nanofiber mat, and the results are shown in Fig. 4.

As observed in the figure, the elastic modulus, yield strength, rupture strength, and rupture elongation were 1.48 ± 0.14 GPa, 54.1 ± 5.7 MPa, 54.1 ± 5 MPa, and 6.3 ± 1.0%, respectively. These results indicate that the prepared PBO nanofiber mat had excellent mechanical properties and also retained a high level of porosity. In addition, PBO nanofibers were clearly observed both on the surface and in the cross-sectional SEM images of the tensile fracture surface of the PBO nanofiber mat (Fig. 5).

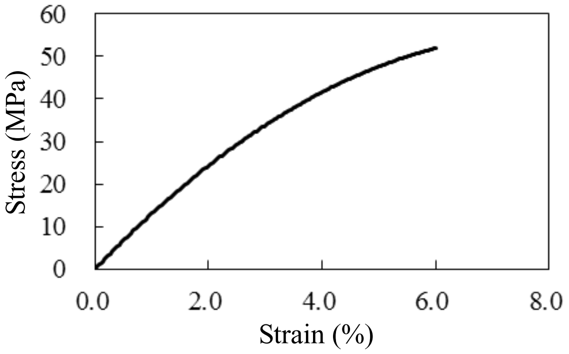

Fig. 4. Stress-strain curve for the PBO nanofiber mat.

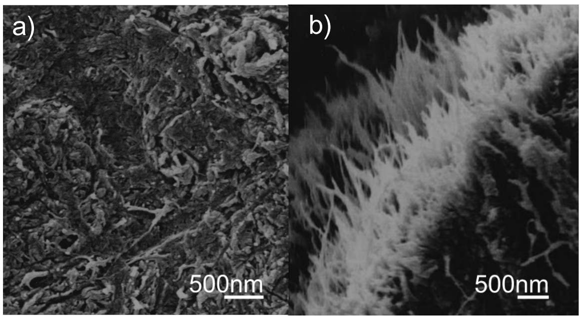

Fig. 5. SEM images of the a) surface and b) tensile fracture surface of the PBO nanofiber mat.

The data obtained for the thermogravimetric analysis of the PBO nanofiber mat are shown in Fig. 6. The 5% and 10% weight loss temperatures for the PBO nanofiber mat were 610 °C and 650 °C, respectively, which confirmed that the mat possessed high thermal stability.

Furthermore, the results of the viscoelastic modulus analysis revealed that the elastic modulus of the PBO nanofiber mat remained stable at temperatures up to 400 °C (Fig. 7).

Finally, the PBO nanofiber mat was found to exhibit a high thermal diffusivity of 5.36 ± 0.38 × 10^{-6} m^2/s in the in-plane direction and 0.29 ± 0.04 × 10^{-6} m^2/s in the thickness direction, indicating a large difference in the thermal diffusivity depending on the measurement direction.

Based on the results described above, it was concluded that the PBO nanofiber mat exhibited excellent properties (Table 2).

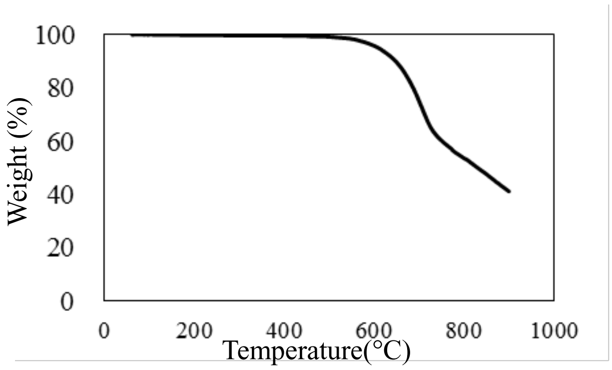

Fig. 6. Thermogravimetric analysis results for the PBO nanofiber mat.

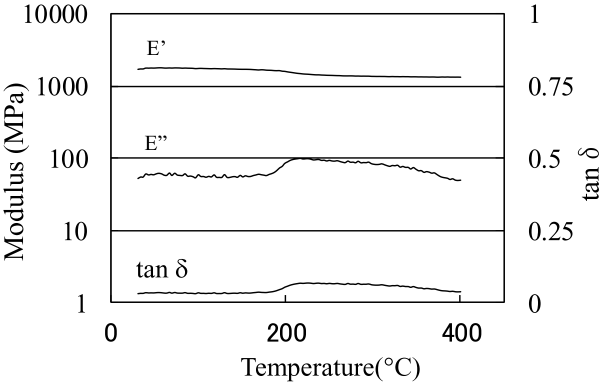

Fig.7. E', E", and tan δ for the PBO nanofiber mat.

Table 2. Properties of the PBO nanofiber mat.

	Physical property
Density	1.10 ± 0.07 g/cm^3
Porosity	28.7% ± 4.2 %
Elastic modulus	1.48 ± 0.14 GPa
Thermal resistance:	
5% weight loss	610 °C
10% weight loss	650 °C
Specific surface area	42.6 g/m^2
Thermal diffusivity:	
In-plane direction	5.36 ± 0.38 × 10^{-6} m^2/s
Thickness direction	0.29 ± 0.04 × 10^{-6} m^2/s

4. Conclusion

We have developed a method for the preparation of PBO nanofibers with molecular chains crystallized in a highly oriented manner via the crystallization (self-assembly) of the rigid polymer without the need for the use of a high voltage or special equipment. In addition, a PBO nanofiber mat were simply prepared using filtration and a vacuum heating press. The PBO nanofiber mat prepared from the PBO nanofibers exhibited excellent mechanical properties, high thermal stability, and high porosity. Notably, the thermal diffusivity was found to be anisotropic, with the value in the in-plane direction of the film greater than that in the thickness direction.

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