HIGHLY ORIENTED AND HIGHLY GRAPHITIZED CARBON FIBER PREPARED FROM PBO FIBER

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Introduction

Poly-p-phenylenebenzobisoxazole (PBO) is one of polybenzazoles containing aromatic heterocyclic ring as shown in Fig. 1. The PBO fiber is known to exhibit excellent physical properties, such as high thermal stability (thermal decomposition temperature being 650°C), high Young's modulus and high tensile strength, due to the rigid rod molecules aligned parallel to the fiber axis [1-3]. In the cross section of the fiber, the a-axes of the PBO crystals show a remarkable radial orientation [2]. Rogers et al. and Newell et al. investigated the carbonization behavior of the PBO fiber, and examined the structure, morphology, mechanical properties and electrical resistivity of the carbonized PBO fiber [4,5]. The PBO-based carbon fibers (PBOCF's) showed a radial texture similar to pitch-based carbon fibers. PBOCF's, especially for the fibers heat-treated above 1600°C, exhibit lower tensile modulus and tensile strength than those for the precursor PBO fiber. Both studies were made for PBOCF's heat-treated at various temperatures up to 2000°C, and it was revealed that PBOCF's have turbostratic structure. Rogers et al. concluded that PBOCF does not graphitize [4]. However, no investigation has been made for PBOCF's heat-treated at temperatures above 2000°C. In the present study, PBOCF was heat-treated at temperatures up to 3000°C and examined the texture and graphitizability, because graphitization temperature is usually higher than 2000°C for aromatic polymers and it has been known that a rigid aromatic polyimide film PMDA/PPD, which has rigid rod molecules similar to PBO, exhibits excellent graphitizability [6,7].

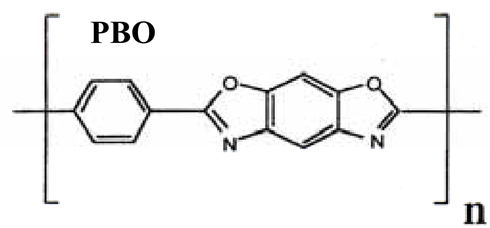


Fig. 1. Molecular structure of PBO

Experimental

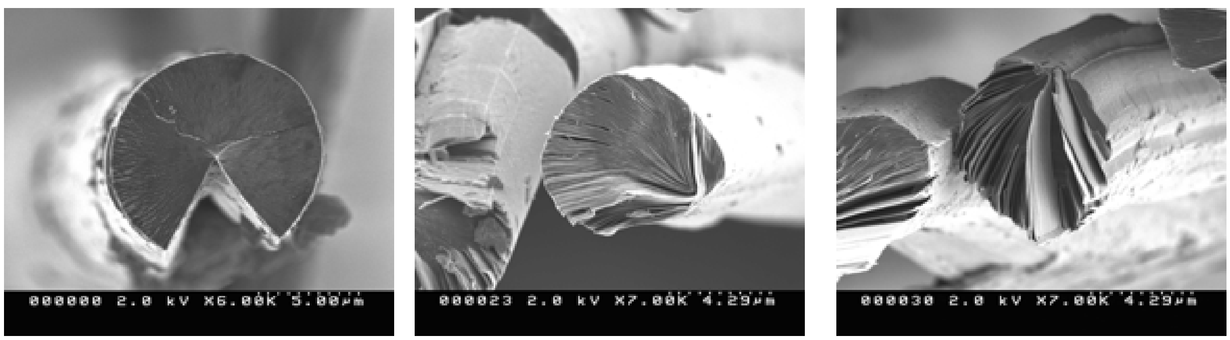
Zylon HM, a commercially available high modulus PBO fiber with mean diameter of 12 μm produced by Toyobo Co. Ltd., was used for the present study [2,3]. Zylon HM was wound onto a rectangular plate of artificial graphite. The windings were heated up to

900°C in an infrared radiation furnace in a flow of nitrogen with a heating rate of 2°C/min and kept for 1hr at the top temperature for carbonization. From the carbonized windings, sections of about 3 cm long were cut out. In the sections, single fibers were aligned almost parallel. Using graphite resistance furnace, each section was sandwiched between two artificial graphite plates and heated further up to a desired temperature between 2400 and 3100°C with a heating rate of 2000°C/hr in a flow of argon and kept for 30 min at the top temperature. PBOCF's thus obtained were denoted as Zylon-HM followed by each heat treatment temperature (HTT). Another 3000°C-treatment was made by the same method, but the graphite resistance furnace was broken when the temperature reached to 3000°C. The samples thus heat-treated are denoted as 3000°C-2.

SEM observations were carried out for the surfaces and cross sections of these PBOCF's. X-ray diffraction (XRD) measurements were made for the bundle (3cm-section-cut-out) of PBOCF's mounted on a specially designed sample holder using CuKα radiation in reflection and transmission modes. Mosaic spread (MS) was also measured for each bundle. MS is originally defined for well-oriented materials with plane orientation, by full width at the half maximum of the peak intensity of the 002 diffraction plotted against rotation angle of the sample, keeping the diffractometer at the Bragg condition [7], but it can be measured for carbon fibers with an axial orientation. Maximum transverse magnetoresistance $(\Delta\rho/\rho)_{max}$ and two minimum magnetoresistance values $(\Delta\rho/\rho)_{Tmin}$ and $(\Delta\rho/\rho)_{TLmin}$ were measured at 77K and in a magnetic field of 1T for each single fiber of PBOCF's. In the case of Zylon-HM 3000-2, measurements were made for a bundle of a few fibers. $(\Delta\rho/\rho)_{TLmin}$ was obtained when the field was parallel to the fiber axis and $(\Delta\rho/\rho)_{Tmin}$ was obtained in the field direction perpendicular to both directions obtaining $(\Delta\rho/\rho)_{max}$ and $(\Delta\rho/\rho)_{TLmin}$ [8]. The anisotropy ratios r_{TL} and r_T, as a measure of orientation of carbon layers along the fiber axis and across, were obtained from the ratio of $(\Delta\rho/\rho)_{TLmin}$ and $(\Delta\rho/\rho)_{Tmin}$ to $(\Delta\rho/\rho)_{max}$, respectively. The average crystallite transverse magnetoresistance $(\Delta\rho/\rho)_{cr}$, a measure of graphitization degree, is also obtained by the sum of $(\Delta\rho/\rho)_{max}$, $(\Delta\rho/\rho)_{TLmin}$ and $(\Delta\rho/\rho)_{Tmin}$ [8]. In order to examine the surface structure of carbon fibers, first order Raman spectra were measured for each single fiber at room temperature in air using a 514.5nm line of an argon ion laser.

Results and Discussion

Figure 2 shows examples of the SEM photographs for Zylon-HM900, 2400 and 3000. Two different textures were found on the cross sections of the Zylon-HM900; one is a so-called open wedge texture (Fig. 2 (a)) as observed in mesophase pitch based-carbon fibers [9], and another is a modified texture of the open wedge. The mean diameter is about 8~10 μm for both type of the cross sections. The fibers having the open wedge texture were frequently found, while those with the modified open wedge were rare. On the other hand, the mean diameter of Zylon-HM2400 and 3000 is about 5 μm, and most of these fibers have a texture spreading relatively thick carbon layers (graphite ribbons) from one definite axis (fiber axis) and extending the graphite ribbons along this axis (Fig. 2 (b) and (c)). In the cross-sectional texture, graphite ribbons align like leaflets of the palm-leaf fan. The morphology suggests a highly oriented and highly graphitized structure of Zylon-HM2400 and 3000.



Zylon-HM900 Zylon-HM2400 Zylon-HM3000-1

Fig. 2 SEM photographs for heat-treated PBO fibers.

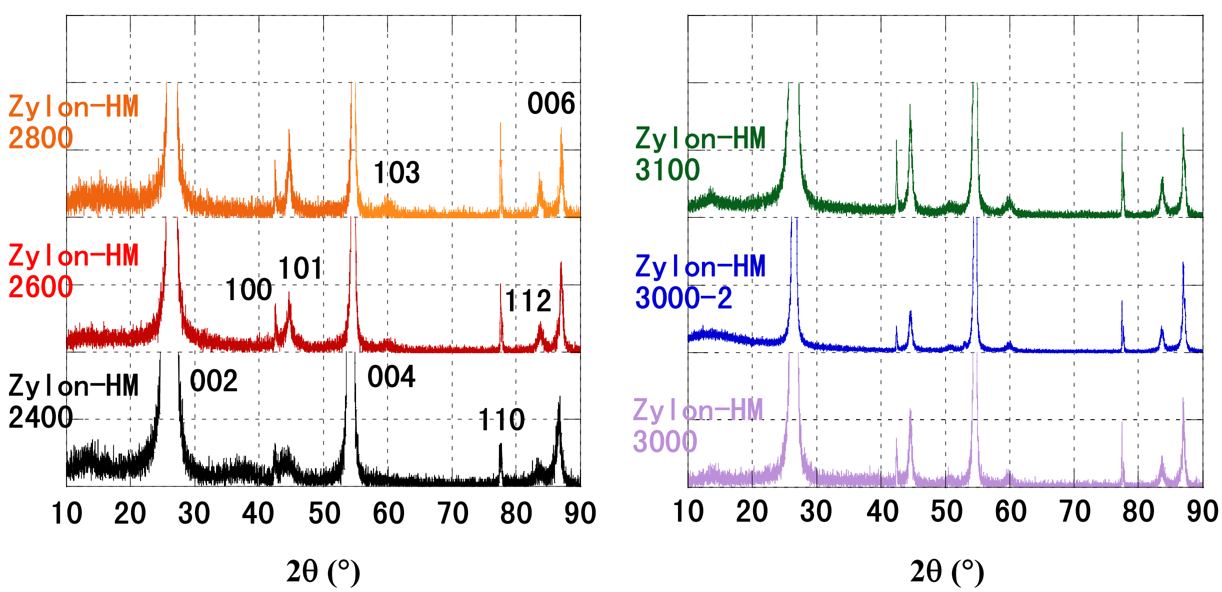


Fig.3 X-ray diffraction patterns for heat-treated Zylon HM carbon fibers.

Table.1 Values of MS, $(\Delta\rho/\rho)_{cr}$, r_T, r_{TL} and I_D/I_G.

Sample	MS ($^\circ$)	$(\Delta\rho/\rho)_{cr}$ (%)	r_T	r_{TL}	I_D/I_G
Zylon-HM2400	**3.6**	**4.79**	**0.988**	**0.059**	**0.31**
Zylon-HM2600	**4.0**	**33.7**	**0.903**	**0.039**	**0.06**
Zylon-HM2800	**4.7**	**43.04**	**0.676**	**0.041**	**0.06**
Zylon-HM3000	**4.1**	**45.92**	**0.690**	**0.007**	**0.06**
Zylon-HM3000-2	**3.9**	**60.44**	**0.822**	**0.009**	
Zylon-HM3100	**4.7**	**75.45**	**0.018**	**0.577**	**0.07**

The XRD patterns in reflection mode for PBOCF's are shown in Fig. 3. A very strong 002 line and a relatively strong 004 line were observed with a quite weak 006 line in each pattern. In addition to these 00*l* lines, weak 100, 101, 102, 103, 110 and 112 lines were measured as quite weak peaks. In the transmission mode, however, only 100 and 110 peaks were observed. The average values of the interlayer spacing d_{002} and lattice constant a_0 were determined to be 0.3355 nm and 0.2461 nm for Zylon-HM3000, as an example, after correction of the pattern for Lorentz polarization and atomic scattering factors, referring to the external standard of an HOPG specimen. The MS values for PBOCF's were around 4 – 5^o as listed in Table 1. Thee MS values correspond to those for the highly crystallized graphite films prepared by heat treatment above 3000^{o}C [10,11]. These results indicate that PBOCF's are graphitized at HTT's above 2400^{o}C at least and have a quite high orientation of carbon layers along the fiber axis.

The field dependence of $(\Delta\rho/\Delta\rho)_{max}$ at 77K for PBOCF's is shown in Fig.3 and the values of $(\Delta/\Delta\rho)_{max}$, $(\Delta/\Delta\rho)_{cr}$, r_T and r_{TL} for each PBOCF in a field of 1T are shown in Table 1. $(\Delta/\Delta\rho)_{max}$ increases remarkably with increasing HTT. The large positive $(\Delta/\Delta\rho)_{max}$ and very small r_{TL} reveal that PBOCF is graphitizable enough and highly oriented carbon fiber, and agree well with the results of the X-ray diffraction and SEM. The r_T values indicate that some degree of preferred orientation exists in the cross sections of PBOCF's, and should be related to the palm-leaf fan texture in the cross section observed in each PBOCF by SEM. We can compare the magnetoresistance value between any graphite materials with different textures by $(\Delta\rho/\rho)_{cr}$ obtained at the same temperature and in the same magnetic field [8,11]. The $(\Delta\rho/\rho)_{cr}$ value of PBO3000 is higher than that for the vapor grown carbon fibers (VGCF's) heat-treated at 2600^{o}C and much higher than those for any other carbon fibers heat-treated at 3000^{o}C, such as stretched PAN-based carbon fibers and mesophase pitch-based carbon fibers [11].

The first-order Raman spectra for PBOCF's are shown in Fig. 4. The ratio of the D band to G band, I_D/I_G, in each spectrum is listed in Table 1. The I_D/I_G values for the fibers heat-treated at temperatures above 2600°C are below enough 0.1. The value obtained for VGCF's heat-treated at 2600°C is about 0.2 [4]. The small I_D/I_G values for the present PBOCF's reveal that the fibers have highly graphitized carbon surfaces.

We can conclude that a highly graphitized fiber with high degree of axial orientation can be obtained from the PBO fiber.

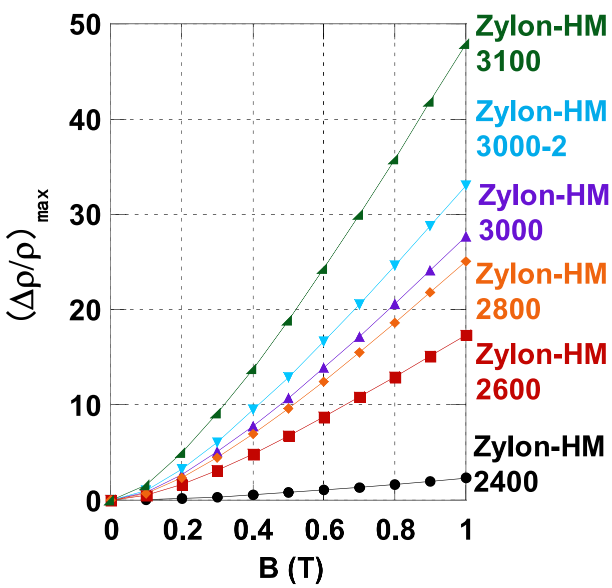


Fig.3 Filed dependence of $(\Delta\rho/\rho)_{max}$ at 77K for PBOCF's

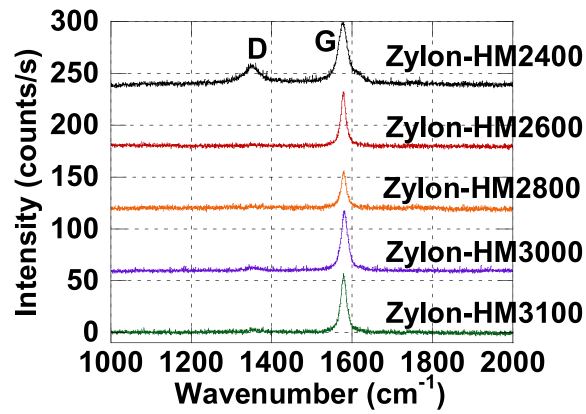


Fig.4 First-order Raman spectra for PBOCF's

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