

Preparation of Carbon Fiber from Heavy Oil Residue through Bromination

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Abstract: A pitch precursor for a general purpose carbon fiber was prepared by condensation of pyrolyzed fuel oil (petroleum residual oil) with bromine under nitrogen blowing. Such a condensation raised the softening point of the pitch from 40°C to 265°C with a yield of 43%. The pitch precursor showed an enhanced aromaticity and enlarged molecular size, which led to a reduction in molecular mobility and optical isotropy. The precursor was spun into fibers of 20 µm diameter at a take-up speed of 700 m/min. The fiber was stepwise stabilized in air and carbonized in Ar gas to obtain an isotropic carbon fiber. The carbon fiber exhibited tensile strengths of 500-800 MPa though the fiber was formed via a crude method. The electric conductivity of the carbon fiber was relatively high, 2.2×10^2 S/cm, sufficient to be used as electrode materials.

Keywords: Isotropic carbon, Petroleum pitch, X-ray diffraction, Carbon fiber, Mechanical properties

Introduction

The commercial carbon fibers are classified into three major categories according to their precursors[1,2]: rayon, polyacrylonitrile (PAN), and pitch-based carbon fibers, although the production of rayon-based carbon fiber has diminished. Pitch is readily available in large quantities and is attractive as a precursor for large-scale carbon fiber manufacture because of its significantly low price in comparison with other polymeric fibers. The precursor pitches are originally obtained from petroleum, asphalt, coal tar, and polyvinylchloride (PVC). However, the low price of raw materials is offset by the expenses of the purification and the low yield of the precursor.

Pitch based carbon fiber is usually classified into two categories by their performances[3-6]. One is the high performance carbon fiber (HPCF), which is prepared from optically anisotropic pitch. The fiber exhibits a high modulus, high tensile strength, and high electric and thermal conductivities. The other is the general purpose carbon fiber (GPCF), which is prepared from isotropic pitch. Activated carbon fiber (ACF) is readily prepared from the GPCF due to its isotropically connected network morphology.

Petroleum-derived carbon industry can be huge, based on the amount of heavy residual oils from various petroleum processes. In general, petroleum pitch typically has lower aromaticity and higher degree of substitution of the aromatic ring than coal tar pitch, i.e., it is enriched with more alkyl-substituted polycyclic aromatic hydrocarbons[7,8].

Pyrolyzed fuel oil (PFO) used as the raw material in this work is the heavy residual oil by-product in the manufacturing of ethylene from naphtha. Some portion of the PFO is used as fuel but it causes air pollution due to incomplete combustion. The PFO has high carbon contents, above 92%, which can be an economical benefit.

The precursors with high softening points were normally prepared by condensation of low molecular hydrocarbons, such as coal tar or petroleum residues. Mochida *et al.*[9-12] condensed polycyclic hydrocarbons by using various catalysts. They reported that isotropic precursor could be prepared through condensation from naphthalene with potassium catalysts, and the mesophase from that with Lewis acid catalysts, such as $AlCl_3$ or HF/BF_3 . The $AlCl_3$ in carbon cannot be removed easily due to the high viscosity of the condensed hydrocarbon and cause puffing in the process of carbonization. Even if it can be removed, it cannot be recycled because it is removed in the form of $AlCl_3OH$. The HF/BF_3 also presents some difficulties in processing due to its strong acidity causing corrosion of metals.

Yang *et al.*[13-18] oligomerized coal tar or heavy oil residue to prepare pitch precursors of high softening point, in the presence of nitrobenzene (NB)[13-15], *p*-benzoquinone [16,17], *p*-nitroaniline[15], borontrifluoride/diethyletherate complex (BFDE)[14,15] or halogens[18]. In the carbonization process, an inhibition of molecular stacking due to molecular size increase during the condensation was observed resulting in isotropic pitch, which was explained with the reduced mobility of the enlarged molecules. They proposed that the morphology of carbon materials could be controlled by changing the reaction rates by varying the concentration of catalyst and/or co-catalyst and/or stabilization condition.

In the present study, PFO was oligomerized via a new method comprising of chemical reaction with bromine and removal of volatiles through nitrogen blowing to obtain a pitch precursor with an appropriate softening point (SP) for oxidative stabilization. The precursor was then spun into fibers, stabilized and then carbonized.

Experimental

Precursor Preparation

PFO (Samsung Chemical Co., SP of 40°C) was oligomerized

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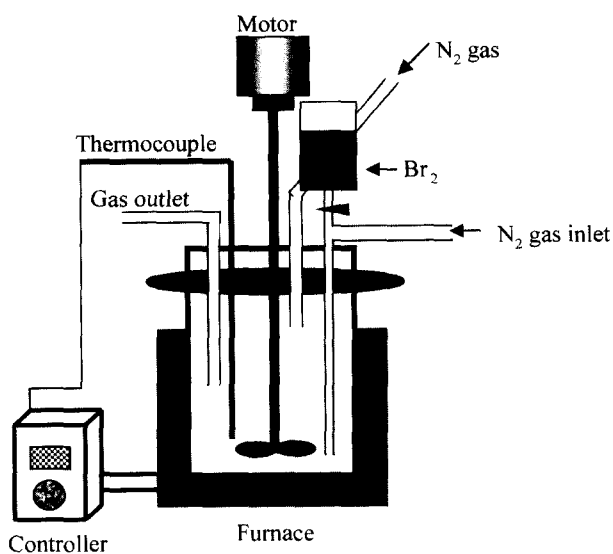


Figure 1. Schematic diagram of reactor.

at 180°C for 2 hours in the presence of 15 wt% bromine (Junsei Chemical Co. Ltd., first-grade), fed into the reactor (Figure 1) with 0.1 ml/min. Nitrogen blowing at a flow rate of 1 l/min at 340°C for several hours at 500±50 rpm was then carried out to obtain a high SP precursor by reduction of volatile components. The MPFO and MPFO-N represent the condensed product and the precursor pitch obtained through nitrogen blowing of MPFO with SP of 265°C, respectively. The product yields of precursors were calculated based on equation (1).

$$\text{Yield}(\%) = \frac{\text{weight of precursor}}{\text{weight of PFO}} \times 100 \quad (1)$$

Spinning, Stabilization, and Carbonization

MPFO-N was melt-spun into fibers through a round-shaped single-hole spinneret ($L/D=2$, $D=0.2$ mm) at 275–295°C using pressurized nitrogen, 20–80 MPa. The pitch fiber was oxidatively stabilized stepwise at 200°C, 280°C and 310°C for 1 hour respectively under air convection.

The stabilized fibers were carbonized at 1000 and/or 1300°C for 1 hour under argon atmosphere at a heating rate of 5°C/min. The carbon yield was calculated on the basis of equation (2).

$$\begin{aligned} \text{Carbon yield}(\%) \\ = \frac{\text{weight of sample after carbonization}}{\text{weight of sample before carbonization}} \times 100 \end{aligned} \quad (2)$$

Characterization

SP was measured by using Mettler FP 90 apparatus (Mettler-Toledo AG, Switzerland). The functional groups of the PFO and the MPFO-N were characterized using a FT-IR spectrometer (Nicolet 520p, USA) with samples in KBr discs and using NMR (Varian XL-400, USA) of the samples

dissolved in CDCl_3 or deuterated pyridine. C , H , N contents of samples were determined from elemental analysis (EA1110 CHNS-O, CE Instruments, Italy), and O content was calculated from the difference between 100% and the sum of the fraction of the other elements. From the results of NMR and elemental analysis, aromaticity f_a was calculated on the basis of Brown-Ladner method (equation (3)) [19],

$$f_a = \frac{C/H - H_\alpha^*/x - H_0^*/y}{C/H} \quad (3)$$

where C =mol % carbon, H =mol % hydrogen, H_α^* =mol fraction hydrogen α to aromatic ring, H_0^* =mol fraction of aliphatic hydrogen not α to aryl ring, x =average ratio of hydrogen to carbon on carbons α to aryl ring and y =average ratio of hydrogen to carbon on aliphatic carbons not α to aryl ring.

Thermogravimetry analysis (STA 1640, Stanton Redcroft) was performed under air or nitrogen atmosphere to find optimal stabilization condition or to measure the thermal stability of the samples.

Optical texture of the stabilized and carbonized fibers were observed under a polarized-light microscope (AFX-II, Type-104, Nikon, Japan), after imbedding and polishing them in unsaturated polyester resin. The topological structures of carbon fiber were observed on a SEM (Hitachi, S-4700, Japan). X-ray diffraction (Dmax 1200, Rigaku, Japan) was also used to characterize the morphological structure. The interlayer spacing d_{002} and the crystalline thickness $Lc_{(002)}$ were calculated on the basis of Bragg's law (equation (4)) and Scherrers formula (equation (5)), respectively.

$$d_{002} = \frac{n\lambda}{2\sin\theta} \quad (4)$$

$$Lc_{(002)} = \frac{k\lambda}{\beta\cos\theta} \quad (5)$$

where n and k are constant, λ is the wavelength of x-ray, θ is the Bragg angle and β is the width of scattering peak.

Tensile strength was measured using a lab-scale tensile tester (Nano Technics Co, Korea) with 150 g load cell at a cross head speed of 2.5 mm/min (JIS R 7601 method). Average strength was taken from 5 samples.

Electrical conductivity of the carbon fiber was measured by a 4-probe method, which measures the voltage (Digital multimeter, Model 2041, Kotronix, Japan) with applied DC current (Model 3387-11, Kotronix, Japan). Electrical conductivity was calculated from reciprocal value of ρ obtained from equation (6),

$$\rho = R \times A/L \quad (6)$$

where ρ is resistivity, R is resistance, A is cross-section area of specimen in cm^2 and L is length in cm between the probes. The resistance R was calculated on the basis of Ohm's law.

Results and Discussion

The condensation of the PFO increased the SP from 40°C to 85°C (MFPO), and the nitrogen blowing further increased the SP proportionally to the blowing time (Figure 2). Though the production yield decreased with increase in blowing time, a relatively high yield above 40% was obtained with a sample having a SP of 265°C. These results suggest that average molecular size is increased through the condensation reaction of the PFO in the presence of bromine and subsequent nitrogen blowing. Mochida *et al.* [20,21] reported that the nitrogen blowing also proceeded cross-linking and condensation reaction suppressing the growth of mesophase spheres in the isotropic matrix.

Some characteristics of PFO and MPFO-N are compared in Table 1. SP and aromaticity increased from PFO to MPFO-N through condensation and nitrogen blowing. The results indicate that condensation and aromatization were occurred during the procedures.

The FT-IR spectra of PFO and MPFO-N are shown in Figure 3. The spectra show aromatic C-H stretching at 3040 cm^{-1} , aliphatic C-H stretching at 2920 cm^{-1} , aromatic C=C stretching at 1630 cm^{-1} and C-H bending (out of plane) at 750-872 cm^{-1} . The results indicate that PFO and MPFO-N consist of a variety of complex aromatic ring with aliphatic side chain, and the aromaticity calculated from the ratio of

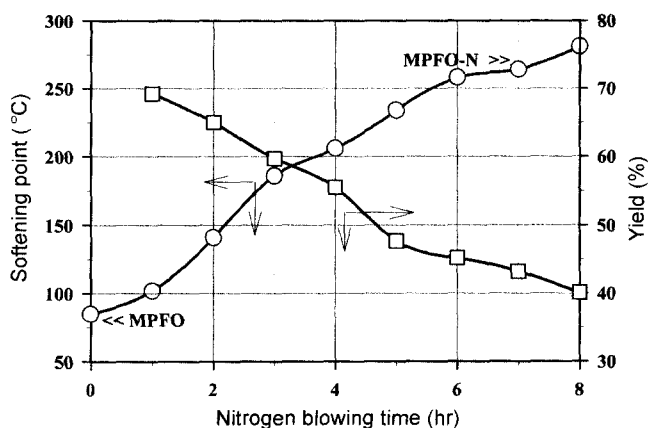


Figure 2. The effects of nitrogen blowing on SP and product yield.

Table 1. The characteristics of PFO and pitch precursor (MPFO-N)

Sample	Yield (%)	SP (°C)	C_{ar}/C_{al} *	H_{ar}/H_{al} *	f_a **
PFO	-	40	1.268	1.499	0.70
MPFO-N	43	265	1.492	1.645	0.75

*Determined by ^{13}C -NMR and ^1H -NMR, C_{ar} : aromatic carbon, C_{al} : aliphatic carbon, H_{ar} : aromatic hydrogen, H_{al} : aliphatic hydrogen, **Aromaticity was calculated from ^1H -NMR based on the Brown-Ladner method.

the intensities of Ar-(C-H)/Al-(C-H) increased from 0.493 to 0.674 by the condensation reaction.

As shown in Figure 4, under air atmosphere, a weight gain of 1.5% was observed in the range of 250-350°C due to oxygen uptake, then the weight decreased rapidly above 350°C due to combustion. Under nitrogen atmosphere, weight loss started from 330°C, the weight was nearly constant at 51% above 450°C, showing relatively high thermal stability. Based on the TGA results, stabilization temperature was set in the range of 200-330°C.

The suitability of pitch for the production of carbon fibers is determined by its spinnability and dimensional stability in the oxidative stabilization and carbonization procedures [22]. MPFO-N was spun at a take-up speed of above 700 m/min, indicating good spinnability. The average diameter of pitch fiber was about 20 μm . The pitch fibers were oxidatively stabilized in air, followed by carbonization.

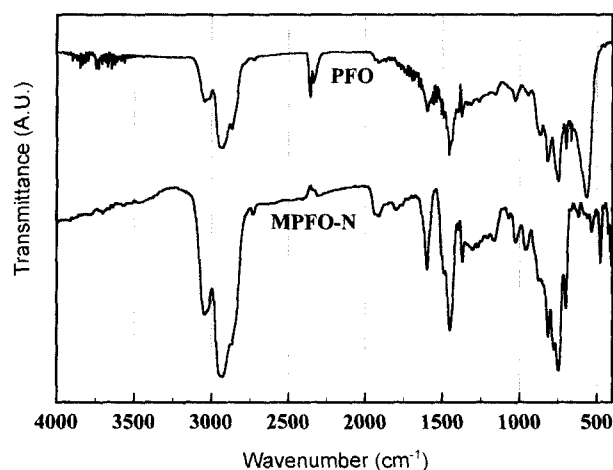


Figure 3. FT-IR spectra of PFO and MPFO-N.

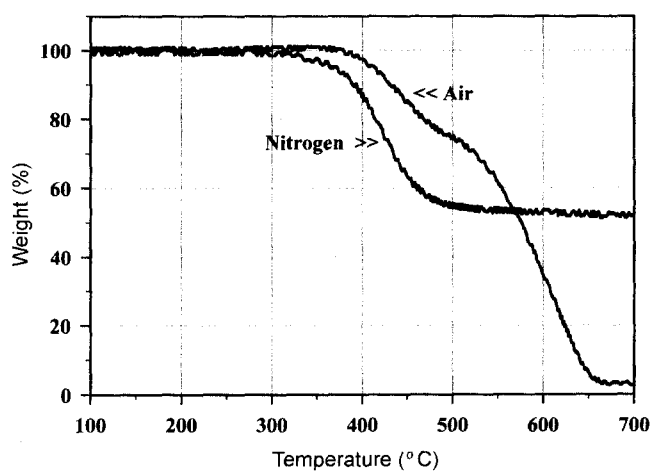
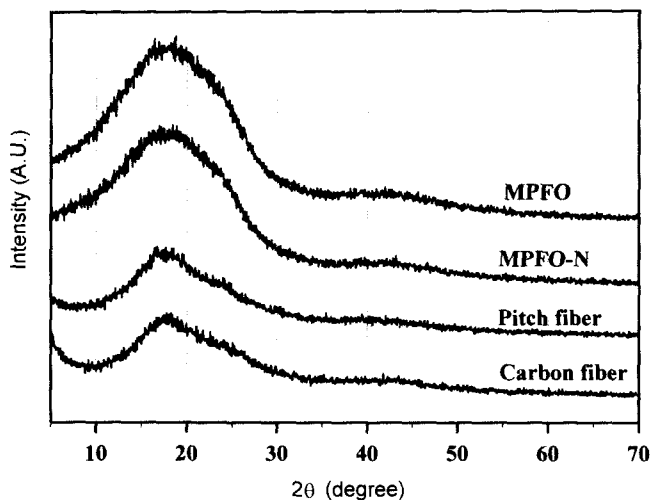


Figure 4. Thermogravimetric profiles of MPFO-N under air or nitrogen atmosphere; heating rate, 5°C/min.

Table 2. Elemental contents of the samples

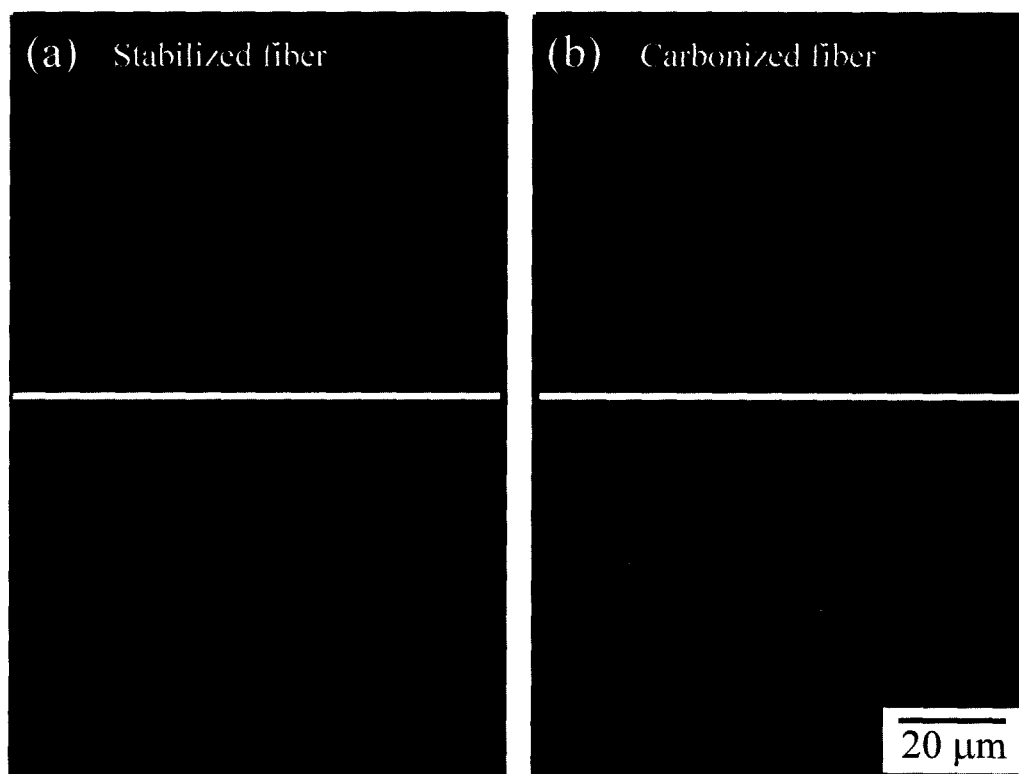
	C (%)	H (%)	N (%)	O (%)
PFO	92.62	7.25	0.07	0.06
MPFO-N	92.64	6.20	0.01	1.55
Pitch fiber	91.07	6.09	0.04	2.8
Stabilized fiber	74.10	2.95	0.02	22.93
Carbonized fiber at 1,000°C	93.10	0.12	0.12	6.7

**Figure 5.** XRD curves of the samples.

Elemental compositions of each sample are summarized in Table 2. Most samples except stabilized fiber exhibit the carbon content above 90%. The oxygen uptake of the stabilized fiber was above 20%. Generally, the stabilization reaction proceeds via diffusion of oxygen and oxidative reaction, which results in a variety of oxygen containing functional groups on the aromatic rings, dehydration and cross-linking of the oligomers[1,21]. Insufficient stabilization results in deformation of the fiber shape during the successive carbonization. Excess stabilization reduces the alignment of mesogen molecules by enlarging the molecular size and leads to poor mechanical properties.

The layer spacings ($d_{(002)}$) of MPFO-N, pitch fiber and carbon fiber were about 4.92 Å, which is large, and the stacking heights ($L_{c(002)}$) were 6.36, 10.91 and 10.51 Å, respectively (Figure 5). These results represent a disordered morphological structure, which is difficult to graphitize. The polarized light microphotographs of stabilized and carbonized fibers (Figure 6) also indicate isotropic texture, being suitable for preparation of ACF.

The carbon fibers do not exhibit highly ordered structure (Figure 7). Carbon fibers have diameters of 15-20 μm. Holes formed in the fiber (Figures 7 (c) and (d)) were observed and considered to be defects, which cause the reduced tensile strength. Through reductions in the defects of the fiber, tensile strengths of the fibers are expected to approach to

**Figure 6.** Polarized light microphotographs of cross-sectional and longitudinal direction of fibers: (a) stabilized fiber, (b) carbonized fiber.

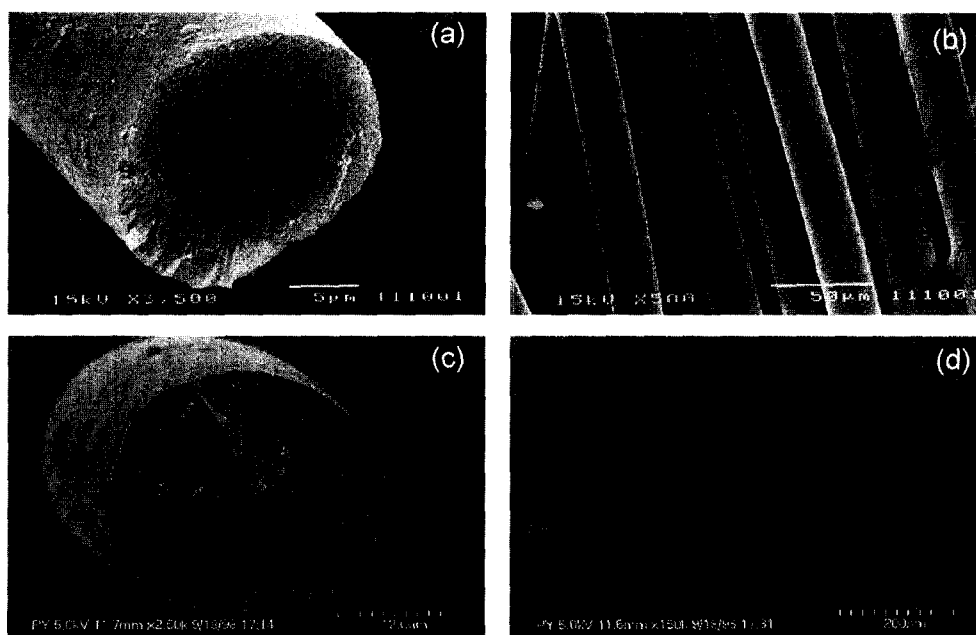


Figure 7. SEM microphotographs of fiber carbonized at 1300°C: (a) cross-section, (b) longitudinal, (c) popped structure, (d) magnified popped structure (square region of (c)).

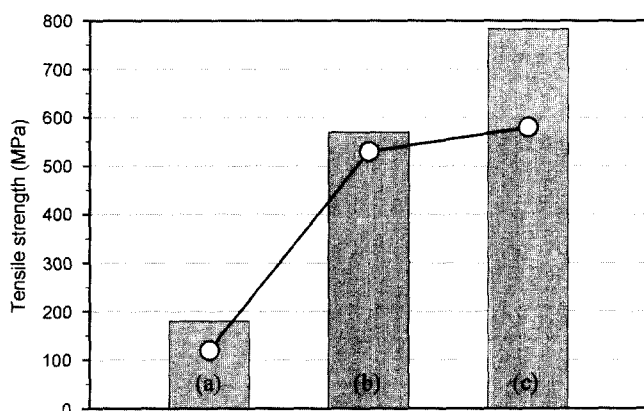


Figure 8. Tensile strength of stabilized and carbonized fibers: (a) stabilized fiber, (b) carbonized fiber at 1000°C, (c) carbonized fiber at 1300°C (bar: maximum tensile strength, circle symbol: average tensile strength).

those of the commercialized GPCF. The microstructure may be suitable for creation of high surface area by activation process.

The tensile strengths of stabilized and carbonized fibers heat-treated at two different temperatures are shown in Figure 8. The maximum tensile strength were 180, 570 and 780 MPa for the stabilized fiber and fibers carbonized at 1,000°C and 1300°C, respectively (diameter, 20 μm). The tensile strength of the fiber carbonized at 1000°C from the commercialized isotropic pitch (Osaka Gas Chemical Co., SP 312°C) was also measured under identical conditions. Its

strength (diameter, 10 μm) was 1,250 MPa which was 2.2 times higher than that of the PFO-based. The smaller the fiber diameter, the larger the tensile strength expected, reflecting the structural dependence of the fiber on the diameter. The difference may originate from the higher carbon yield (about 75%) and the smaller diameter with reduced defects from the commercialized pitch.

The electric conductivity of carbon fiber was about 2.2×10^2 [S/cm], which was high enough for applications in various kinds of electrodes. Especially, on activation this carbon fiber may be applied to electrodes of supercapacitor on the basis of its high electric conductivity and large surface area from micropores[23].

Conclusions

The reaction of PFO with bromine led to oligomerization of PFO, and its heat treatment and nitrogen blowing made it possible to prepare a isotropic precursor pitch with high enough SP for stabilization. The take-up speed of the fiber through single-hole spinneret was above 700 m/min. The precursor (MPFO-N) showed enhanced aromaticity and increased molecular size compared with the raw material, PFO. Such increased molecular weight led to less ordered carbon materials due to the restricted mobility of the constituent molecules in the carbonization process. All the fibers prepared showed an optically isotropic texture. They exhibited relatively high conductivity of 2.2×10^2 [S/cm] and tensile strengths of 500-800 MPa, in spite of the presence of some defects and large diameters of the carbon fiber. The

carbon fibers seem to be suitable for preparations of ACFs for gas adsorption and for electrodes of double layer supercapacitors.

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