# Isotropic Carbon and Graphite Fibers from Chemically Modified Coal-Tar Pitch

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**Abstract**–A precursor for a general purpose carbon fiber was prepared from coal tar pitch (CP) modified with 10 % p-benzoquinone (BQ) at 380 °C for 3 hours. Such a modification raised the softening of the pitch from 85 °C to 271 °C at a yield of 43 %. The modified pitch was spun smoothly at a rate of 480 m/min into a fiber of 20 $\mu$m diameter. The fiber was stepwise stabilized at 236 °C (5 °C/min) and 312 °C (1 °C/min) for 3 hours at each temperature. Successively, carbonization and graphitization were performed at 1,000 °C and 2,400 °C, respectively, for one hour. Both the carbonized and graphitized fibers exhibited tensile strength of 570 MPa. The structural parameters of carbon and graphite fibers were their orientation values of 56.2 and 58.1 %, relatively low Lc(002) of 11.24 and 25 Å, and large interlayer spacing ($d_{002}$) of 3.86 and 3.49 Å, respectively.

Key words : Coal Tar Pitch, Chemical Modification, Benzoquinone

## INTRODUCTION

The general performance of carbon fiber (CF) from pitch was first proposed by Otani and assigned to Kureha Chemical Industry Co. [Otani, 1971]. The spinnability of pitches is dependent on their chemical composition and molecular weight distribution [Donnet et al., 1990]. Although any spinnable pitch with high carbon yield can be used as a precursor of general purpose carbon fiber in principle, a qualified precursor must satisfy the following two requirements. A higher softening point is preferable as far as stable spinning is assured, since stabilization at higher temperature is allowed for such a pitch precursor to complete its stabilization in a shorter time. In general, the pitch must be completely isotropic, because contamination by any mesophase spheres at which viscosity-temperature relationship is very different from that of the isotropic part, severely deteriorates the spinnability of the whole pitch. Komatsu et al., 1997, reported that the precursor containing sphere was spinnable to give a graphite fiber of 9.5 $\mu$m diameter.

Air blowing has been successfully applied in manufacturing paving asphalt, in preparing precursors of isotropic carbon materials, and in raising the softening point of coal tar or petroleum feed stocks. Cross-linking and condensation reaction are suggested to take place during the air blowing and to suppress the growth of mesophase spheres in the isotropic matrix. Some authors obtained coal tar pitch precursor with softening point of 280 °C by air-blowing. The air-blowing increased molecular size through dealkylation, dehydration and aromatization [Toyohiro et al., 1993; Zeng et al., 1993a, b]. However, the air blowing method requires severe control of conditions in a blowing time and

temperature as well as vigourous agitation to avoid heterogeneity.

The present authors [Yang et al., 1994] reported that a coal tar pitch (CP) was polymerized with p-benzoqinone (BQ) at about 150 °C resulting in an increase in molecular size and suppressing development of anisotropy.

Though the carbon fibers from the isotropic pitch show relatively low mechanical properties in comparison with the carbon fibers from mesophase pitch, the fiber can be selecting gasified to give a fibrous type of adsorbent activated carbon fiber (ACF). ACF can be a molecular sieve carbon because there can be excellent selectivity of planar molecules [Mochida et al., 1995].

In the present study, an isotropic precursor pitch was prepared through oligomerization of the CP through reaction of 10 wt% BQ. The precursor was spun into pitch fibers, carbonized, and graphitized by following heat treatment.

## EXPERIMENTAL

### 1. Precursor Preparation

THF soluble fraction of the coal tar pitch (CP, softening point of 85 °C, Jung-u Coal Chemical Co.) was separated by filtration from insoluble fraction and followed by removal of the THF by using a rotary evaporator. The CP was oligomerized stepwise in the presence of 10 wt% BQ at 121 °C and 131 °C for 1 hour at each temperature and it was designated as modified coal tar pitch (MCP). Softening point elevation was performed by nitrogen bubbling at 380 °C and at 1 *l*/min, MCP-380. The characteristics of the precursor are shown in Table 1. The concentration of BQ was expressed in weight ratio between BQ and CP, such as BQ10/CP100 representing the weight ratio of 10/100.

### 2. Spinning

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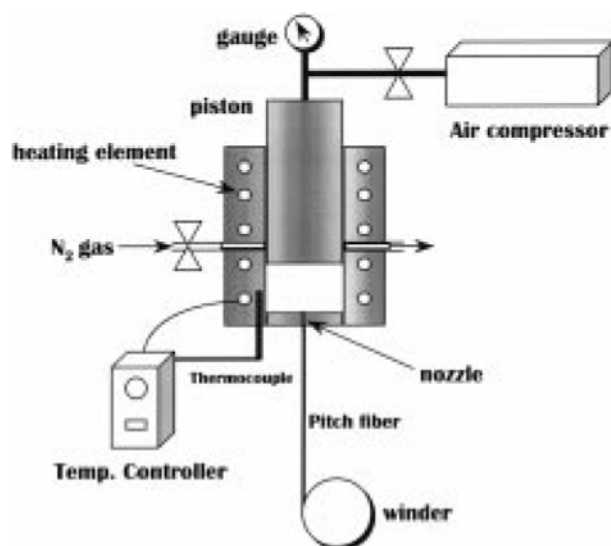E-mail : ksyang@chonnam.chonnam.ac.kr

**Fig. 1. Schematic diagram of spinning apparatus.**

The precursor pitch was aged in a reservoir for 3 hrs at 330 °C under nitrogen atmosphere. It was spun through a circular nozzle (D−0.3 mm, L−0.6 mm) at 285 °C, 10 Kgf/cm² as shown in Fig. 1. There was a mass outflow of 160 mg/min and a spin-draw ratio of 84, respectively. The parameters of the spinning were calculated on the basis of the Poiseuille equation [Brydson, 1981].

### 3. Stabilization, Carbonization and Graphitization

The pitch fibers were stabilized stepwise in an oven by convection of air in the temperature range of effective oxidative reaction but not combustion. The conditions chosen were temperatures of 236 °C and 312 °C for 3 hours at each temperature, followed by carbonization at 1,000 °C (5 °C/min) and graphitization at 2,400 °C for one hour. Finally, isotropic carbon and graphite fibers were obtained.

### 4. Analysis and Characterization

The reactivity of CP with BQ was investigated by determining the heat of reaction by using differential scanning calorimetry (DSC-200, Seiko Inco., Japan). The softening points of CP and MCP were measured by using a Mettler FP83 apparatus.

The $f_\alpha$ values were calculated on the basis of Brown-Lander method [Eq. (1)].

$$f_\alpha = \frac{C/H - H\alpha'/x - H_i'/y}{C/H} \tag{1}$$

The solubility of the precursor pitches was determined by Soxhlet extraction. Molecular distributions of the samples were measured with gel permeation chromatography (GPC, Shodex Degas). C, H, N contents were measured from elemental analysis, and O content was obtained from the difference from the sum of the C, H, N wt%.

Rheological properties of the precursor pitches were examined by using capillary rheometer (Instron 3211, USA) at softening point plus 30 °C. The stabilization behaviour of the pitch fiber was studied by using DSC (PL-Thermal Sciences, U.S.A.) and thermogravimetry (TG, Atantron Redcrost, U.K.) under air to find optimum stabilization temperatures.

The optical textures of carbonized samples were observed under a polarized-light microscope (Nikon, Japan, AFX-II, Type-104). The surfaces of the samples were investigated by SEM (JSM 5400, Japan) and atomic force microscopy (AFM, Nanoscope III, Digital Instruments Inc.). X-ray diffraction (Rigaku, Japan) was also used to characterize the morphological structures such as $d_{(002)}$ and $Lc_{(002)}$.

The $\pi$ of the carbon and graphite fiber were determined by X-ray diffraction by Eq. (2).

$$\pi = \frac{(180 - H)}{180} \times 100 \tag{2}$$

The tensile properties were measured by Instron (4200 Series, Full Scale Load Range ; 0.250 kgf) on the basis of a single filament standard method (KS K 0327), gauge length of 25 mm, a stretching rate of 0.5 mm/min. An average was taken from 15 tests.

## RESULTS AND DISCUSSION

### 1. Reactivity of CP and BQ

Fig. 2 represents the DSC thermal behavior of a mixture of CP and BQ (50 wt% of BQ). One endothermic peak at 99.6 °C and two exothermic peaks at 154.7 °C and 167.9 °C were observed. The endothermic peak represents the melting of BQ and the endothermic peaks imply Diels Alder reactions at 154.7 °C and dehydration at 168 °C evolving the total amount heat of 422 mJ/mg. Some properties of the pitches used are tabulated in Table 1. The solubilities represent that the BQ/CP reaction mainly increased the PI fraction and the following heat treatment at 380 °C increased the BI-PS fraction sustaining the PI fraction. In comparison with CP-380, the MCP-380 contains higher fractions of BI-PS and PI instead representing effective increase in molecular weight through the chemical modification.
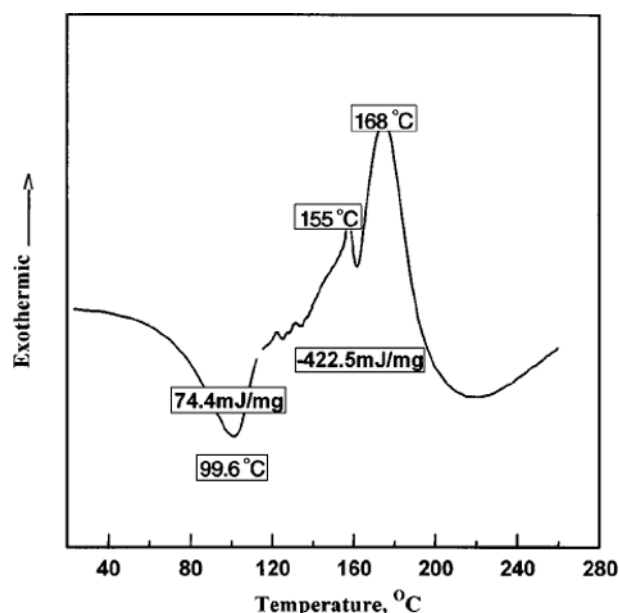


**Fig. 2. DSC thermal diagram of a mixture of BQ100/CP100 ; heating rate, 10 °C/min.**

**Table 1. Some properties of the precursor pitch**

| Elemental analysis (wt%) | | | | H/C | SP[a] (°C) | AP[b] (%) | Soubility (wt%) | | |
|---|---|---|---|---|---|---|---|---|---|
| H | C | N | diff. | | | | BS | BI-PS[c] | PI |
| 3.93 | 92.99 | 0.94 | 2.14 | 0.51 | 271 | 0 | 29 | 38 | 33 |

[a]softening point by Mettler, [b]anisotropic %, [c]β-resin %

An increase of the softening point by heat treatment was more significant for MCP (from 100 °C to 271 °C) than CP (from 85 °C to 214 °C). It was reported that the BQ/CP reaction increased the radical concentration and the increase contributed to a drastic increase in molecular weight resulting in increased softening point [Yang et al., 1994].
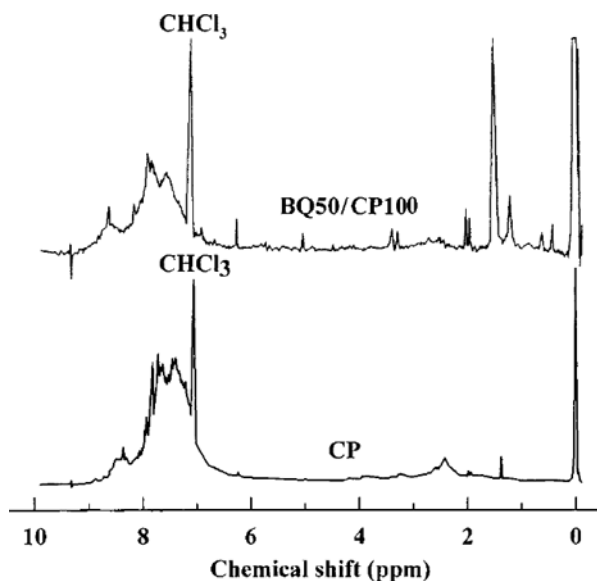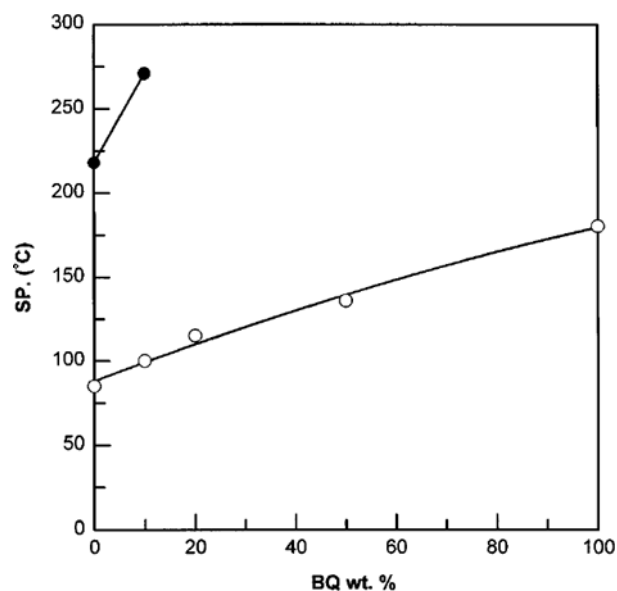
$^1$H-nmr spectra of CP and MCP are shown in Fig. 3. 7.3 ppm is assigned to aromatic hydrogens, 2.3 ppm and 1.2 ppm are assigned to $\alpha$ and other aliphatic hydrogens, respectively [Davidson, 1986]. The $f_\alpha$ values calculated on the basis of Brown-Lander method, 1960, was 0.963 for CP and 0.983 for BQ10/CP100. This implies that the chemical reaction increased the aromaticity.

The elemental analysis of chemically modified CP and MCP is summarized in Table 2. Though the oxygen content increased with an increase of BQ concentration, the two different reaction temperatures (140 °C, 180 °C) did not have significant effects

on elemental compositions.

As the concentration of BQ increased, the softening point of the sample increased (Fig. 4). When the BQ/CP was step-wise oligomerized at 10/100, 50/100 and 100/100, the softening point of the modified pitch increased from 85 °C to 100 °C, 124 °C, 176 °C respectively. When the BQ10/CP100 sample was nitrogen blown at 380 °C, the softening point increased from 100 °C for MCP to 271 °C for MCP-380, sustaining isotropic phase.

The molecular weight distributions of CP and MCP, and then MCP-380, are shown in Fig. 5. Though only the THF soluble fractions are experimented, it is recognized that the CP was oligomerized by the chemical reaction with BQ showing a shoulder in the upper region of molecular weight. The heat treatment at 380 °C not only increased but also broadened the



Fig. 3. $^1$H NMR spectra of CP and MCP.



**Fig. 4. Softening point dependence of modified pitch on the concentration of BQ.**
○: stepwise modified at 121 °C and 131 °C, ●: modified and followed by nitrogen blown at 380 °C

**Table 2. Elemental analysis of CP and the CP chemically modified with BQ**

| Elements | CP | BQ30/CP100 180 °C | BQ50/CP100 140 °C | BQ50/CP100 180 °C | BQ500/CP100 180 °C |
|---|---|---|---|---|---|
| N (%) | 1.05 | 0.98 | 0.94 | 0.97 | 0.25 |
| C (%) | 90.58 | 87.98 | 85.97 | 86.87 | 70.62 |
| O (%) | - | 5.52 | 8.17 | 7.92 | 26.16 |
| H (%) | 4.71 | 4.53 | 4.09 | 4.24 | 2.99 |
| H/C (mol) | 0.64 | 0.62 | 0.57 | 0.59 | 0.51 |
| O/C (mol) | - | 0.047 | 0.071 | 0.068 | 0.245 |
| (O/C)$_i$/(O/C)$_f$(%) | - | 78 | 79 | 76 | 93 |

(O/C)$_i$: the O content remained. (O/C)$_f$: the O content remained.

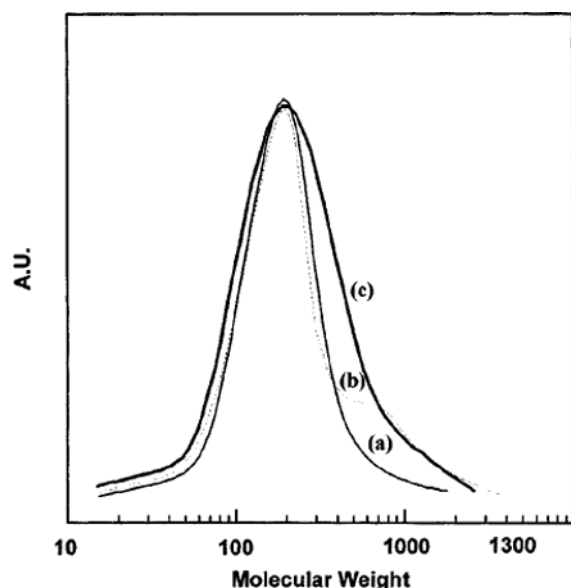Fig. 5. Molecular weight distribution
of the THF soluble fraction of the samples.
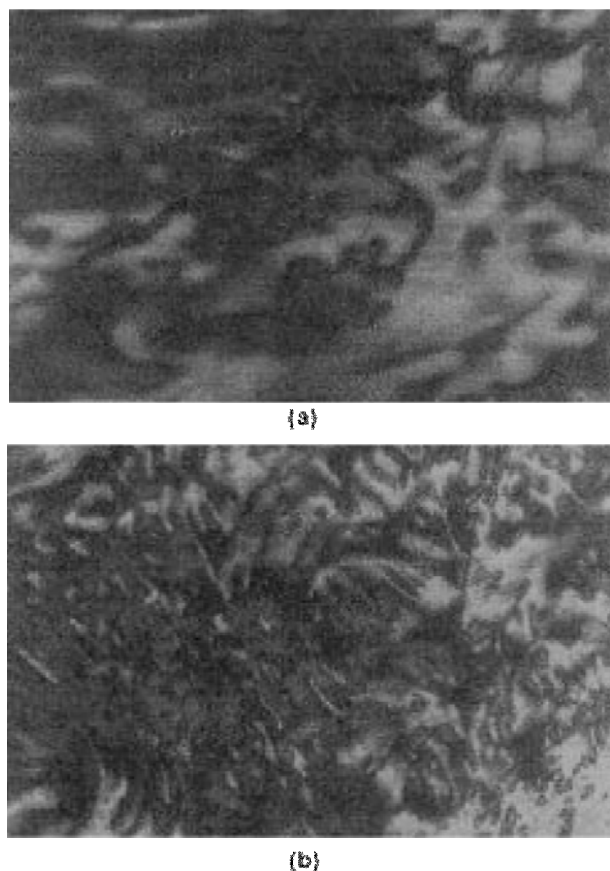(a) CP, (b) MCP, (c) MCP-380



Fig. 7. The relationship between viscosity ($\eta_a$) and shear rate
($\gamma$) of CP-380 ($\bigcirc$) and MCP-380 ($\bullet$) at softening point
plus 30.

the modified MCP has smaller optical domains than those of
CP. This result suggests that CP polymerized by BQ effective-
ly suppressed the development of its anisotropy compared to
CP itself, because of a lower mobility of the increased molec-
ular weights in the reaction procedure.

## 2. Fiber Formation

Fig. 7 shows rheological properties of CP-380 and MCP-380
at the temperatures of softening point plus 30 °C. Though both
of them show shear thinning behaviour, the MCP-380 show-
ed linear decrease with shear rate and that of CP decreased
drastically and then levelled off from ca. 200 sec$^{-1}$ showing
Newtonian behaviour. The shear thinning behavior of MCP-380
with higher molecular weight seems to be less sensitive com-
pared with CP-380 because of the enhanced molecular interac-
tions. The behaviour is considered to be an advantage of using
a resin for composite preparation because the reduced viscos-
ity gives an advantage for easy penetrating and effective wet-
ting. The pitch fibers of 20 $\mu$m could be spun at the speed
of 480 m/min from the MCP-380.

## 3. Stabilization

As shown in Fig. 8, stabilization behavior was studied by
using DSC and TGA under air atmosphere. An endothermic
peak appears near at 187 °C, representing a glass transition tem-
perature, and the exothermic peak was observed at 187-335 °C,
representing an active reaction of the pitch with oxygen and
finally weight loss in the TGA diagram at above the 335 °C
representing predominant combustion.

The elemental analysis data in Table 3 shows variations of
oxygen content in the pitch fiber. As the stabilization time and
temperature increased, the content of oxygen in pitch fibers in-
creased and the maximum content of oxygen was 13.5 % through
the stabilization.

## 4. Characterizations of the Fibers

The X-ray parameters and tensile properties the fibers are tab-



(a)



(b)

Fig. 6. Polarized light microphotographs of (a) CP and (b) MCP
carbonized at 600 °C.

molecular weight distribution.

The optical micrographs of CP and the MCP carbonized at
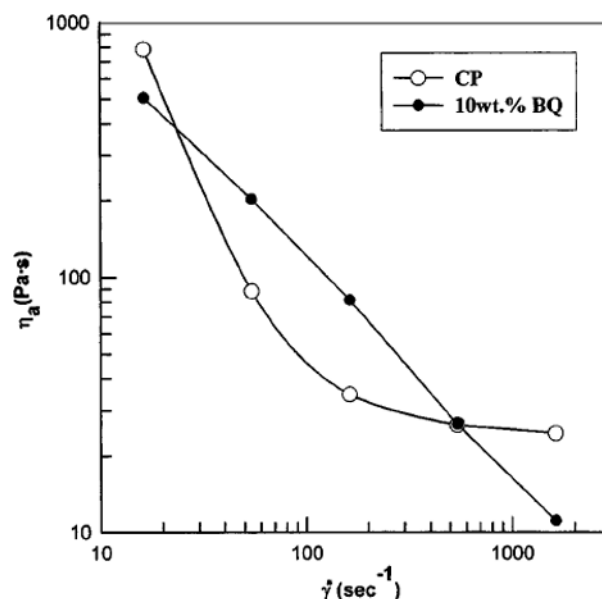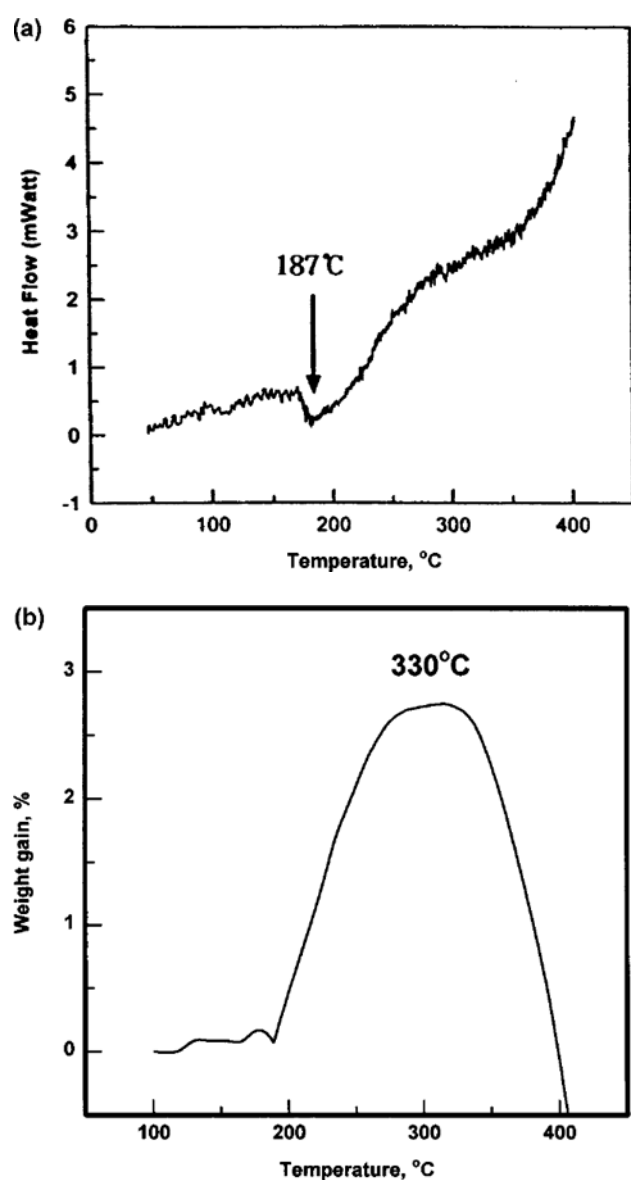600 °C are illustrated in Fig. 6. It shows that the coke from

ulated in Table 4. The $d_{(002)}$ values of carbon and graphite fibers were large as 3.86 and 3.49 Å and their $Lc_{(002)}$ values were small as 11.24 and 25 Å, respectively. Tensile strengths of carbon and graphite fibers were equally 567 MPa, and their Young's moduli were 39.4 and 43.1 GPa, respectively, which are large enough as a precursor for ACF preparation. The tensile properties of general purpose carbon fiber from pitch exhibits 700 MPa in tensile strength and 60 GPa in Modulus [Otani et al., 1983].

SEM microphotographs of carbon and graphite fiber with diameters of 17 $\mu$m and 15 $\mu$m are shown in Figs. 9 and 10. No



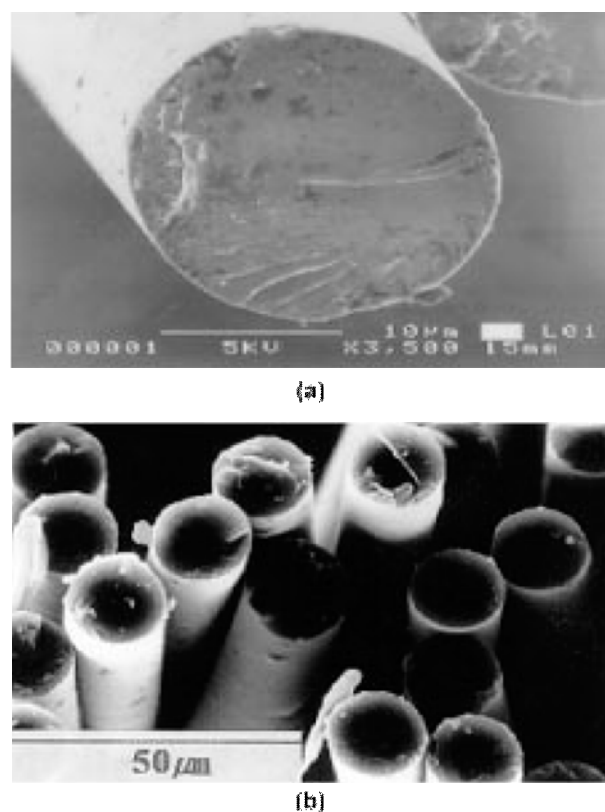Fig. 8. DSC (a) and TGA (b) thermoprofile under air flow ; heating rate, 5 °C/min.

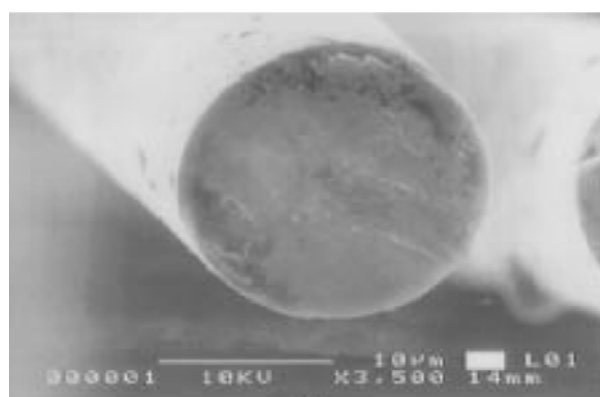Fig. 9. SEM microphotographs of carbonized fibers at 1,000 °C ; (a) monofiber, (b) multifiber.

**Table 3. Elemental analysis of samples in the process of the stabilization**

| Samples | Pitch fiber | Stab. fiber | Stab. fiber | Stab. fiber | Stab. fiber |
|---|---|---|---|---|---|
| Temp. (°C)/Time (hrs) | 285 | 236/3 | 312/0 | 312/1.5 | 312/3 |
| C | 92.7 | 89.6 | 87.7 | 84.5 | 82.1 |
| H | 3.9 | 3.4 | 3.0 | 2.8 | 2.6 |
| N | 1.1 | 1.1 | 1.1 | 1.2 | 1.4 |
| S | 0.4 | 0.4 | 0.5 | 0.4 | 0.3 |
| O | 1.9 | 5.5 | 7.7 | 11.0 | 13.6 |

**Table 4. Properties of carbonized and graphitized fiber**

| | Diameter ($\mu$m) | $d_{(002)}$[1] (Å) | $Lc_{(002)}$[2] (Å) | DO[3] (%) | TS[4] (MPa) | YM[5] (GPa) | UE[6] (%) |
|---|---|---|---|---|---|---|---|
| Carbon fiber | 17 | 3.86 | 11.24 | 56.2 | 567 | 39.4 | 1.44 |
| Graphite fiber | 15 | 3.49 | 25 | 58.1 | 567 | 43.1 | 1.32 |

[1]$d_{(002)}$ spacing, [2]Apparent crystallite stack height, [3]Degree of preferred orientation, [4]Tensile strength, [5]Young's modulus, [6]Ultimate elongation

(a)



(b)

Fig. 10. SEM microphotographs of graphitized fibers at 2,400 ℃;
(a) monofiber, (b) multifiber.



Fig. 11. AFM microphotographs of the fiber carbonized at 1,000
℃.

highly ordered structure of the carbon and graphite fibers was observed. The AFM microphotograph shows that striped pleat units aligned along the fiber direction with repeating distance of ca. 30 nm and deepness of 10 nm which was examined by section analysis (Fig. 11).

## CONCLUSIONS

The reaction of CP with BQ led to polymerization of CP, and its heat treatment made it possible to prepare the isotropic precursor pitch having the enough softening point for stabilization showing good spinnability which resulted in take-up speed of 480 m/min.

The isotropic carbon and graphite fiber which have good physical properties was prepared, i.e., tensile strength of 567 MPa, Young's modulus of 39.4, and 43.1 GPa, and low orientation values of 56.2 and 58.1 %, respectively.

## NOMENCLATURE

ACF : activated carbon fiber
BQ : benzoquinone
BS : fraction benzene soluble
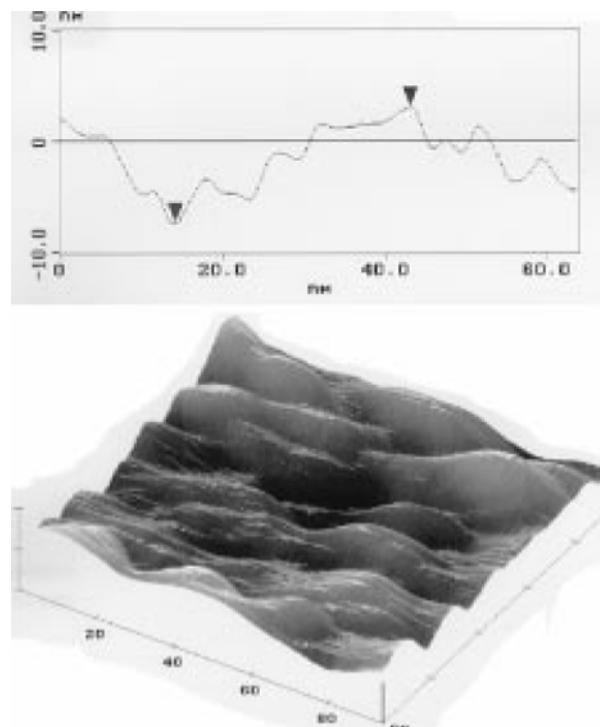BI-PS : fraction of benzene soluble but pyridine insoluble
C : mole % of carbon

CF : carbon fiber
CP : coal tar pitch
CP-380 : CP of nitrogen blown at 380 ℃
$d_{(002)}$ : interlayer spacing
GPa : gigapascal
H : mole % of hydrogen
$H$ : a half width angle for intensity along Debye ring for (h k l) interference
H'$\alpha$ : mole fraction of $\alpha$ hydrogen to aromatic ring
H'o : mole fraction of aliphatic hydrogen not $\alpha$ to aryl ring
$Lc_{(002)}$ : crystalline thickness along the c axis
MCP : chemically modified CP with 10 wt% BQ
MCP-380 : MCP nitrogen blown at 380 ℃
MPa : megapascal
PI : pyridine insoluble
THF : tetrahydrofuran
x : average molar ratio of hydrogen to carbons on carbon $\alpha$ to aryl ring
y : average ratio of hydrogen to carbon on aliphatic carbons not $\alpha$ to aryl ring
$f_\alpha$ : aromaticity calculated based upon Brown Lander equation

**Greek Letters**

$\eta_\alpha$ : apparent viscosity
$\pi$ : preferred orientation parameter

## ACKNOWLEDGEMENT

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