

# Preparation of Activated Carbon Fiber from Chemically Modified Coal-tar Pitch

K. S. Yang, \*S. K. Ryu, D. J. Lee and Y. J. Kim

*Department of Textile Engineering, Chonnam National University  
Yongbong-Dong 300, Puk-ku, Kwangju, 500-757*

*\*Department of Chemical Engineering, Chungnam National University  
Daejeon, 302-764*

## (ABSTRACT)

Carbon fiber of general purpose was prepared from coal tar pitch modified with 10% benzoquinone(BQ) at 380°C for 3 hours. Such a modified pitch raised the softening of the pitch from 85°C to 271°C at the yield of 40%. The modified pitch was spun smoothly at a rate of 480m/min into a fiber of 20 $\mu$ m diameter. The fiber was stabilized stepwise at 236°C (5°C/min) and 312°C(1°C/min) for 3 hours each. Both carbonized and graphitized fibers exhibited tensile strength of 570MPa which appears large enough as a precursor for active carbon fiber.

The activated carbon fiber prepared exhibited relatively high surface area of 2062m<sup>2</sup>/g at 76% burn-off and rather narrow distribution pore size of 20 Å.

## 1. INTRODUCTION

Activated carbons, which carry its large amount of micropore and high surface area, are widely used for gas purification and separation, deodorization, and water purification as the adsorbents and catalyst supports. They are usually in pelletized, granular, powdered, or molded form.

Recent development of activated carbons in fiber form(activated carbon fiber, ACF) is broadening applications of activated carbons due to its unique characteristics. Thin-fiber shape assures fast adsorption and desorption kinetics compared with pelletized or granular activated carbons, reducing the volume of adsorption vessel. The fibrous form is also favored because of facile handling in its felt fabric or other consolidated forms by newly developed molding techniques.

The feedstock precursors for ACF are cellulose(viscose rayon)[1,2], phenolic resin(Novolak)[3,4], polyacrylonitrile(PAN)[5], and isotropic pitch[6]. Productions of polymers based ACFs take high cost, because of a low coking yield(>wt%) and a high price of feedstock itself. On the other hand, coal tar pitch is the cheapest among the precursors of ACFs and the carbonization yield is expected to be high(theoretically 93.1 wt.%), which can contribute to lowering the final cost of the product[7]. However, technology is needed for preparation of

precursor pitch and manufacturing of fiber.

In this research, the precursor pitch showing isotropic character was prepared after the reaction of THF soluble coal tar pitch(CP) with p-benzoquinone(BQ) and then heattreatment at 380°C for 3 hours under nitrogen bubbling. It was spun, stabilized and carbonized, and carbon fiber was activated by H<sub>2</sub>O at 900°C.

## 2. EXPERIMENTAL

### 2.1 Preparation of precursor

The primary QI(quinoline insoluble) free pitch was reacted with 10wt.% BQ stepwise at 121°C and 131°C for 1 hour, respectively. The product was heattreated at a 380°C for 3 hours to increase the softening point of 271°C under nitrogen bubbling at 1 ℓ /min. The characteristics of the precursor were shown in table 1.

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

Elemental Analysis (wt.%)				H/C	SP <sup>a</sup> (°C)	AP <sup>b</sup> (%)	Solubility(wt.%)		
H	C	N	diff.				BS	BI-PS <sup>c</sup>	PI
3.93	92.99	0.94	2.14	0.55	271	0	29	38	33

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

### 2.2 Spinning

The precursor pitch was spun through a circular nozzle (D=0.3mm, L/D=2) at 285°C after soaking at 330°C for 3 hour under nitrogen atmosphere with a take-up velocity of 480m<sup>2</sup>/min and a pressure of 10Kgf/cm<sup>2</sup>.

### 2.3 Stabilization, carbonization, graphitization and activation

The pitch fibers were oxidatively stabilized stepwise at a temperatures of 236°C and 312°C for 3 hours each, in a convection oven under air and followed by carbonization at 1000°C at heating rate of 5°C/min in argon atmosphere. Graphitization was performed at 2400°C for 1hour.

The carbon fibers was activated in steam (H<sub>2</sub>O/N<sub>2</sub>, 0.44molar ratio) at 900°C for a given length of time.

### 2.4 Analysis and characterization

Rheological property of the precursors for spinning was investigated by using capillary rheometer(Instron 3211). DSC and thermogravimetry(TG) were used for determination of oxygen pick-up in stabilization process.

The morphological structures of carbon fibers and graphite fibers were characterized by X-ray diffraction. The tensile properties of the single fibers were measured by Instron on the basis of

KS K 0327. The surface of isotropic carbon fibers was investigated by high resolution SEM and Atomic force microscopy(AFM).

Adsorption behaviors of activated carbon fiber(ACF) were characterized from  $N_2$  adsorption, and BET specific surface area was calculated from the results, and evaluated by using  $\alpha_s$  - method[8].

### 3. RESULTS AND DISCUSSION

#### 3.1 Fiber formation

Fig. 1 shows rheological properties of modified CP and CP at the temperature of above 30°C of each softening points. Though both of them show shear thinning behaviour, the modified pitch showed less shear thinning comparing with the CP itself. The modified pitch with increased molecular weight would be less sensitive in shear because of the increased molecular interactions.

The pitch fibers of 20 $\mu$ m could be spun at 480m/min.

In Fig. 2, stabilization behavior was resembled by using DSC under air atmosphere. An endothermic peak appears near at 187°C, representing a glass transition temperature, and the exothermic behavior becomes more significant at 187°C - 335°C, representing a active reaction of oxygen with pitch.

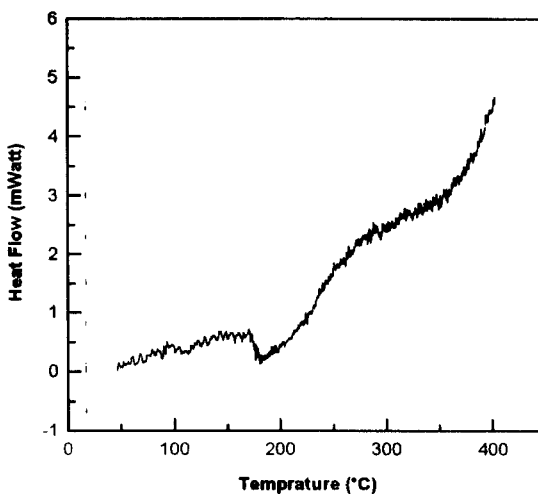
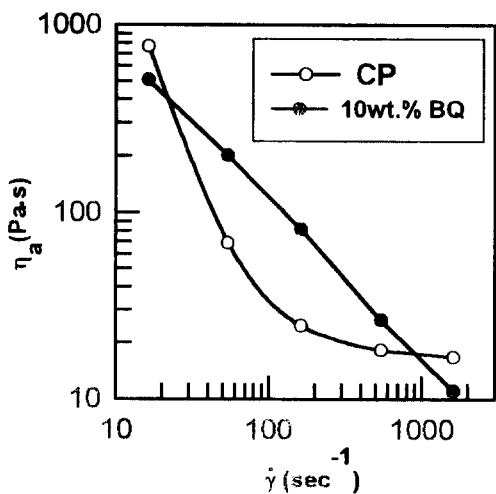


Fig.1. The relationship between  $\eta_a$  at SP+30°C and  $\dot{\gamma}$  of the samples heattreated at 380°C.

Fig.2. DSC thermoprofile of oxidation, heating rate, 5°C/min.

The stabilization and combustion behavior is also verified by the results of TGA(Fig. 3). Negligible weight gain upto 187°C, rather significant 2.6% weight gain from 187°C to 335°C, and finally weight loss representing combustion were observed. The elemental analysis data in Table 2 shows variations of oxygen content in the pitch fiber. As the stabilization time and temperature increase, the contents of oxygen in pitch fibers increase, and 13.5% oxygen content was obtained through the stabilization.

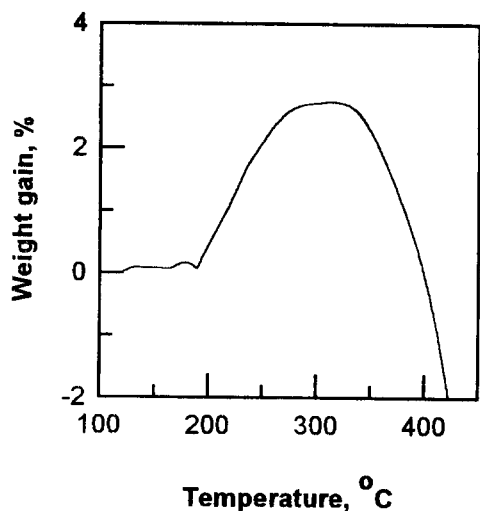


Fig.3. TGA oxidation thermoprofile, heating rate 5°C/min.

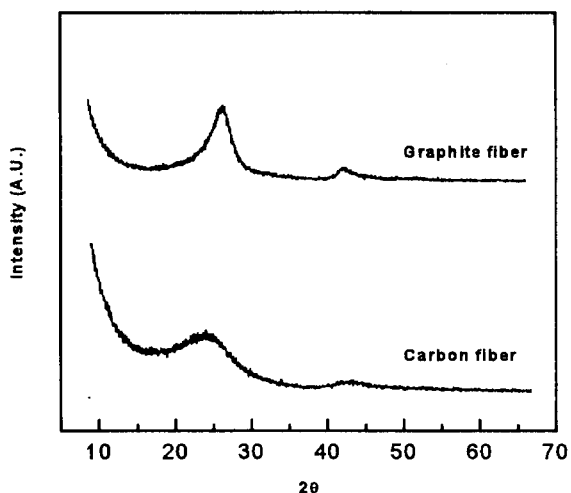


Fig.4. X-ray diffraction curves of the carbon and graphite fibers.

Table 2. Properties of carbon and graphite fiber.

	Diameter ( $\mu\text{m}$ )	$d_{(002)}$ <sup>(1)</sup> ( $\text{\AA}$ )	$L_{C(002)}$ <sup>(2)</sup> ( $\text{\AA}$ )	$DO$ <sup>(3)</sup> (%)	$TS$ <sup>(4)</sup> (MPa)	$YM$ <sup>(5)</sup> (GPa)	$UE$ <sup>(6)</sup> (%)
Carbon Fiber	17	3.86	11	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

### 3.2 Characterization

X-ray diffraction data of the fibers are shown in Fig. 4. The  $d_{(002)}$  values of carbon fiber and graphite fiber were large as 3.86 and 3.49  $\text{\AA}$ , and their  $L_{C(002)}$  value were small as 11.24 and 25  $\text{\AA}$ , respectively.

The tensile properties of the fibers are tabulated in Table 2. Their tensile strengths were equally 567 MPa, and their Young's modulus was 39.4 and 43.1 GPa, respectively, which appeared large enough as a precursor for ACF.

Isotropic carbon and graphite fiber having each diameter of 17  $\mu\text{m}$  and 15  $\mu\text{m}$  were prepared (Fig. 5). AFM microphotographs (Fig. 6) represent the isotropic carbon fiber consists of

pleat units in a irregular alignment.

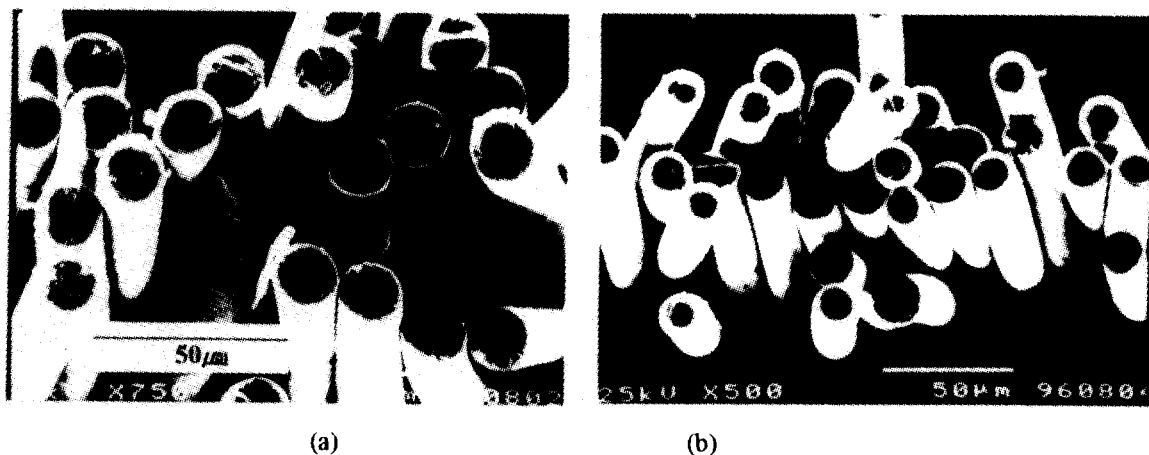


Fig.5. SEM microphotages of (a) the carbon and (b) graphite fibers.

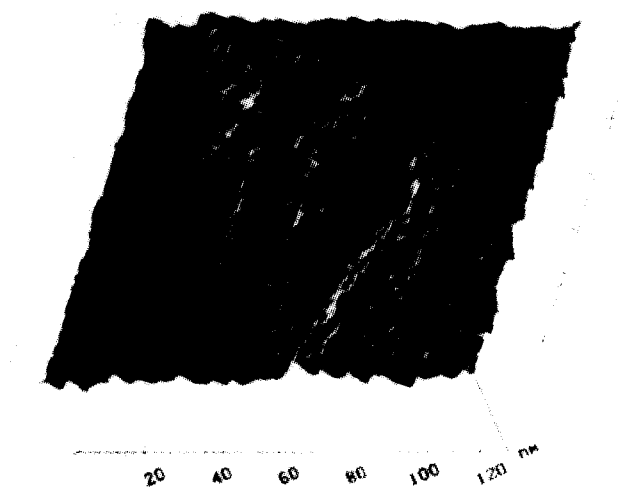


Fig.6. AFM microphotographs of the carbon and graphite fibers.

### 3.3 Activated carbon fiber

Fig. 7 shows a dependence of burn-off on activation time at 900°C. As the activation time increased upto 55minutes, the burn-off was 76%. Gas adsorption characteristics of activated carbon fiber are tabulated in Table 3. Average pore size remained almost unchanged as about 20 Å irrespective of the burn-off %. As the burn-off increased from 30 to 76%, specific surface area increased from 954 to 2062m<sup>2</sup>/g which values are more excellent than commercial ACF.

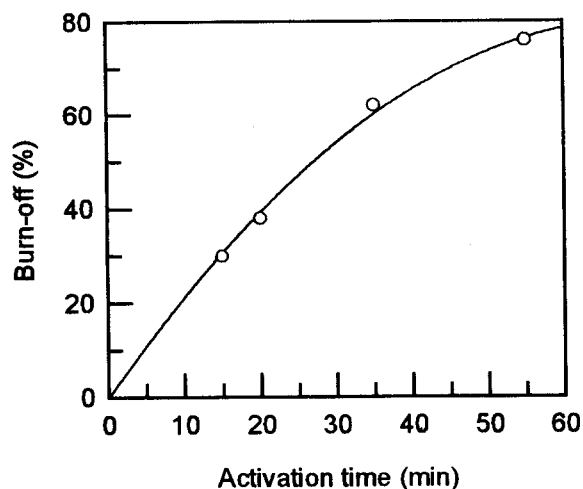


Fig. 7. Burn-off of carbon fiber with respect to activation time at 900°C, H<sub>2</sub>O/N<sub>2</sub> : 0.44.

Table 3. Gas adsorption characteristics of activated carbon fibers.

Weight loss (%)	S <sub>BET</sub> (m <sup>2</sup> /g)	Average pore dia. (Å)	Total pore volume (cm <sup>3</sup> /g)	Sext (m <sup>2</sup> /g)
0	0.2	-	-	-
30	954	18.6	0.44	9
38	976	20.4	0.50	12
62	1865	19.4	0.91	26
76	2062	21.6	1.11	39

#### 4. CONCLUSIONS

The isotropic carbon fiber and graphite fibers were obtained. Both carbonized and graphitized fibers exhibited tensile strength of 567MPa which appeared large enough as a precursor for ACF. The ACF showed a specific surface area of 2062m<sup>2</sup>/g exhibiting consistence of the pore size of about 20Å irrespective of the burn-off %.

#### 5. REFERENCE

1. E.G. Doying, *US Patent 3,256,206*, Union Carbide Corp.(1996).
2. E.M. Peters, *US Patent 3,235,323*, Minnesota Mining&Manufacturing.
3. J. Economy and R.Y. Sin, *German Patent 2,246,572*(1973).
4. R.N. Mcnair and G.N. Arons, "Sorptive Textile Systems Contaning Activated Carbon Fibers",

Carbon Adsorption Handbook, 819, Ann Arbor Science Pub., Ann Arbor, 1997.

5. K.Saito, M. Hirai, and Shimazaki, Industrial Fabrics Association International '72nd Annual Convention, Oct. 7-10(1984).
6. N. Shindo, K. Tai, and Y. Matsumura, *Chim. Eng.*, 10, 28(1987).
7. N. Shindo, K. Tai, and Y. Matsumura, *Kemkaru Enginiaringu*, 1, 28(1987).
8. Rodriguez-Reinoso, F., Martin-Martinea, J. M., Prado-Burguete, C. and McEnaney B. : *J. Physical Chemistry*, 91, 515(1987).