

# NOTE

## Conversion of Polyacrylonitrile Fibers to Activated Carbon Fibers: Effect of Preoxidation Extent

### INTRODUCTION

Due to their excellent surface properties, high adsorption capacity, and great flexibility in converting into a wide variety of textile forms, activated carbon fibers (ACFs) have attracted increasing attention.<sup>1-3</sup> Polyacrylonitrile (PAN)-based fibers has been one of the main precursors for developing ACFs. Conversion of PAN-based fibers to ACFs usually include three steps: preoxidation in air at a temperature region of 200–300°C, low-temperature carbonization (< 1000°C), and an activation treatment in an oxidizing medium. In the manufacture of carbon fibers from PAN-based fibers, the extent of preoxidation must be controlled at a certain range.<sup>4,5</sup> Over- and underoxidation would be unfavorable to the mechanical properties of carbon fibers. However, in the manufacture of activated carbon fibers, the concern is focused on the development of porosity and, thus, the surface properties of ACFs. Therefore, the requirement for the preoxidation may not be identical as in the case of carbon fibers. In this work, the effect on low-temperature carbonized fibers and activated carbon fibers of a preoxidation extent induced during the continuous thermal oxidative stabilization stage was studied. Preliminary results are reported here.

### EXPERIMENTAL

A special grade of PAN-based fiber, Courtelle fiber, containing 6000 filaments with 1.22 dtex fineness was used as the precursor fiber. The PAN fibers were preoxidized and carbonized using a continuous process. The preoxidation constituted four independent furnaces.<sup>6</sup> The extent of preoxidation of PAN fibers could be adjusted by monitoring the temperatures at each furnace. In this work, four combinations of temperatures in the preoxidation stage were chosen and are given in Table I. The preoxidized fibers thus obtained were designated as A, B, C, and D, respectively. The preoxidized fibers were then continuously carbonized by passing through a low-temperature carbonization furnace with temperature increasing from 300°C to about 900°C in argon. The processing rate was controlled at 10 m/h. The activated carbon fibers were

obtained by activating the carbonized fibers using a batch scale in a mixture of steam–argon.

Densities of preoxidized PAN fibers were measured by the density gradient column method with a mixture of *n*-heptane and carbon tetrachloride. Elemental analysis of fibers was performed with a Perkin–Elmer 240C elemental analyzer. The oxygen content was determined by the difference.

Wide-angle X-ray diffraction (WAXD) measurements were obtained by a Rigaku rotating anode X-ray diffractometer of the D/MAX- $\gamma$ A type using Ni-filtered CuK $\alpha$  radiation ( $\lambda = 0.154$  nm). The stacking height ( $L_c$ ) was calculated by the Scherrer formula.<sup>7</sup> The experiment was conducted on fiber bundle. The specific surface area of ACFs was measured by adsorption of nitrogen at 77 K with an application of the BET equation using a domestically produced ST-03 surface-area analyzer.

### RESULTS AND DISCUSSION

Results of densities and elemental analysis on preoxidized fibers are given in Table II. With increase in preoxidation temperature, fiber density shows a significant increase from sample A to D. Meanwhile, the oxygen content increases simultaneously, while hydrogen content decreases monotonically. On the other hand, the nitrogen ratio remains practically constant. These results indicate that the extent of oxidation of PAN fibers increased with increase in oxidation temperature.

Results of elemental analysis and WAXD measurement on low-temperature carbonized fibers obtained from the

**Table I** Preoxidation Temperatures

Sample Code	Temperature in Preoxidation Stage			
	1 <sup>a</sup>	2	3	4
A	215	230	250	250
B	215	230	250	270
C	215	230	250	290
D	215	230	255	300

<sup>a</sup> The furnace.

**Table II Elemental Analyses of Preoxidized Fibers**

Sample Code	Densities (g/cm <sup>3</sup> )	C (wt %)	H/C	N/C	O/C
A	1.385	59.73	0.76	0.31	0.19
B	1.429	58.94	0.71	0.31	0.21
C	1.480	57.67	0.65	0.31	0.24
D	1.502	57.45	0.61	0.31	0.25

above preoxidized fibers with different preoxidation extents are shown in Table III. Compared with the data in Table II, the carbon content markedly increases after the carbonization treatment, whereas the other elements like hydrogen, nitrogen, and oxygen decrease dramatically. It has been well studied that a series of reactions of cross-linking, aromatization, and condensation occur during the carbonization stage.<sup>8,9</sup> As a result, various gaseous products of a large amount as well as of a trace amount, such as water, carbon oxides, cyanide, ammonia, and nitrogen, were liberated and driven off the fiber. Meanwhile, the carbon basal planes were gradually formed, ordered, and thickened due to these reactions.<sup>8,9</sup> As a consequence, the noncarbon elements were tremendously ejected from the body of the fibers. The consequence was the significant decrease in content of these noncarbon elements and the marked increase in carbon content as demonstrated in Table III. In comparing the elemental analysis data among four carbonized fibers in Table III, one finds that the oxygen level shows a general trend of increase from samples A to D, which seems to correspond to that in the preoxidized fibers (Table II). Comparatively, the nitrogen content slightly increases, whereas the carbon content gradually decreases. As mentioned above, the carbonization treatment of preoxidized fibers leads to evacuation of noncarbon elements in the forms of various gases and volatiles. Thus, it may be inferred that more oxygen incorporated into the preoxidized fibers might cause more losses of small oxygen-containing molecular pieces such as water

and carbon oxides from the fiber body during the carbonization treatment. This leads to a decrease in carbon content as shown in Table III. Besides, since more volatiles were evolved in the case of higher oxygen content of preoxidized fibers, the carbonized fiber diameter would be expected to be reduced as is evidenced in Table III. Results of the WAXD measurement on the carbonized fibers are given in Table III. The influence of the preoxidation extent (or oxygen content) on the morphological structure of the carbonized fibers is not significant, probably because the difference in the preoxidation extent of the preoxidized fibers was not significant enough to cause an evident measured difference in the morphological structure of the carbonized fibers.

Compared with the surface area of carbonized fibers, which was generally negligible in the surface area measurement,<sup>10</sup> steam activation leads to a significant increase in surface area (Table III). Elemental analysis of the activated carbon fibers as shown in Table III indicates that the nitrogen level markedly decreased upon activation treatment in comparison to that of carbonized fibers. This result suggests that, during the activation, nitrogen continued to be eliminated from the fiber body. On the other hand, the level of oxygen and hydrogen was somewhat increased during the activation treatment. This simultaneous increase in oxygen and hydrogen seems to point out that there might be some oxygen-containing groups or functionalities being introduced onto the fibers with the proceeding of activation. As is accepted, the surface prop-

**Table III Elemental Analyses of Low-temperature Carbonized Fibers and Activated Carbon Fibers**

Sample Code	Low-temperature Carbonized Fibers							Activated Carbon Fibers					
	Elemental Analysis (wt %)				WAXD Measurement		Diameter (μm)	Specific Surface Area (m <sup>2</sup> /g)	Elemental Analysis (wt %)				
	C	H/C	N/C	O/C	fwhm <sup>a</sup> (Degree)	Lc (nm)			C	H/C	N/C	O/C	
A	75.37	0.21	0.17	0.081	6.6	1.37	8.36	280	74.76	0.26	0.13	0.12	
B	74.07	0.20	0.18	0.091	7.2	1.26	8.27						
C	73.36	0.21	0.19	0.097	6.9	1.31	8.14	278	75.97	0.24	0.13	0.11	
D	73.58	0.20	0.19	0.094	6.8	1.33	8.27						

<sup>a</sup> Full-width at half-maximum in the X-ray scan.

erties, such as surface area and surface chemical and microstructure, have a significant effect in determining the application of the potential of activated carbon fibers. Further works on these aspects are in progress.

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