Effects of the Oxidation Temperature on the Structure and Properties of Polyacrylonitrile-Based Activated Carbon Hollow Fiber

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ABSTRACT: Polyacrylonitrile (PAN) hollow fibers were pretreated with ammonium dibasic phosphate, oxidized in air, carbonized in nitrogen, and activated with carbon dioxide. The effects of the oxidation temperature of the PAN hollow fiber precursor on the microstructure, specific surface, pore size distribution, and adsorption properties of PAN-based activated carbon hollow fiber (PAN-ACHF) were studied. When PAN hollow fibers were oxidized at 270°C, because of drastic oxidation, chain scission occurred, and the number of pores within and on the surface of the resultant PAN-ACHF increased, but the pores were just in the thinner region of the skin of PAN-ACHF. The surface area of PAN-ACHF reached a maximum when the oxidation temperature was 270°C. The adsorption ratios to creatinine were all higher than 90% at all oxidation temperatures, and the adsorption ratio to VB_{12} reached a maximum (97%) at 230°C. The dominant pore sizes of the mesopores in PAN-ACHF ranged from 2 to 5 nm. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 203–207, 2005

Key words: oxidation; polyacrylonitrile; activated carbon hollow fiber; adsorption properties

INTRODUCTION

Activated carbon fibers have played a major role in adsorption technology over the last few years. These fibers have uniform slit-shaped micropores and great surface area. Activated carbon fibers are produced by the carbonization of raw materials such as polyacrylonitrile (PAN), cellulose, phenolic, or pitch fibers. The advantage of fibrous active carbon over finely powdered active carbon is the higher bulk volume of the former, which can lead to higher adsorption rates because of the more open base structure.[1–4] Recently, PAN-based activated carbon hollow fiber (PAN-ACHF) has attracted many investigators' interest[5–10] because PAN-ACHF shows the largest adsorption capacity among the carbon surfaces.

The thermal oxidation of PAN has attracted much interest because of its importance in carbon-fiber production. For this process, one has to choose the correct or optimum conditions of the temperature, oxidizing gas, heating rate, and oxidation duration. Some authors have tried to show why it is important to oxidize PAN fibers before carbonization.[11–13] A low-temperature treatment leads to the formation of a cyclized structure because of additional polymerization of the nitrile side group. The cyclized structure is stable toward heat and is converted to turbostratic carbon.[14]

In this research, PAN hollow fibers were dipped in an ammonium dibasic phosphate aqueous solution, oxidized at temperatures ranging from 190 to 290°C, carbonized in nitrogen, and activated with carbon dioxide. This study examined the effects of the oxidation temperature of PAN hollow fibers on the adsorption and structural properties, such as the specific surface area, pore size distribution, and morphology, of PAN-ACHF.

EXPERIMENTAL

PAN (a copolymer of acrylonitrile, methyl methacrylate, and itaconic acid) hollow fiber spun by a dry–wet spinning setup was used as the precursor. The resultant hollow fiber had an inside diameter of 400 μm and an outside diameter of 500 μm. Figure 1 shows the porous structure of the PAN hollow fiber.

Virgin PAN hollow fibers were first dipped in an ammonium dibasic phosphate aqueous solution of 4% (wt %) concentration for 30 min. Afterwards, the pretreated fibers were oxidized at different temperature for 2 h in air, carbonized at 900°C for 30 min in nitrogen, and activated at 800°C for 40 min with carbon dioxide.

A JEOL Model JSM-5600LV scanning electron microscope (Tokyo, Japan) was used to examine the cross section and external surface of the fibers.
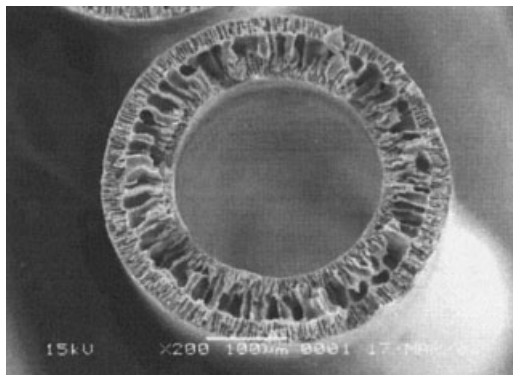
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Figure 1 Cross section of virgin PAN hollow fiber (200×).

An adsorption study of creatinine and VB_{12} was carried out by a static process. A known quantity of the activated carbon hollow fiber was immersed in a known volume of an aqueous solution at 37°C for 24 h. The amount of creatinine and VB_{12} adsorbed was determined by the difference in the concentrations before and after immersion in the solution. The creatinine and VB_{12} concentrations of the solution were determined with a Techcomp Corp. 7500 ultraviolet–visible spectrophotometer (Shanghai, China) at wavelengths of 510 and 361 nm, respectively. The absorbency of creatinine and VB_{12} in the aqueous solutions reflected the differences in the solution concentrations. Then, the adsorption ratio was calculated as follows:

Adsorption ratio (wt %)

$$= \frac{\text{Absorbency before adsorption} - \text{Absorbency after adsorption}}{\text{Absorbency before adsorption}} \times 100\%$$

Samples of PAN-based activated carbon hollow fiber (PAN-ACHF) were characterized by the measurement of the specific Brunauer–Emmett–Teller (BET) surface area and pore size distribution with a Micromeritics Tristar 3000 autoadsorption apparatus. The surface area was calculated with the multipoint BET method. The pore volume and pore size distribution were determined from the nitrogen adsorption isotherms with the Barrett–Joyner–Halenda method.[15]

RESULTS AND DISCUSSION

Surface area and adsorption properties of PAN-ACHF

When PAN hollow fibers were thermally oxidized in air, the color gradually changed uniformly to black. Chemical reactions such as dehydrogenation, oxidation, degradation, and crosslinking also took place, causing the wall of the PAN hollow fibers to contract and thus making their texture denser and their pore diameters smaller. During the oxidation stage, the molecular structure of the polymer changed from linear to cyclic, and the structure of the ladder polymer was formed.

Figure 2 shows the variation of the burn-off and shrinkage ratio of PAN-ACHF with the oxidation temperature. The weight loss and the shrinkage ratio were determined from changes in the weight and length before and after activation. As shown in Figure 2, the weight loss and shrinkage ratio of PAN-ACHF changed little as the oxidation temperature increased. The oxidation temperature had little influence on the weight loss and shrinkage of the resultant PAN-ACHF.
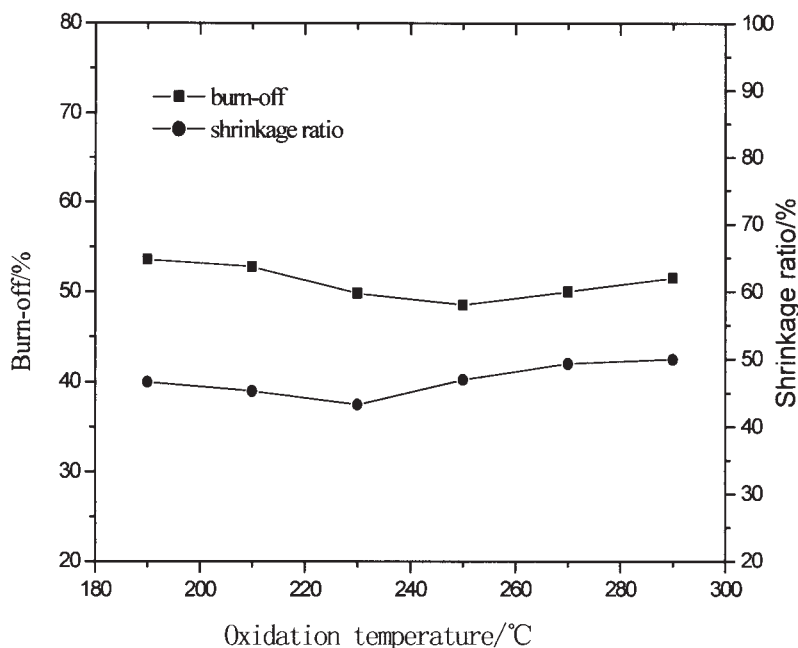

Figure 2 Burn-off and shrinkage ratio of PAN-ACHF versus the oxidation temperature (oxidation time = 2 h).
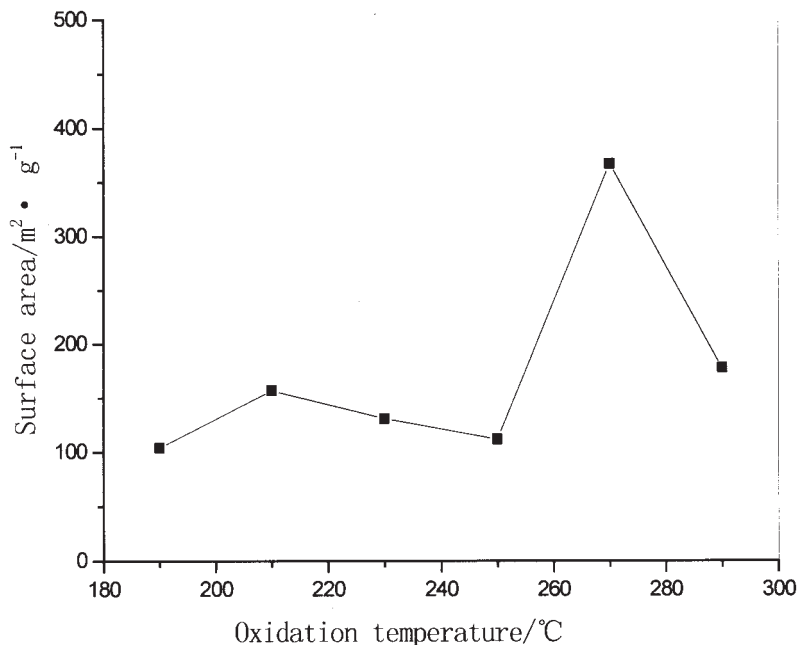
Figure 3 Specific surface area of PAN-ACHF versus the oxidation temperature (oxidation time = 2 h).

Figure 3 shows the variation of the specific surface area of PAN-ACHF with the oxidation temperature. The surface area ranged from 100 to 150 m^2/g with the oxidation temperature increasing from 190 to 250°C, reached a maximum (368 m^2/g) at 270°C, and decreased at 290°C. Because the molecular chains were not susceptible to chain scission in oxidation at low temperatures[6] and the occurrence of chain scission facilitated the formation of the pores, the surface area of PAN-ACHF made of fibers oxidized at a low tem-

perature was low. When the PAN hollow fibers were oxidized at 270°C, because of drastic oxidation, chain scission occurred, and the number of pores within and on the surface of the resultant PAN-ACHF increased.

Figure 4 shows the variation of the adsorption ratio with the oxidation temperature. The adsorption ratios to creatinine were all higher than 90% at all oxidation temperatures. The adsorption ratio to VB_{12} increased with the oxidation temperature from 190 to 230°C, reached a maximum (97%) at 230°C, and then gradu-
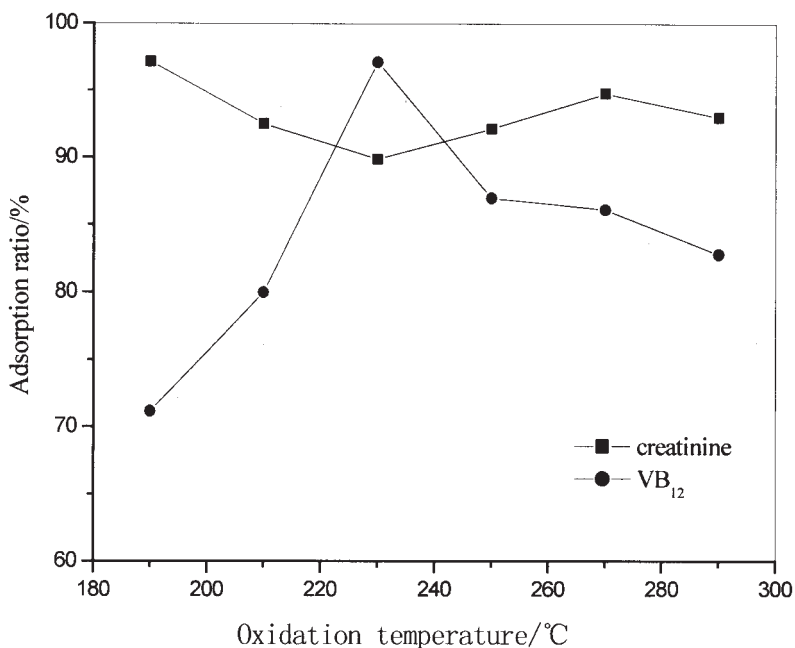

Figure 4 Adsorption ratio of PAN-ACHF versus the oxidation temperature (oxidation time = 2 h).
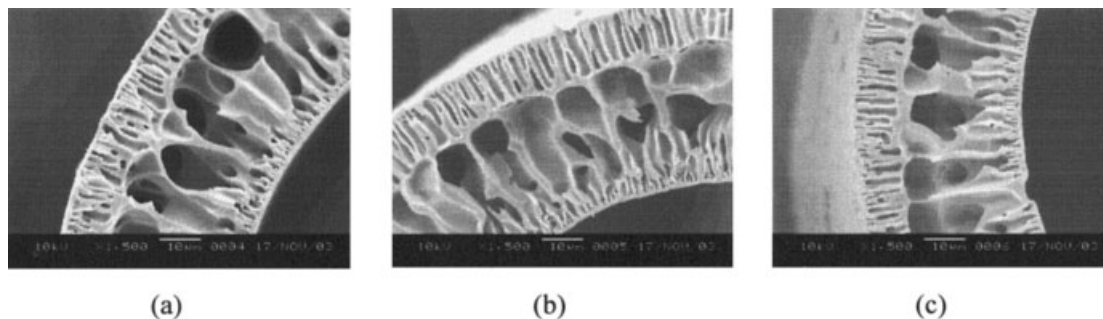
Figure 5 Scanning electron micrographs (1500×) of cross sections of PAN-ACHF at oxidation temperatures of (a) 190, (b) 230, and (c) 270°C (oxidation time = 2 h).

ally decreased as the oxidation temperature increased. According to their molecular sizes (creatinine < VB_{12}), the molecular size of creatinine is less than 2 nm, and creatinine is primarily adsorbed by micropores (<2 nm). However, the molecular size of VB_{12} is larger than 2 nm, and VB_{12} is primarily adsorbed by mesopores (2–50 nm). This indicates that there are more mesopores in PAN-ACHF made of fibers oxidized at 230°C than in PAN-ACHF made of fibers oxidized at other temperatures.

Morphology of PAN-ACHF

Figures 5 shows cross sections of PAN-ACHF made of fibers oxidized at 190, 230, and 270°C. The cross-sectional shape of the activated carbon hollow fiber in Figure 5(a–c), a difinger-like, porous structure, was preserved after oxidation. As shown in Figure 5, the thickness of the fiber wall did not change much as the oxidation temperature increased.

Figure 6 shows the external surface of PAN-ACHF made of fibers oxidized at 190, 230, and 270°C. As shown in Figure 6(a,b), there were no apparent pores on the surface of PAN-ACHF for activation temperatures of 190 and 230°C. After oxidation at 270°C, pores began to appear on the surface of PAN-ACHF, but the pores were just in the thinner region of the skin of PAN-ACHF, as shown in Figure 6(c). The pores in the

thinner region of the skin of the hollow fiber may have been activated and sintered.

Pore size distribution of PAN-ACHF

Figure 7 shows the pore size distribution of PAN-ACHF made of fibers oxidized at 190, 230, and 270°C. Because of the limits of the apparatus, pore diameters of less than 2 nm could not be tested. However, the distribution of mesopores (2–50 nm) can be observed in Figure 7. The maximum of the incremental pore volume increased with the oxidation temperature and reached 0.0078 mL/g when the oxidation temperature was 270°C. Figure 7 shows that the incremental pore volume of the mesopores gradually decreased with the average diameter, and the dominant pore sizes of the mesopores in PAN-ACHF ranged from 2 to 5 nm. Moreover, a mass of micropores existed in PAN-ACHF, and the number of macropores was much lower.

CONCLUSIONS

The oxidation temperature had little influence on the weight loss and shrinkage of resultant PAN-ACHF. When PAN hollow fibers were oxidized at 270°C, because of drastic oxidation, chain scission occurred, and the number of pores within and on the surface of the resultant PAN-ACHF increased, but the pores were just
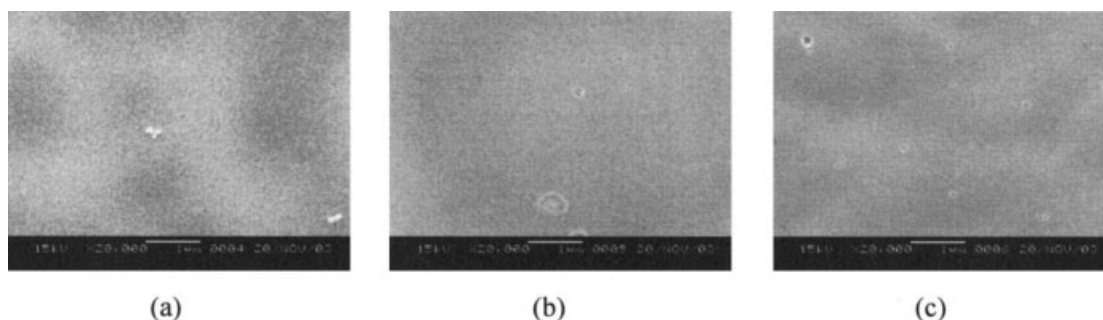

Figure 6 Scanning electron micrographs (20,000×) of the external surface of PAN-ACHF at oxidation temperatures of (a) 190, (b) 230, and (c) 270°C (oxidation time = 2 h).
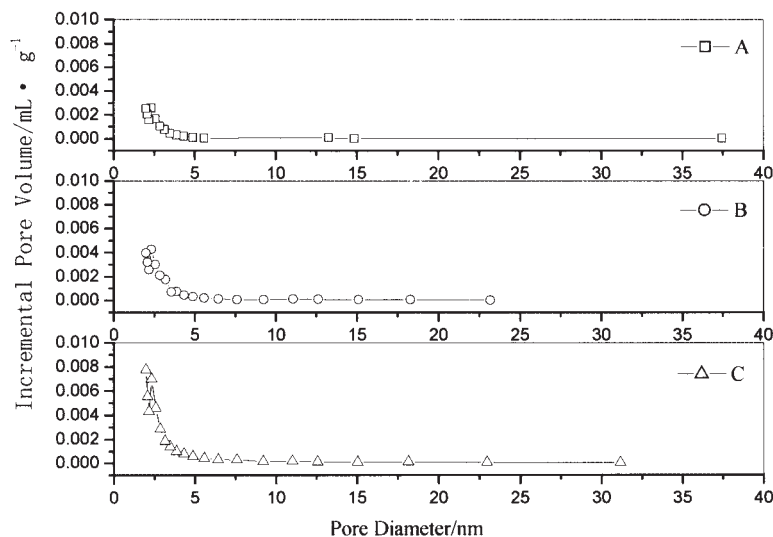
Figure 7   Pore size distribution of PAN-ACHF at oxidation temperatures of (A) 190, (B) 230, and (C) 270°C (oxidation time = 2 h).

in the thinner region of the skin of PAN-ACHF. The adsorption ratios to creatinine were all higher than 90% at all oxidation temperatures. The adsorption ratio to VB_{12} increased with the oxidation temperature from 190 to 230°C, reached a maximum (97%) at 230°C, and then gradually decreased as the oxidation temperature increased. The dominant pore sizes of the mesopores in PAN-ACHF ranged from 2 to 5 nm.

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