

The Traps in Characterisation of PAN and Carbon Fibers by the Mercury Porosimetry Method

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Abstract: The mechanical properties of a fiber relate to an average pore size or the pore size distribution in the fiber. In this study, the effects of testing sample preparation, crystallization rate, humidity, sizing agent, composition and processing conditions on the pore size distribution measurements were analyzed and discussed.

Keywords: Carbon fiber, Polyacrylonitrile fiber, Pore size distribution, Mercury porosimetry.

Introduction

Porosity is a property of solids that is due to their structure and is expressed in the presence of voids (pores) between separate grains, layers, crystals and other elements of a coarse structure of a solid. There are several methods of estimating the parameters of porosity that have been worked out for mineral sorbents and been used also for polymers. Each of them covers a definite range of pore dimensions as follows [1]:

<u>Method</u>	<u>Pore size (cm)</u>
Sorption	10^{-7} – 10^{-5}
Mercury porosimetry	10^{-7} – 10^{-3}
Electron microscopy	10^{-6} – 10^{-4}
Optical microscopy	10^{-4}
X-raying	10^{-8} – 10^{-5}

The most direct method is electron microscopy, which makes it possible to determine not only the dimensions, but also the shape of pores. It is used for studying mineral sorbents and polymers. However, a method of preparing objects have still not been worked out sufficiently well for polymer sorbents. Use is also made of the X-raying which makes it possible to determine the radii of fine pores. But the most common ones are the classical sorption method and mercury porosimetry.

If the surface nature of a fiber or filament is not well-known, the intrusion data obtained from mercury porosimetry may give an error in the information. In this paper, the porosity of the fibers is discussed by the

mercury method in detail, which gives an aid for correctly using porosity data to confirm the other fiber properties. For example, the tensile strength of carbon fiber is also affected by the pore size [2-4].

Experimental

The acrylonitrile-vinylidene chloride copolymer as modacrylic was copolymerized by the suspension method with redox catalysts, such as sodium hydrogen sulfite, ammonium persulfate and ferrous sulfate, at 25 °C under a nitrogen gas. The slurry of the polymer was filtered by centrifuge to form the polymeric powder, simultaneously the polymeric powder was washed several times by water, then dried in a vacuum oven at 100 °C. The dried polymer powder was dissolved in N,N-dimethylacetamide (DMAC), and the dope with 24 % of polymer content was spun in a coagulation bath to form modacrylic fiber.

The polyacrylonitrile (PAN) copolymers with different comonomers, such as methyl acrylate (MA), ethyl acrylate (EA), 2-ethyl hexyl acrylate (2-EHA) and itaconic acid (IA), were polymerized in the mixed solvent of acetone and dimethyl sulfoxide (DMSO) at 60 °C with α , α -azobis (isobutyronitrile) as initiator under an inert atmosphere of nitrogen. The resulting polymerization solution was directly spun through a 10 % DMSO coagulation bath at 5 °C to form PAN precursor fiber, which was stretched in boiling water and dried at 120 °C in hot air. PAN precursor was stabilized at 250 °C for 30 min, then stabilized again at 270 °C for 1 hr in air, under 0.15 g/d tension. The

oxidized PAN fiber was carbonized to 1200 °C under a high-purity nitrogen atmosphere. The carbon fibers were treated by a sizing agent (epoxy) after the carbonization, then dried at 80 °C in air. The activated carbon fiber used in this study is a commercial product made in Japan.

The pore size of various fibers was measured using a Micromeritics Autopore II 9220 with a pressure from 0 to 413.5 MPa. The fibers used to measure the pore size distribution were cut into small pieces for discussing the factor of the testing sample weight. The lighter the sample weight, the shorter the fiber length. An optical microscope, Zeiss MC63, was used to observe the surfaces of fibers. X-ray data were determined by a Scintage DMS 2000 X-ray diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation. The crystallite size (L_c) was calculated from the following equation:

$$L_c = K \lambda / (B \cos \theta)$$

where λ is the wavelength of $\text{CuK}\alpha$ X-ray; B is the width at half-maximum intensity of the peak at $2\theta = 17^\circ$ for modacrylic fiber; and K is 0.89 (a constant). The crystallinity index for modacrylic fiber was measured by Bell's method [5].

Results and Discussion

The rate of the crystallization during wet-spinning for modacrylic fiber can be controlled by the temperature and solvent concentration of a coagulation bath. The fiber spun with a lower coagulation rate exhibits a higher crystal size and degree of crystallinity (or crystallinity index) [6], as shown in Table I, but these fibers are stuck together, as shown in Figure 1. From Figure 2, it can be seen that the fibers stuck

together have a distribution of the larger pores than 6 μm of diameter, due to these larger pores with vacant spaces among the sticking fibers. Since these larger pores are not true pores in and on the fiber, incorrect data will be obtained, as shown in Table II. Generally, the fiber with a higher crystal size and crystallinity index has a small pore distribution such as the pore distribution of smaller than 6 mm in Figure 2. The water content also affects the distribution of pore size for modacrylic fiber, as shown in Figure 3. When the fibers adsorb a higher water content, the fibers tend to stick together, and have the distribution of the pore size involving pores (no true pores) larger than 6 mm in diameter, but the number of the pores smaller than 6 μm is considerably decreased due to the water molecules intrusion in the pores.

The distribution curve of the pore size for carbon fiber is affected by the weight of the sample tested, as shown in Figure 4. The larger the weight, the smaller the pore size for the distribution. This is because after the fibers are cut into small pieces for a lower weight of the sample, some closed pores inside the fiber, not intruded by mercury previously, become opened pores, which can be intruded by mercury.

The distribution of the pore size for carbon fiber is affected by the treatment of the epoxy sizing agent, as shown in Figure 5. If the fibers are treated with a

Table I. Crystal size and crystallinity index of modacrylic fibers

Sample	2θ (deg)	Crystal Size (nm)	Crystallinity Index
PNDC1	16.45	4.33	0.49
PNDC2	16.76	3.65	0.40
PNDC3	16.85	3.46	0.36

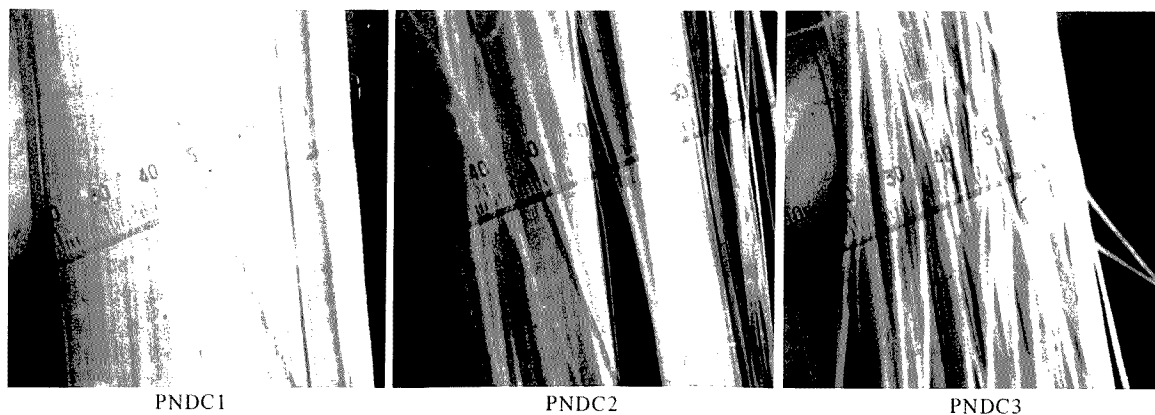


Figure 1. The optical photographs of modacrylic fiber strand ($\times 20$).

low content of epoxy sizing (1.4 %), the surfaces of the fibers are stuck together. Therefore, the distribution of the pore size exhibits the pores (no true pores) larger than 6 μm, but the amount of the pores smaller than 6 μm also decreases.

From Figure 6, it can be seen that the polyacry-

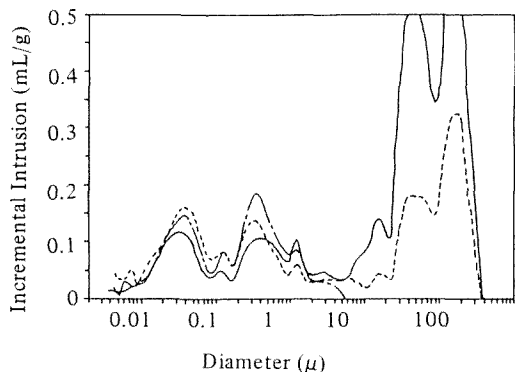


Figure 2. The distribution of the pore diameter for modacrylic fibers; sample PNDC1 (—), sample PNDC2 (---), sample PNDC3 (—·—).

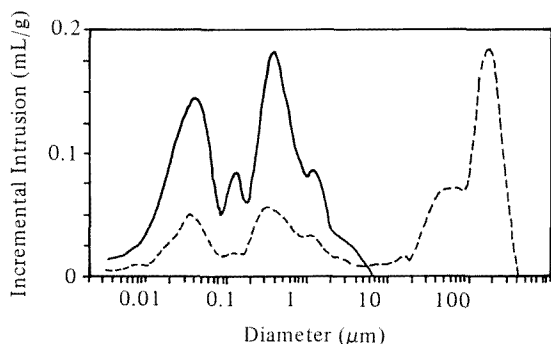


Figure 3. The distribution of the pore diameter for modacrylic fibers; dried sample PNDC3 (—), sample PNDC3 with a higher water content (---).

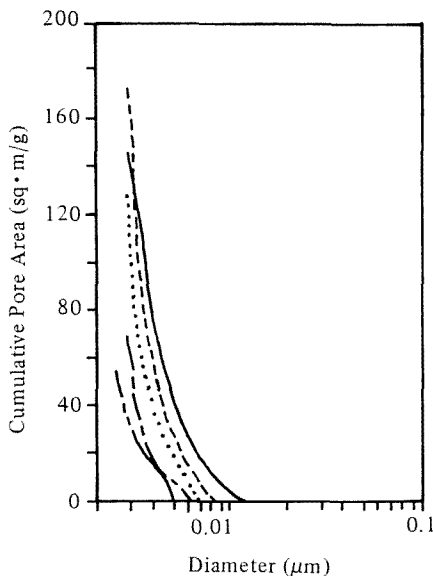


Figure 4. The cumulative pore area of carbon fibers; sample weight: 0.02 g (—), 0.05 g (---), 0.08 g (—·—), 0.11 g (— · — · —), 0.2 g (— · — · —).

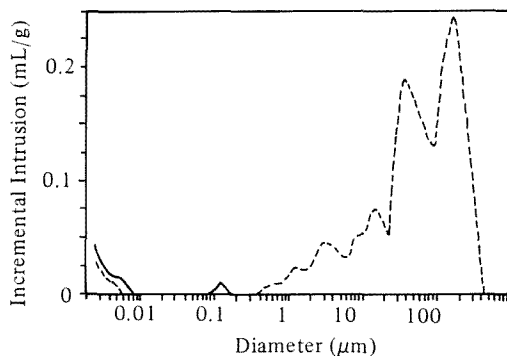


Figure 5. the distribution of the pore diameter for carbon fibers; with no sizing agent (—), with 1.4 % of epoxy sizing agent (---).

Table II. Pore data for modacrylic fibers

Sample	Total Intrusion Volume (ml/g)	Total Pore Area (sq·m/g)	Median Pore Diameter ^(a) (μm)	Median Pore Diameter ^(b) (μm)	Average Pore Diameter ^(c) (μm)
PNDC1	4.46	100.7	44.0	0.0081	0.1772
PNDC2	2.72	164.5	9.17	0.0074	0.0061
PNDC3	1.33	146.2	0.28	0.0061	0.362

(a) Calculated by volume (V)

(b) Calculated by area (A)

(c) Calculated by (4V/A)

lonitrile fiber with a larger side chain of the comonomer has a higher amount of larger pore between 0.01 and 6 μm . These pores are surrounded by an amorphous phase [2]. This is because the comonomer exists in the amorphous region, and a larger side chain of the comonomer has the larger free volume. The density of carbon fiber gradually increases with the increase of carbonization temperature, because the polyacrylonitrile fiber evolves from a linear polymer into a layered graphite structure after carbonization. Thus, after carbonized to carbon fiber from PAN fiber, the size and amount of the pore for carbon fiber is considerably decreased due to the increase of the density, as shown in Figure 7.

The mat of a commercial activated carbon fiber does not exhibit any pores smaller than 3 μm in diameter, as shown in Figure 8. This is because the activated carbon fiber has some closed pores [7], which can not be detected by the mercury porosimetry.

From the above results, one must carefully use the mercury porosimetry for the fiber, especially if the pore size is larger than 6 μm , which may not be true pores.

Conclusion

The weight of the testing sample for carbon fiber has an effect on the distribution of the pore size. The larger the weight of testing sample, the smaller the distribution of larger pore sizes is. After the treatment of fiber strand, such as sizing agent, water content,

coagulation rate, the sticking together of fiber strand produces a distribution of the pores over 6 mm, which are not the pores inside the fiber, but are the voids among the surfaces of the filaments. In addition, an increase in the amount of sizing agent and water content results in a decrease in the amount of the distribution of pore size. The PAN fiber with a larger side chain of comonomer exhibits the distribution of the larger pore size in the amorphous phase.

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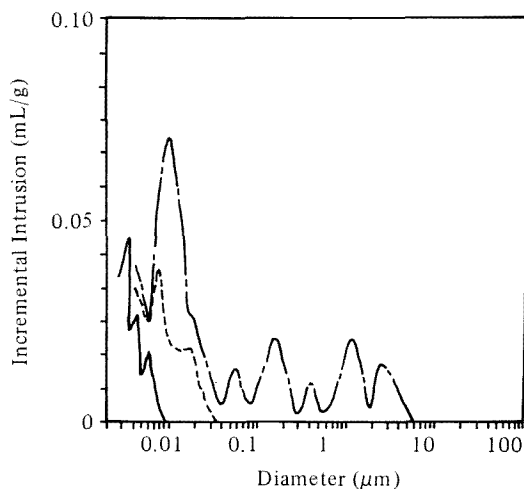


Figure 7. The distribution of the pore diameter for carbon fibers; 3.5 mol % of MA comonomer (—), 3.5 mol % of EA comonomer (---), 3.5 mol % of 2-EHA comonomer (—·—).

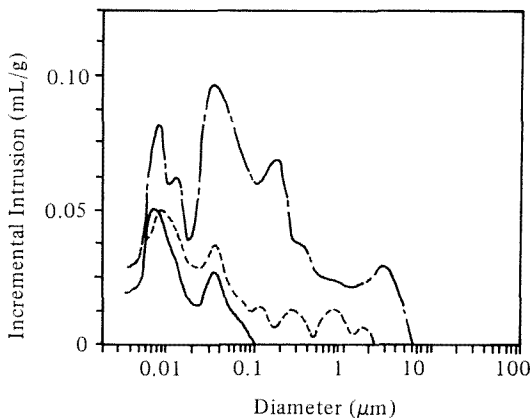


Figure 6. The distribution of the pore diameter for polyacrylonitrile fibers; 3.5 mol % of MA comonomer (—), 3.5 mol % of EA comonomer (---), 3.5 mol % of 2-EHA comonomer (—·—).

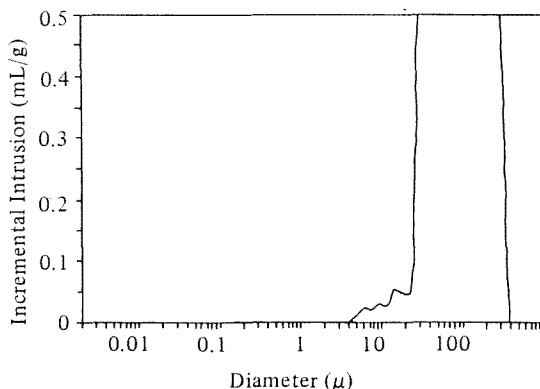


Figure 8. The distribution of the pore diameter for activated carbon fiber.

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