Microporous Polypropylene Hollow Fibers with Double Layers

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SYNOPSIS

Microporous polypropylene hollow fibers with double layers were prepared by stretching double-layered polypropylene microtubes containing polymethylsilsesquioxane fillers: the relatively smaller filler in the inner layer and relatively larger filler in the outer layer. The resultant hollow fibers have a finely interconnected fibrous structure parallel to fiber axis. Their N_2 gas permeabilities were measured to estimate the fibrous structure: tortuosity factor, effective porosity, and pore size. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Many investigators have studied microporous hollow fibers as key materials for separation technologies.[1-3] We have already reported on microporous polypropylene (PP) sheets, prepared by biaxially stretching PP sheets containing fillers such as $CaCO_3$, SiO_2, and polymethylsilsesquioxane (PMSO). These sheets have a layered structure and the pore shapes in the surfaces are rounded by adjusting the balance of the stretching degrees in machine and transverse directions.[4-6] Furthermore, we recently extended this stretching process to prepare microporous PP hollow fibers, which were single layer,[7,8] namely, microporous PP hollow fibers were prepared by monoaxially stretching PP microtubes containing $CaCO_3$ and PMSO fillers.

These microporous PP hollow fibers have an interconnected fibrous structure parallel to the fiber axis and the pores in the surface are long, elliptical, and parallel to the fiber axis. On the other hand, hollow fibers generally have a thin and very fine porous layer on their surfaces—a skin layer, in other words—in order to endow the hollow fibers with a preferable balance of separability and permeability. In the cases of the microporous PP hollow fibers,[7,8] the microporous structure and the permeability are controllable by adjusting the content and size of the filler and the stretching degree. However, there is a limit to obtaining the preferable balance of permeability and separability. It is noteworthy that the stretching process described above is one of the simplest processes to prepare microporous hollow fiber. Accordingly, we tried to prepare microporous PP hollow fibers with double layers (an inner layer with a relatively smaller pore and an outer layer with a relatively larger pore) in order to get rid of the limit. This article is concerned with the preparation of the microporous PP hollow fibers with double layers and their characterization.

EXPERIMENTAL

Materials

The PP powder used was PN-120 (MFI, 1.2) from Tokuyama Corp. The PMSO fillers were Trefil R-923 (0.5 μm^{ϕ}) and R-930 (1.0 μm^{ϕ}) from Dow Corning Toray Silicon Co. and Tospal 120 (1.6 μm^{ϕ}) from Toshiba Silicone Co. Polybutadiene GI-1000 from Nippon Soda Co. (polymerization degree, 1000) and a surfactant, Elegan 2000 (R_2CHSO_3Na, R : C_{10}–C_{20}), from Nippon Oil & Fat Co. were used as additives. The antioxidant used was 2,6-di-*t*-butyl-4-methylphenol of commercial grade.

Preparation of Microporous PP Hollow Fibers

The PP powder (*A*, 35 wt %), the PMSO filler (*B*, 65 wt %), polybutadiene (2 wt % for *A* + *B*), the

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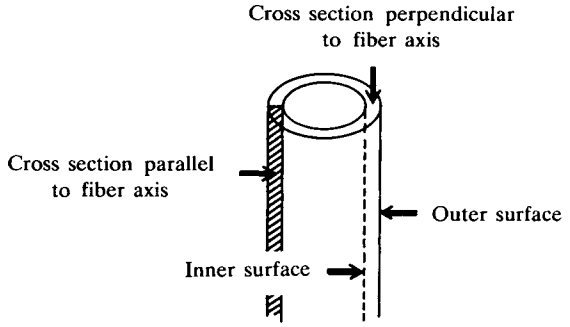

Figure 1 Sampling for scanning electron microscopy.

surfactant (5 wt % for $A + B$), and the antioxidant (1.3 wt % for A) were well mixed in advance, and then extruded at 230°C to prepare the pellets. PP microtubes were prepared by extruding the pellets at 230°C and the resultant PP microtubes were stretched at 120°C with the aid of a pair of Nelson rolls (stretching degree, ×5) to prepare microporous PP hollow fibers. Here, the extrusion was carried out through a double-layered nozzle by using a pair of extruders. The microtubular N_2 gas feeder was set at the center of the nozzle. The thickness ratio of the inner layer/outer layer was controlled by adjusting the extruding speeds of the extruders. The filler of 0.5 μm^{ϕ} was used for the inner layer and the other fillers were used for the outer layer.

Measurement

Scanning Electron Microscopy

The structure of the microporous PP hollow fibers was observed with the aid of a scanning electron microscope, JSM-220, from JEOL Ltd. The accelerated voltage and the probe current were 15 kV and 5 mA, respectively. Pretreatment of each sample was carried out with gold ion sputtering for 3 min at 1.2 kV and 8–10 mA. The sample was observed from various directions, as shown in Figure 1.

Porosity

Porosity was measured with the aid of a Hg porosimeter, Poresizer 9310, from Shimadzu Corp.

Maximum Pore Size (D_{max})

Microporous PP hollow fiber was dipped in methanol and N_2 gas was fed into the hollow fiber. N_2 gas pressure was increased at the rate of 1 kg/cm^2 per min. When three continuous bubbles were generated through the sample, N_2 gas pressure (Pj) was measured. D_{max} was estimated by the following equation (ASTM F-316):

$$D_{max}\ (\mu m) = 0.9388 \cdot Pj^{-1} \qquad (1)$$

N_2 Gas Permeability

The apparatus used was the same as that shown in the previous article.[9] N_2 gas was supplied into the module through a pressure regulator (accuracy, 0.02 kg/cm^2). The volume flow rate of N_2 gas flux (Q) was measured at 20°C under a definite pressure with the aid of a digital flowmeter, Model 2500 SS, from Sogo Rikagaku Industry Co. The effective surface area of the hollow fibers was 30 cm^2.

Table I Dimensions of Microporous PP Hollow Fibers

No.	Outside Diameter[a] (μm)	Inside Diameter (μm)	Thickness[a] (μm)	Thickness Ratio of Inner Layer/Outer Layer
S	362 ± 30	230 ± 20	66	10/0
A-1	394 ± 30	241 ± 20	77	7/3
A-2	394 ± 30	266 ± 20	64	5/5
A-3	386 ± 30	213 ± 20	87	3/7
A-4	418 ± 30	249 ± 20	85	0/10
B-1	378 ± 30	201 ± 20	89	7/3
B-2	442 ± 30	241 ± 20	101	5/5
B-3	447 ± 30	249 ± 20	99	3/7
B-4	418 ± 30	249 ± 20	85	0/10

Filler size was 0.5 μm^{ϕ} in the case of No. S and the inner layer of all the others. Filler sizes in the outer layers were 1.0 and 1.6 μm^{ϕ} in the cases of Nos. A-1–A-4 and B-1–B-4, respectively.

[a] Determined with the aid of scanning electron micrographs showing the cross section of microporous PP hollow fibers.

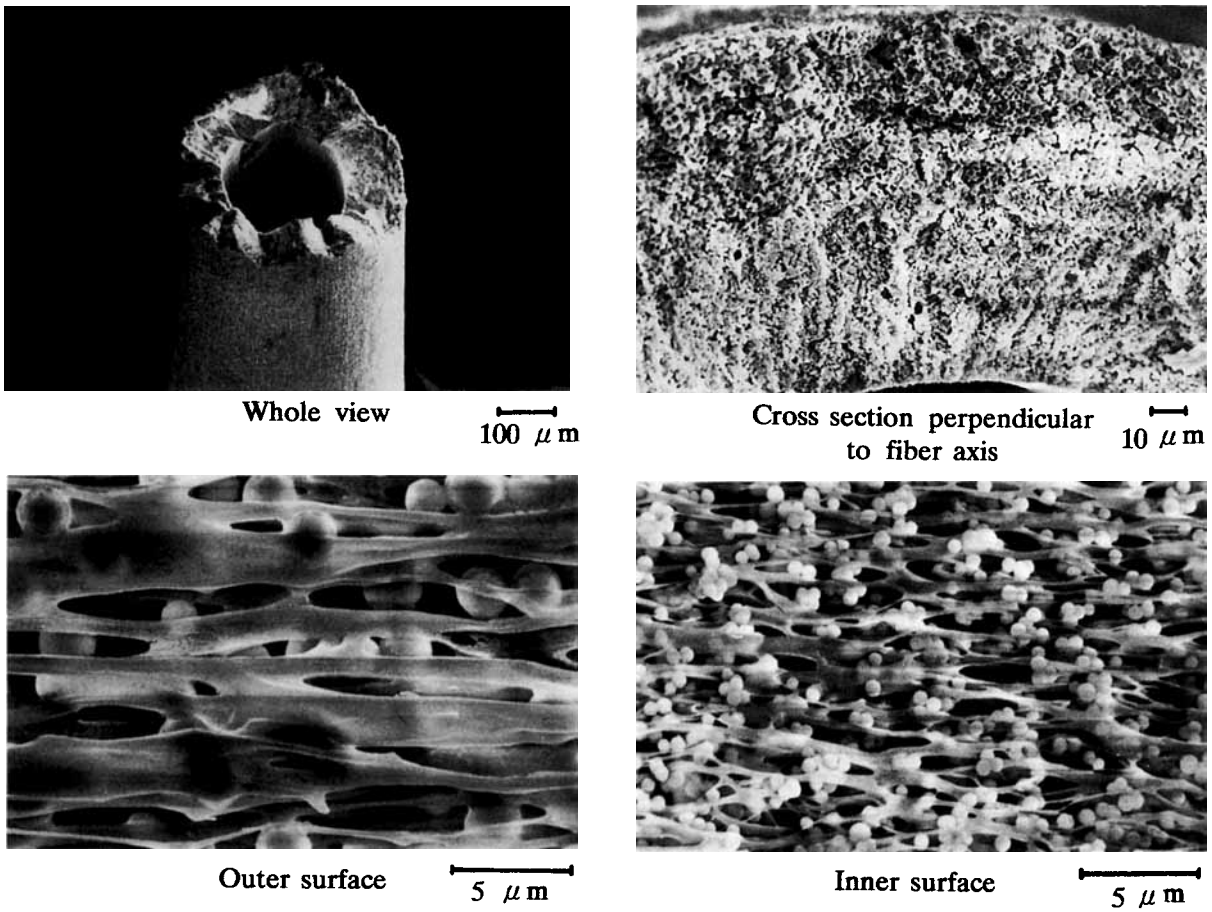

Figure 2 Scanning electron micrographs of a microporous PP hollow fiber: whole view, cross sections perpendicular and parallel to fiber axis, and inner and outer surfaces.

Determination of Pore Structure

To study the pore structure of the microporous PP hollow fibers, gas permeability was measured by a standard method: Yasuda and Tsai[9] and Cabasso et al.[10] studied gas permeation through various Millipore filters and a polysulfone membrane, respectively, and derived following equations:

$$J = QA^{-1} = K\Delta Pl^{-1} \tag{2}$$

where J is the gas flux (cm^3/cm^2 s); Q, the volume flow rate of N_2 gas (cm^3/s); A, the effective surface area of the sample (30 cm^2); K, the permeability coefficient (cm^2/s); ΔP, the pressure difference across the sample (kg/cm^2); and l, the thickness of a sample (cm).

The permeability coefficient (K) of a microporous hollow fiber can be shown as follows:

$$K = K_0 + B_0\eta^{-1}\bar{P} \tag{3}$$

where K_0 is the Knudsen permeability coefficient (cm^2/s); B_0, the geometric factor of the sample (cm^2); $\bar{P}$, the mean pressure (kg/cm^2), and η, the viscosity of N_2 gas (1.75×10^{-4} dyne s/cm^2 at 20°C). K_0 and B_0 can be estimated from the plot of K to $\bar{P}$.

The porosity of the hollow fiber (ε) and the tortuosity factor of the pore (q) can be related to K_0 and B_0 as follows:

$$K_0 = (4/3)(\delta/k_1)(\bar{v}/q^2)\varepsilon m \tag{4}$$

$$B_0 = (m^2/k)(\varepsilon/q^2) \tag{5}$$

where δ/k_1 and k are constants (0.8 and 2.5, respectively) as estimated by Carman,[11] and m, the equivalent pore size.

The average molecular velocity of a gas ($\bar{v}$; molecular weight, M) is shown as follows:

$$\bar{v} = (8RT/\pi M)^{0.5} \tag{6}$$

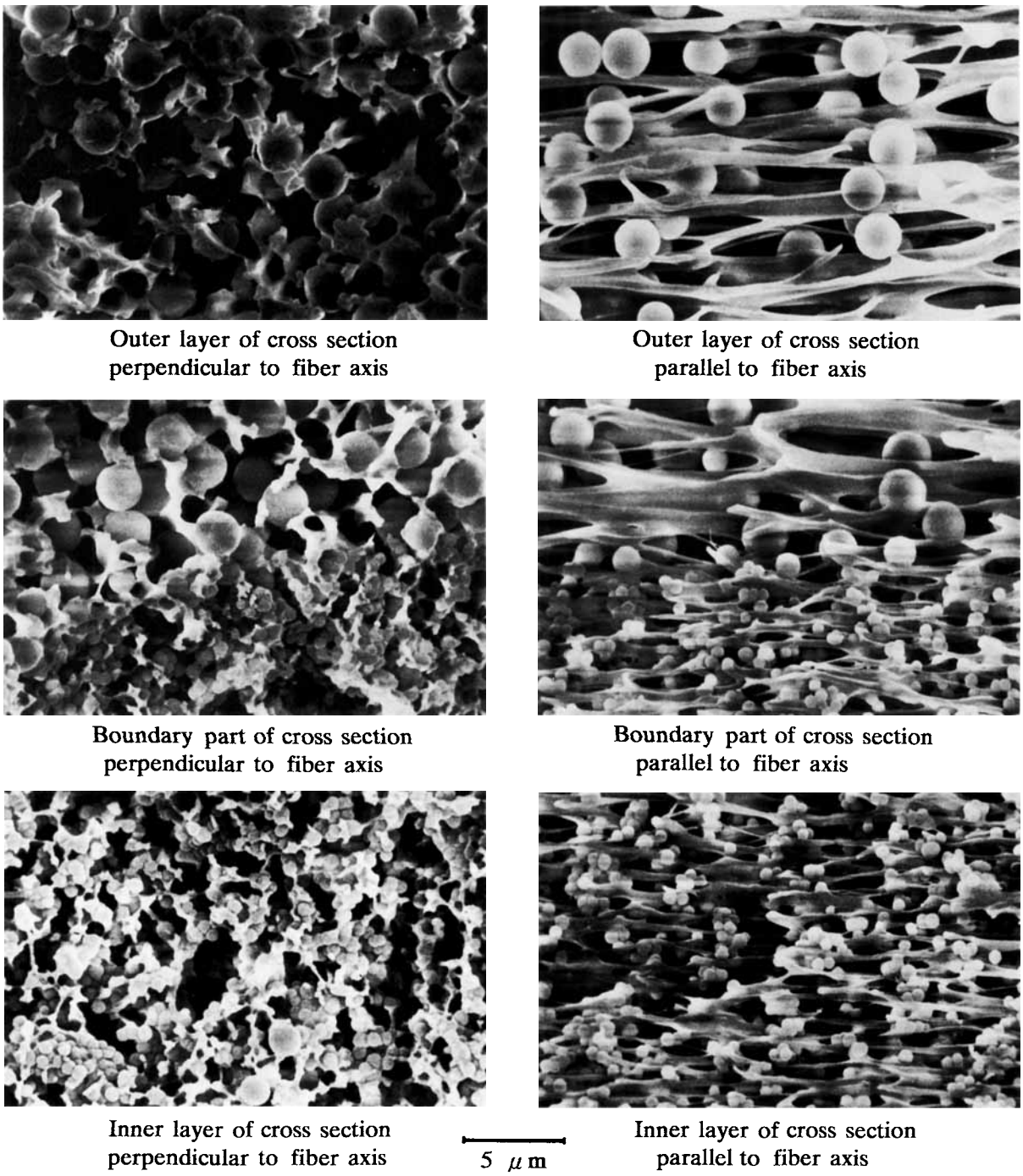

Figure 2 *(Continued from the previous page)*

The equivalent pore size (m) can be calculated by combining eqs. (4)–(6):

$$m = (16/3)(B_0/K_0)(2RT/\pi M)^{0.5} \quad (7)$$

Thus, eq. (8) can be derived for measurement with N_2 gas at 20°C:

$$m = 1.256 \times 10^5 (B_0/K_0) \quad (8)$$

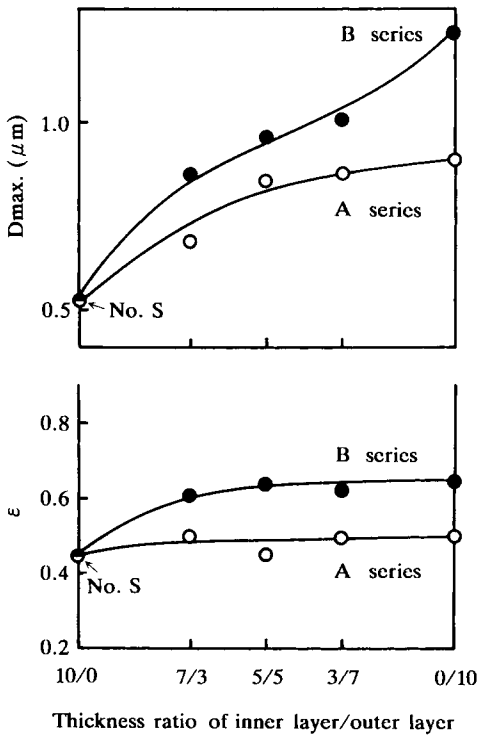

Figure 3 Dependency of maximum pore size (D_{max}) and porosity (ε) on thickness ratio of inner layer/outer layer.

Furthermore, the following equations are derived from eqs. (4)–(6) to estimate the effective porosity (ε/q^2) and the tortuosity factor of pore (q):

$$\varepsilon/q^2 = 2.5B_0/m^2 \tag{9}$$

$$q = 0.63m(\varepsilon/B_0)^{0.5} \tag{10}$$

RESULTS AND DISCUSSION

Properties of Microporous PP Hollow Fibers

Preliminarily, we checked the composition of the hollow fibers to determine which is preferable: the hollow fiber having an inner layer with a relatively smaller pore and an outer layer with a relatively larger pore, or the opposite case. It was confirmed that the former is preferable from the estimation of the water permeability by using tap water containing some suspended materials.

Table I shows the dimensions and compositions of the microporous PP hollow fibers. The thickness fluctuates to some extent, but it is noteworthy that the decrease of the thickness ratio makes the inner layer thinner.

Figure 2 shows scanning electron micrographs of a microporous PP hollow fiber, which show an interconnected fibrous structure parallel to the fiber axis. The fibrous structure of the inner layer, containing a relatively smaller filler, is finer than that of the outer layer containing a relatively larger filler. The cross sections perpendicular and parallel to the fiber axis show the boundary of the inner and outer layers.

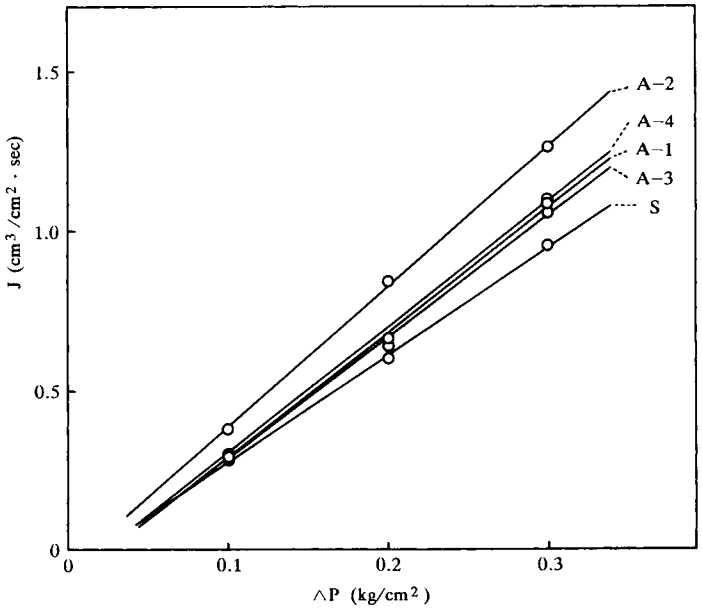

Figure 4 Relation between N_2 gas flux (J) and pressure difference (ΔP).

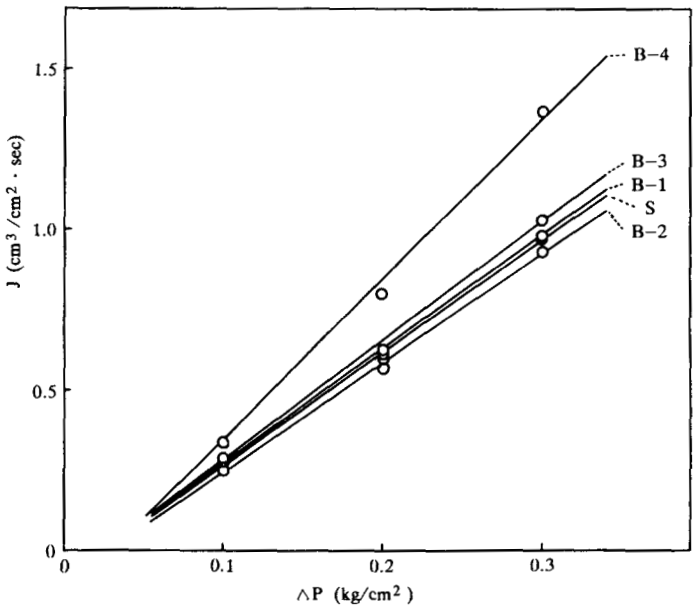

Figure 5 Relation between N_2 gas flux (J) and pressure difference (ΔP).

Figure 3 shows the dependency of D_{max} and porosity on the thickness ratio of the inner layer/outer layer. Evidently, the smaller the thickness ratio, the larger the D_{max}. It is considered that D_{max} should be regulated by the relatively finer texture of the inner layer. Then, the obtained tendencies are inexplicable, but it is presumed that the pore structure of the inner layer might be affected by the formation of

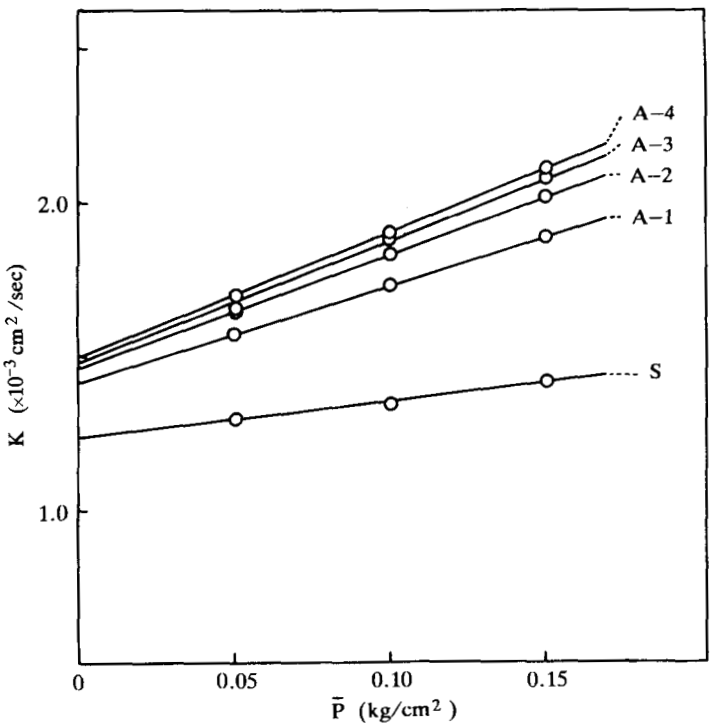

Figure 6 Relation between permeability coefficient (K) and mean pressure ($\bar{P}$).

the pore structure of the outer layer containing relatively larger filler particles. Also, it is interesting that the porosities of Nos. A-1–3 and B-1–3 are about same as those of Nos. A-4 and B-4, respectively, and a little larger than that of No. S. The porosities of the B-series are larger than those of the A-series. Therefore, the porosity of the double-layered hollow fibers seems to be regulated by the size of the relatively larger filler particles, and it probably relates to the tendencies of D_{max} described above. However, the details are obscure.

Figures 4 and 5 show the relations between the N_2 gas flux and the pressure difference. Linear relations are obtained, but there are no definite tendencies in relation to the thickness ratio of the inner layer/outer layer. It comes from the difference in the thickness of the microporous PP hollow fibers. Permeability coefficients can be obtained from the slopes of the linear lines.

Figures 6 and 7 show the relationships between the permeability coefficient and the mean pressure. Linear relationships are obtained. The Knudsen permeability coefficient and B_0/η are estimated from the intercept of the linear line on the vertical axis and its slope, respectively. Here, definite trends of the Knudsen permeability coefficient and the geometric factor are obtained in relation to the thickness ratio of the inner layer/outer layer: The decrease in the thickness ratio, i.e., the decrease in the thickness of the inner layer, causes increases both of the Knudsen permeability coefficient and the geometric factor, but the former increase is slight, as shown in Figure 8. These results mean that N_2 gas permeation is regulated by the inner layer with a relatively finer structure. Also, both values of the B-series are larger than those of the A-series, when the thickness ratio is the same. This means that the particle size of the filler in the outer layer affects N_2 gas permeation through the microporous PP hollow fibers with a double layer.

Figure 9 shows the estimated values of the pore size, effective porosity, and tortuosity factor in re-

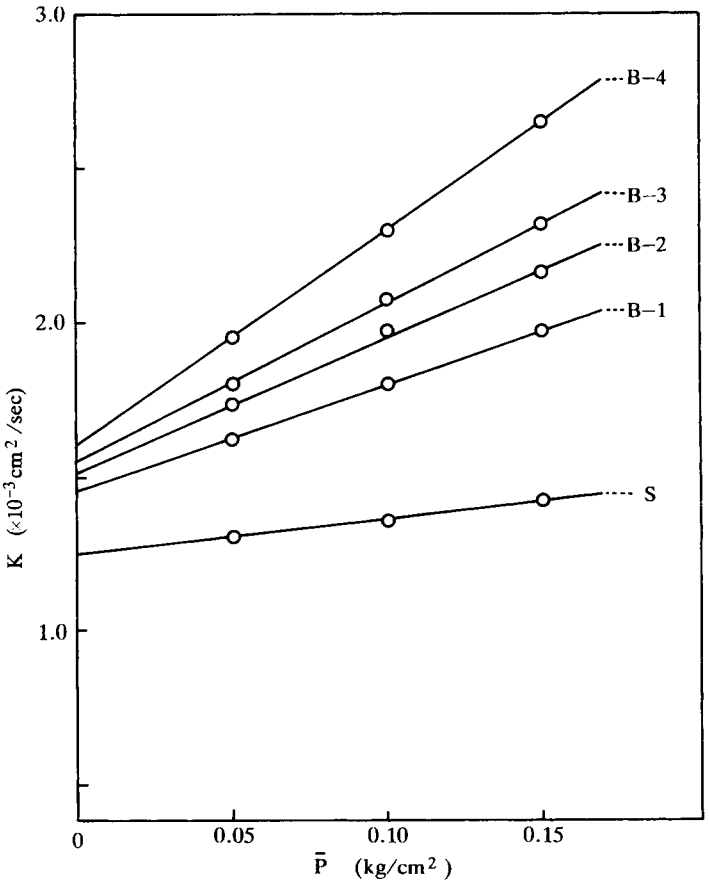

Figure 7 Relation between permeability coefficient (K) and mean pressure ($\bar{P}$).

lation to the thickness ratio of the inner layer/outer layer. With decreasing thickness ratio, the tortuosity factor and the pore size increase and the effective porosity contrarily decreases. Their orders of the hollow fibers with a single layer are as follows:

Pore size: No. B-4 > No. A-4 > No. S
Effective porosity: No. S > No. A-4 > No. B-4
Tortuosity factor: No. B-4 > No. A-4 > No. S.

The obtained tendencies are understandable as follows: Here, the filler contents are taken to be the same. Thus, when the particle size of filler is relatively smaller, the particle number of the filler becomes relatively larger. This means that stretching microtubes containing the smaller filler particles result in many more splitting points of the PP phase at the peripheries of the filler particles. Accordingly, the resultant fibrous texture of the hollow fiber becomes relatively finer; namely, when the particle size of the filler used is relatively smaller, the microporous PP hollow fiber contains relatively finer and

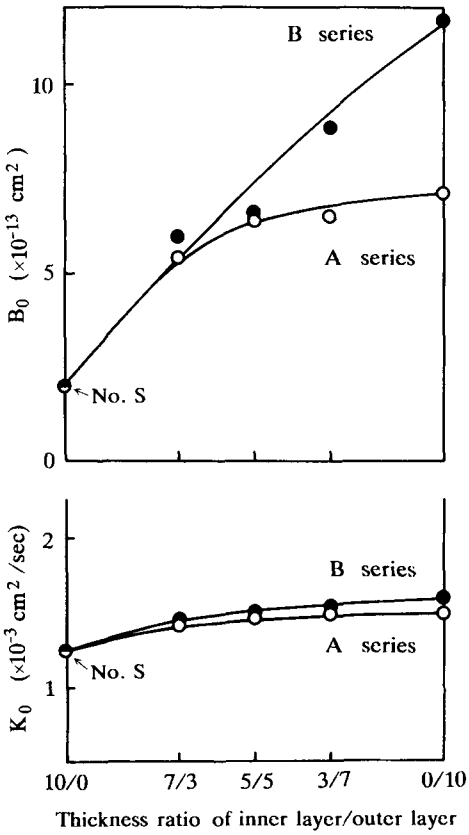

Figure 8 Knudsen permeability coefficient (K_0) and geometric factor (B_0) in relation to thickness ratio of inner layer/outer layer.

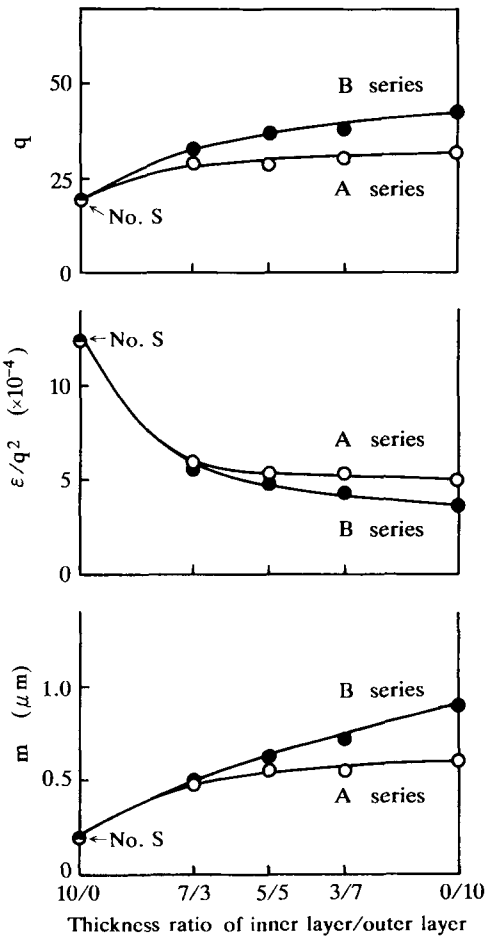

Figure 9 Pore size (m), effective porosity (ε/q^2), and tortuosity factor (q) in relation to thickness ratio of inner layer/outer layer.

less tortuous pores and, as a result, the effective porosity becomes relatively larger.

Then, in cases of the hollow fibers with double layers, the effect of the particle size of the filler used in the outer layer is elucidated: When the relatively larger filler is used in the outer layer (B-series), the hollow fibers have a larger pore size, a larger tortuosity factor, and a smaller effective porosity than those of the A-series at the same thickness ratio. However, details should be elucidated further.

CONCLUSION

Microporous PP hollow fibers with double layers were prepared by stretching double-layered microtubes: the inner layer with a relatively finer fibrous

texture and the outer layer with a relatively coarser fibrous texture. N_2 gas permeability was studied to elucidate the microporous structure in relation to the particle sizes of fillers. The smaller the particle size of the filler, the finer and less tortuous the fibrous texture of the resultant hollow fiber. Practical applicability should be studied further in relation to the balance of separability and permeability.

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