Microporous Polypropylene Hollow Fibers Containing Poly(methylsilsesquioxane) Fillers

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SYNOPSIS

Microporous polypropylene hollow fibers were prepared by stretching polypropylene microtubes containing poly(methylsilsesquioxane) fillers with uniform particle sizes. The properties of the resultant hollow fibers are controllable by adjusting the particle size of the filler, the filler content, and the stretching degree. Also, it is elucidated that the hollow fibers have a fine texture of split PP fibrils, in which the filler particles are dispersed.

INTRODUCTION

Many investigators have been studying hollow fibers as key materials for separation technology.[1,2] Generally, microporous hollow fibers are prepared by the phase inversion method[3] or the stretching method[4] and are used in various ways.

On the other hand, we have reported the preparative method of microporous polypropylene (PP) sheets: thin PP sheets containing filler are biaxially stretched.[5,6] Furthermore, we have studied the dependency of some properties of these sheets on the preparative conditions and their microporous structure.[7-9]

In this article, we report the preparation of microporous PP hollow fibers by stretching PP microtubes containing poly(methylsilsesquioxane) (PMSO) fillers, the properties, and the structure of the resultant microporous PP hollow fibers.

EXPERIMENTAL

Materials

PP powder was PN-120 (MFI, 1.2) from Tokuyama Corp. PMSO fillers with uniform particle sizes were from Toshiba Silicone Co., Ltd. and their particle sizes were 0.3, 0.8, and 2.0 μm, as shown in Figure 1. Some commercial grade additives were used: Ca-stearate, poly(butadiene) (GI-1000 from Nihon Soda Co., Ltd.), and 2,6-di-*t*-butyl-4-methylphenol (antioxidant).

Preparative Procedure

The preparative procedure is as follows. PP powder, filler, and additives were well mixed and then extruded at 230°C. A pellet was extruded at 230°C through a cylindrical double nozzle (internal diameter, 0.5 mm; slit distance, 0.1 mm), supplying N_2 gas into the central part. A microtube was stretched at 120°C with the aid of two pairs of Nelson rolls (cross-axis rolls parted upper and lower sides) to form a microporous hollow fiber. Here, the PMSO filler was pretreated with the poly(butadiene) (2 wt % of the PMSO filler). The amounts of Ca-stearate and 2,6-di-*t*-butyl-4-methylphenol were 0.3 and 0.8 wt % of PP, respectively.

Measurement

Maximum Pore Size (D_{max})

Microporous PP hollow fibers were dipped in methanol and N_2 gas was fed into the hollow fibers. D_{max}

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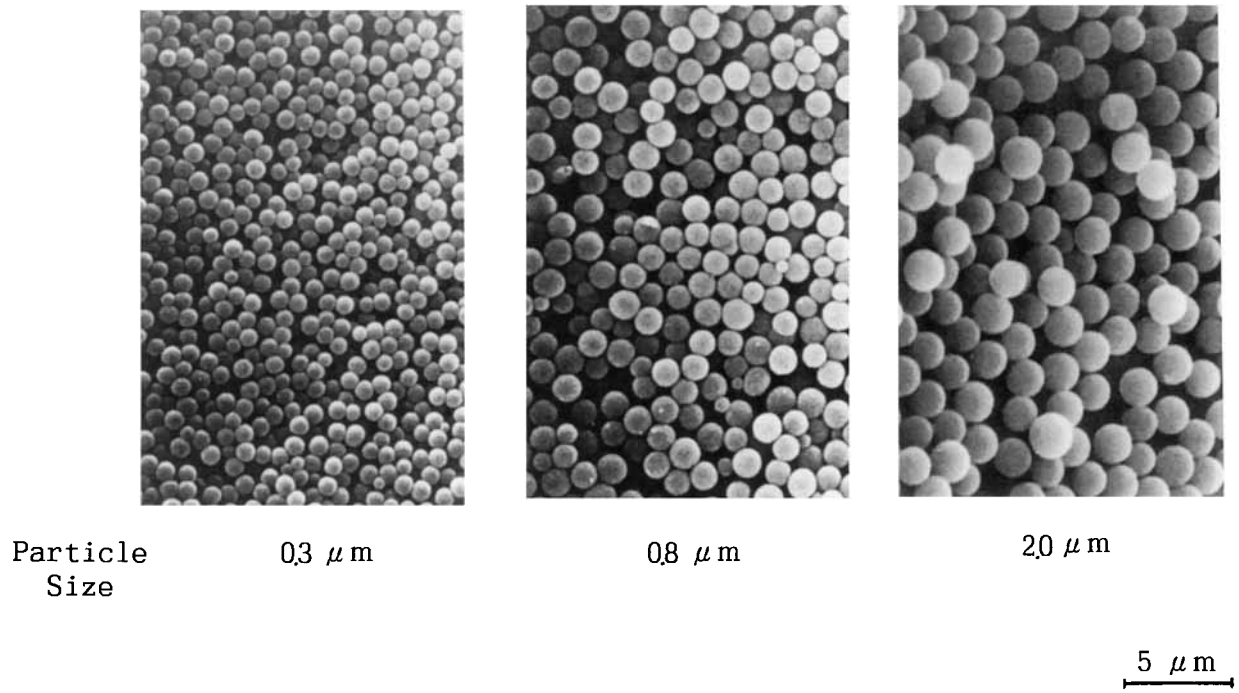

Figure 1 Scanning electron micrographs of PMSO fillers.

was estimated from the N_2 gas pressure (Pj) at the bubbling point as follows (ASTM F-316).

$$D_{max} = 0.9388\ Pj^{-1}. \quad (1)$$

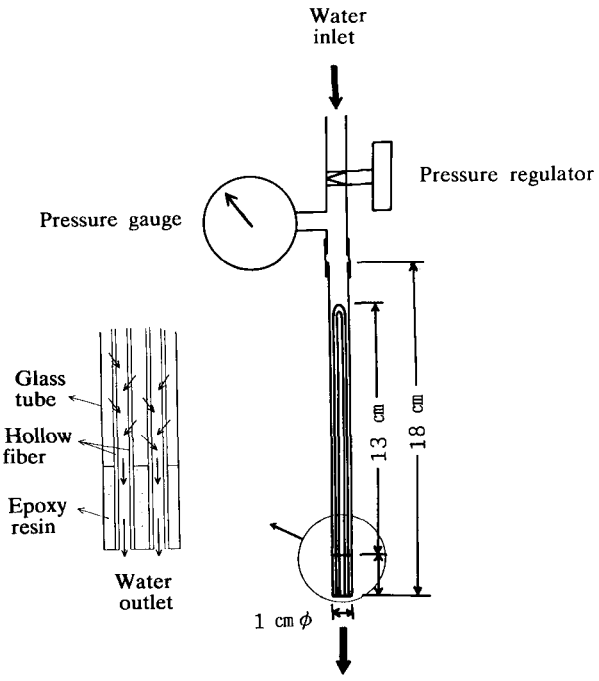

Figure 2 Apparatus to estimate water flux.

Tensile Strength (TS) at Yield and Elongation to Break (Eb)

TS and Eb in machine direction were measured with the aid of an Autograph IS-2000 (Shimazu Seisakusho Co., Ltd.) with the drawing rate of 200 mm/min (JIS K-7127).

Water Permeability

Figure 2 shows the apparatus to estimate water flux at room temperature under N_2 atmosphere (applied pressure, 1 kg/cm^2) by using city water. Here, the hollow fibers were pretreated with an ethanol solution of Na-*n*-dodecylbenzenesulfonate (5 g/100 mL).

N_2 Gas Permeability

Figure 3 shows the apparatus to estimate N_2 gas flux at 20°C under a definite applied pressure.

Structure of Microporous PP Hollow Fibers

Structures of the microporous PP hollow fibers were observed with the aid of a scanning electron microscope (JSM-T-220 from JEOL Ltd.) The samples were taken as shown in Figure 4.

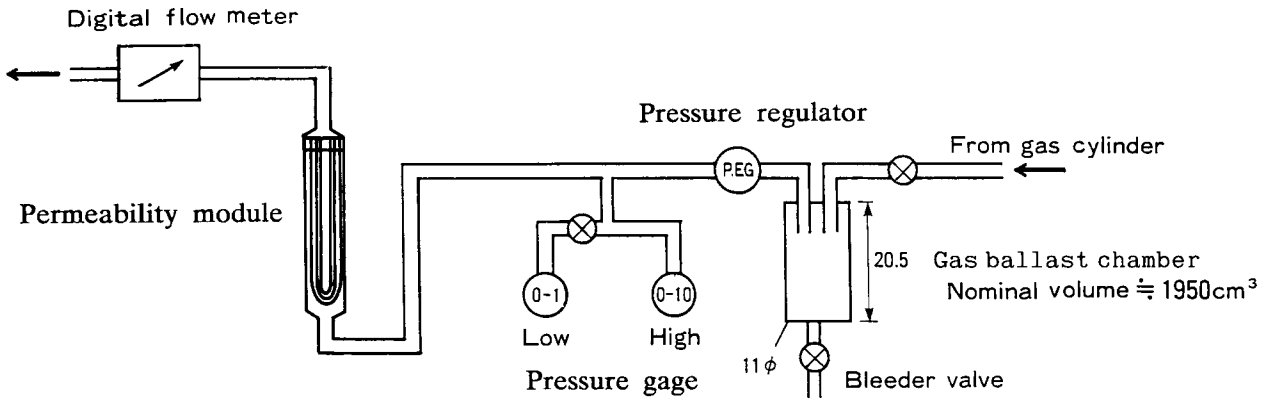

Figure 3 Apparatus to estimate N_2 gas flux.

Determination of Pore Structure

In order to study pore structure of the microporous PP hollow fibers, gas permeability was measured by the ordinary method; namely, Yasuda et al.[10] and Cabasso et al.[11] studied gas permeation through various Millipore filters and polysulfone membrane, respectively, and derived the following equations.

$$J = K\Delta P l^{-1} \tag{2}$$

where gas flux J is expressed in units of volume flow, kg/cm^2·s; K, permeability coefficient (cm^2/s); ΔP, pressure difference across the sample (kg/cm^2); and l, thickness of a sample (cm).

Gas permeability coefficient (K) is determined as follows.

$$K = lPoQ(A\Delta P)^{-1} \tag{3}$$

where Q is the volume flow rate of N_2 gas (cm^3/s) and A, effective area of the sample (30 cm^2).

Permeability coefficient (K) of a microporous hollow fiber can be shown as follows.

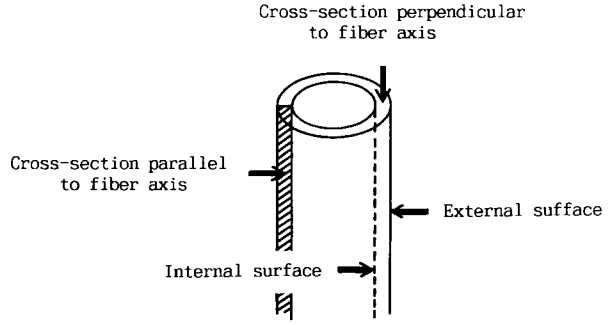

Figure 4 Sampling for scanning electron microscopy.

$$K = \mathrm{Ko} + \mathrm{Bo}\eta^{-1}\bar{P} \tag{4}$$

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

Ko and Bo can be estimated from the plot of K to $\bar{P}$.

Porosity of the hollow fiber (ε) and tortuosity factor of pore (q) can be related to Ko and Bo as follows.

$$\mathrm{Ko} = (4/3)(\delta/k_1)(\bar{v}/q^2)\varepsilon m \tag{5}$$

$$\mathrm{Bo} = (m^2/k)(\varepsilon/q^2) \tag{6}$$

where δ/k_1 and k are constants (0.8 and 2.5, respectively) as estimated by Carman[12]; and m, equivalent pore size as shown below.

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

$$v = (8\mathrm{RT}/\pi M)^{0.5}. \tag{7}$$

The equivalent pore size (m) can be calculated by combining Eqs. (5)-(7).

$$m = (16/3)(\mathrm{Bo}/\mathrm{Ko})(2\mathrm{RT}/\pi M)^{0.5}. \tag{8}$$

Thus, Eq. (9) can be derived for measurement with N_2 gas at 20°C.

$$m = 1.256 \times 10^5\,(\mathrm{Bo}/\mathrm{Ko}). \tag{9}$$

Furthermore, the following equations are derived from Eqs. (5) and (7) to estimate effective porosity (ε/q^2) and tortuosity factor of pore (q).

$$\varepsilon/q^2 = 2.5\ \mathrm{Bo}/m^2 \quad (10)$$

$$q = 0.63m(\varepsilon/\mathrm{Bo})^{0.5}. \quad (11)$$

RESULTS AND DISCUSSION

Properties of Microporous PP Hollow Fibers

Microporous PP hollow fibers are prepared by stretching PP microtubes containing PMSO fillers with uniform particle sizes. The stretching causes splitting of the PP phase at the periphery of the filler particles, and results in a microporous structure as reported in the previous articles.[6,9] Accordingly, the filler content, the size of filler particles, and the stretching degree affect the properties of the resultant microporous PP hollow fibers.

Table I shows the dimensions of the hollow fibers in relation to the stretching degree. As the PP microtubes are stretched much more, the resultant hollow fibers become thinner. It was confirmed that the filler content has little effect on the dimensions. Next, the preparative conditions were investigated by using D_{max} as a measure of the porous structure. Figures 5–7 show the dependencies of D_{max} on the filler content, the particle size of filler, and the stretching degree, respectively. The larger the filler content, the larger D_{max} (Fig. 5). This is reasonable because the increase of the filler content means an increase of the particle number of the filler and an increase of the splitting points of the PP phase described above. Furthermore, the PP phase should be stretched much more with decreasing PP content. When the filler contents are the same, the decrease in the particle size means an increase of the particle number, and then causes the formation of more splitting points of the PP phase. Also, the larger particles engender the formation of larger voids. Accordingly, when the particle size is smaller, the resultant hollow fiber reasonably has smaller

Table I Dimensions of Microporous PP Hollow Fibers

Stretching Degree	Internal Diameter (μm)	Wall Thickness (μm)
0	748 ± 70	102 ± 20
3	397 ± 65	80 ± 12
4	370 ± 63	79 ± 10
5	344 ± 52	75 ± 7
6	334 ± 70	75 ± 10

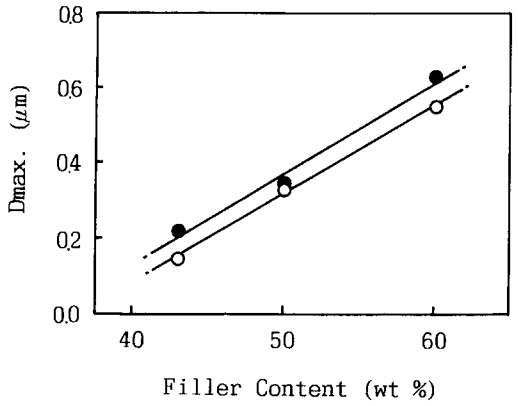

Figure 5 Effect of filler content to D_{max}. Particle size, 0.3 μm and stretching degree: (○) 5 and (●) 6.

D_{max}, a finer texture in other words (Fig. 6). The stretching causes splitting of the PP phase to result in minute voids, which are widened with the increasing stretching degree (Fig. 7). The results described above show that the microstructure of the hollow fiber is controllable by adjusting the filler content, the particle size of the filler, and the stretching degree.

Figure 8 shows the effect of the filler content on the TS of the hollow fibers prepared with various stretching degrees. The increase of the filler content makes TS smaller because of the decrease of the PP content. Also, the larger the stretching degree, the larger the TS, when the filler content is same. Figure 9 shows the relation between Eb and the filler content in relation to the stretching degree. Eb decreases with increasing filler content, and the larger the

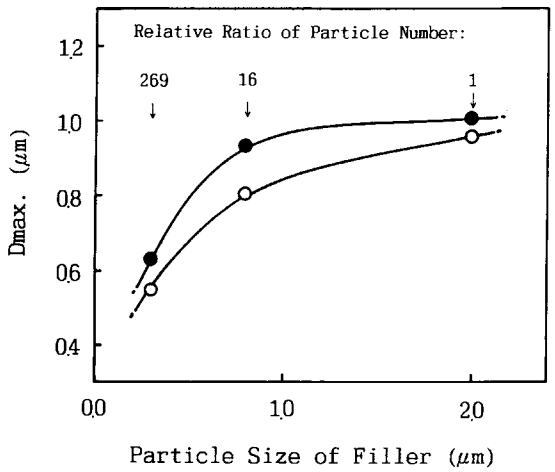

Figure 6 Effect of particle size of filler to D_{max}. Filler content, 60 wt % and stretching degree: (○) 5 and (●) 6.

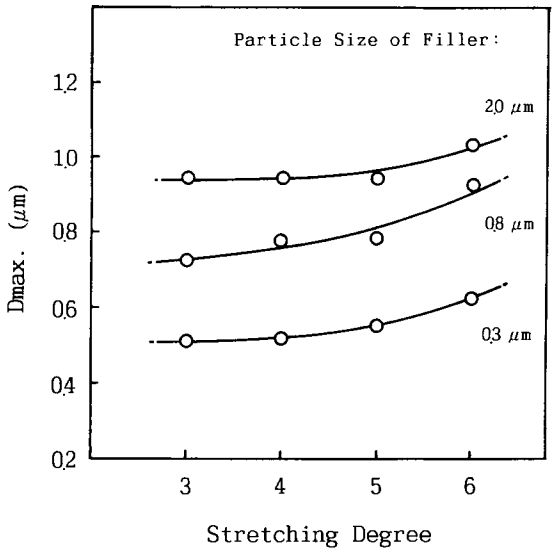

Figure 7 Effect of stretching degree to D_{max}. Filler content, 60 wt %.

stretching degree, the smaller the Eb, when the filler content is same. These results are explicable as follows. The increase of the filler content means a decrease of the PP content, so the relation between TS and the filler content is reasonable. Also, when the PP content is smaller, the PP phase is stretched much more at the same stretching degree, compared with the case where the PP content is larger. Then, Eb decreases with increasing filler content and the

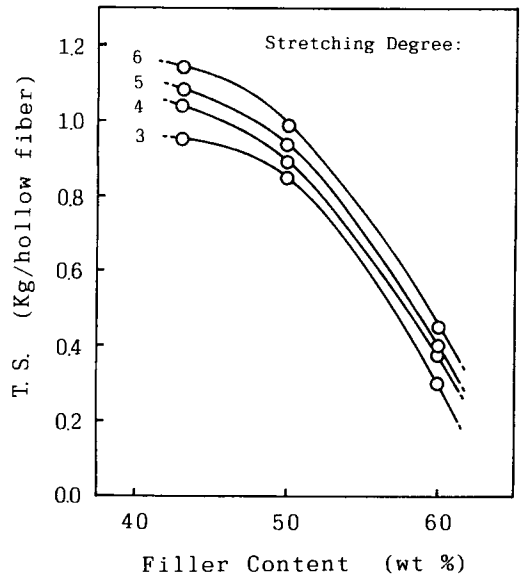

Figure 8 Effect of filler content to TS. Particle size of filler, 0.3 μm.

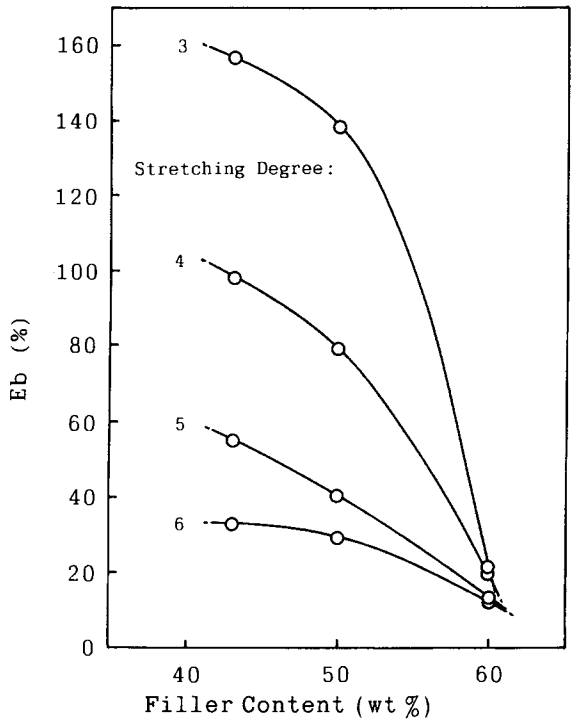

Figure 9 Effect of filler content to Eb. Particle size of filler, 0.3 μm.

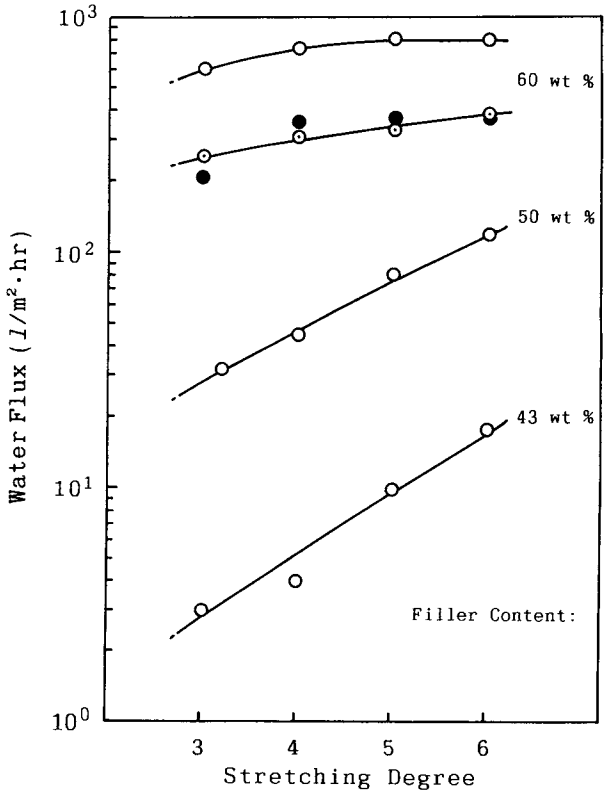

Figure 10 Dependency of water flux on stretching degree. Particle size of filler: (○) 0.3 μm; (⊙) 0.8 μm; and (●) 2.0 μm.

stretching degree and, contrarily, TS increases with increased stretching degree. These results mean that the mechanical properties of the hollow fibers are controllable by adjusting the filler content, the particle size of filler, and the stretching degree.

Water Permeability

Figure 10 shows the effect of the stretching degree on water flux through the microporous PP hollow fiber in relation to the filler content and the particle size of the filler. As described before, D_{max} increases with increasing filler content, the particle size of filler, and the stretching degree, respectively, when the other conditions are same. It is inexplicable that no distinct difference is obtained between the relations in cases of the particle sizes of 0.8 and 2.0 μm. Figure 11 shows the dependency of the water flux on D_{max}. It is reasonable that the water flux increases with increasing D_{max}, but it is obscure why the tendency, with particle size 0.3 μm, is different from the others.

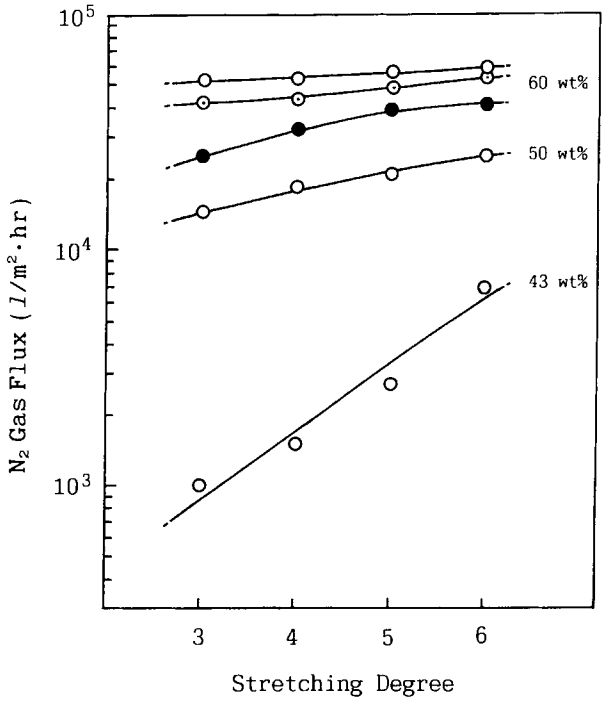

Figure 12 Dependency of N_2 gas flux on stretching degree. Particle size of filler: (○) 0.3 μm; (⊙) 0.8 μm; and (●) 2.0 μm. Δp, 0.5 kg · cm^{-2}.

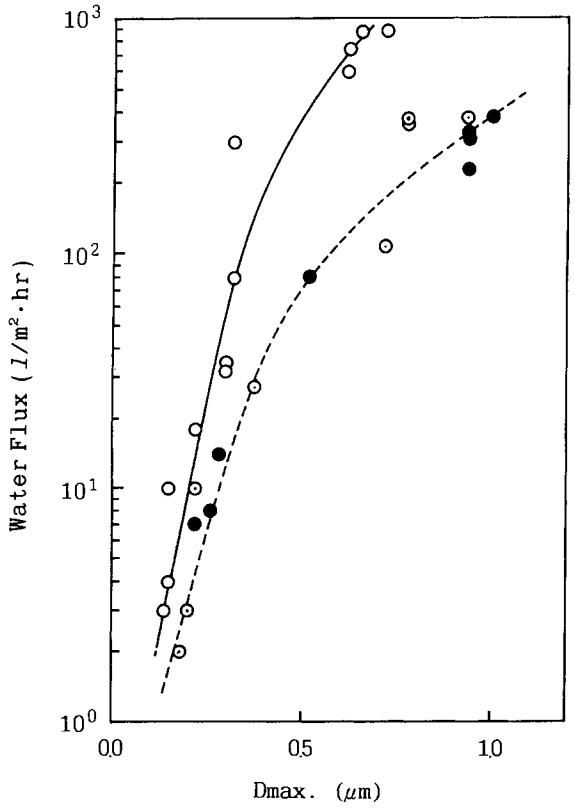

Figure 11 Relations between water flux and D_{max}. Particle size of filler: (○) 0.3 μm; (⊙) 0.8 μm; and (●) 2.0 μm.

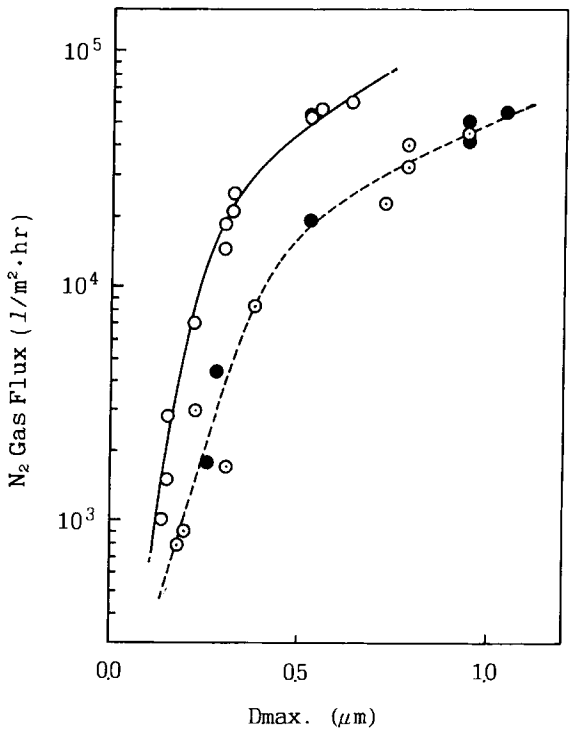

Figure 13 Relations between N_2 gas flux and D_{max}. Particle size of filler: (○) 0.3 μm; (⊙) 0.8 μm; and (●) 2.0 μm.

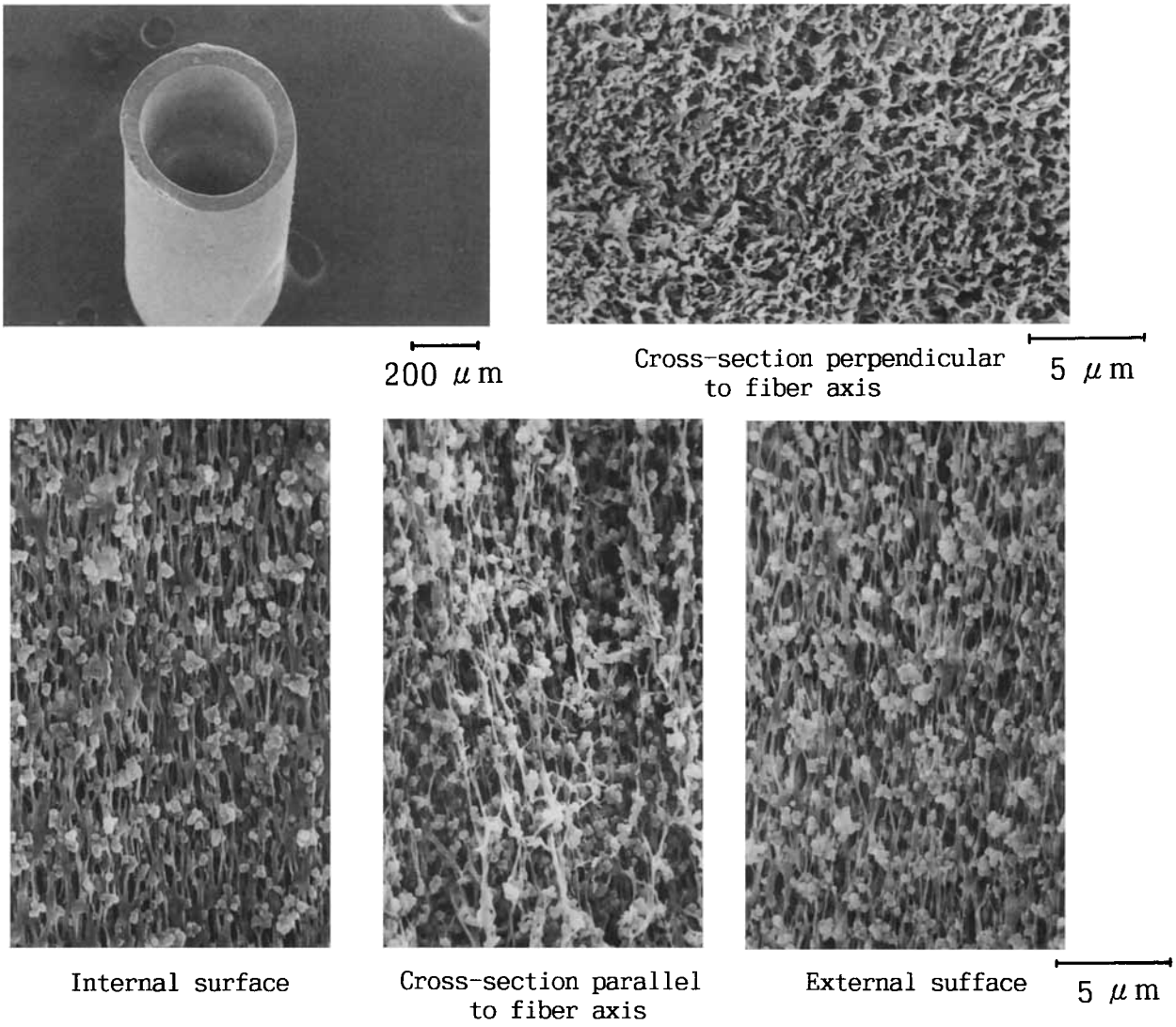

Figure 14 Scanning electron micrographs of a microporous PP hollow fiber.

N_2 Gas Permeability

Figure 12 shows the dependency of the N_2 gas permeability through the microporous PP hollow fiber on the stretching degree in relation to the filler content and the particle size of the filler. These results show tendencies similar to those in the case of the water flux shown in Figure 10. Here, the effect of the particle size of the filler is inexplicable and should be investigated further. Figure 13 shows the dependency of the N_2 gas flux on D_{max}. The increase of D_{max} causes a drastic increase of N_2 gas flux, and

Table II Characteristics of Microporous PP Hollow Fibers

Particle Size of Filler (μm)	Porosity	Ko (cm^2/s)	Bo (cm^2)	Tortuosity Factor (q)	Effective Porosity (ε/q)	Equivalent Pore Radius, m (μm)
0.3	0.43	8.6×10^{-5}	1.6×10^{-15}	24	7.4×10^{-4}	0.23

Filler content, 50 wt %. Stretching degree, 5.5.

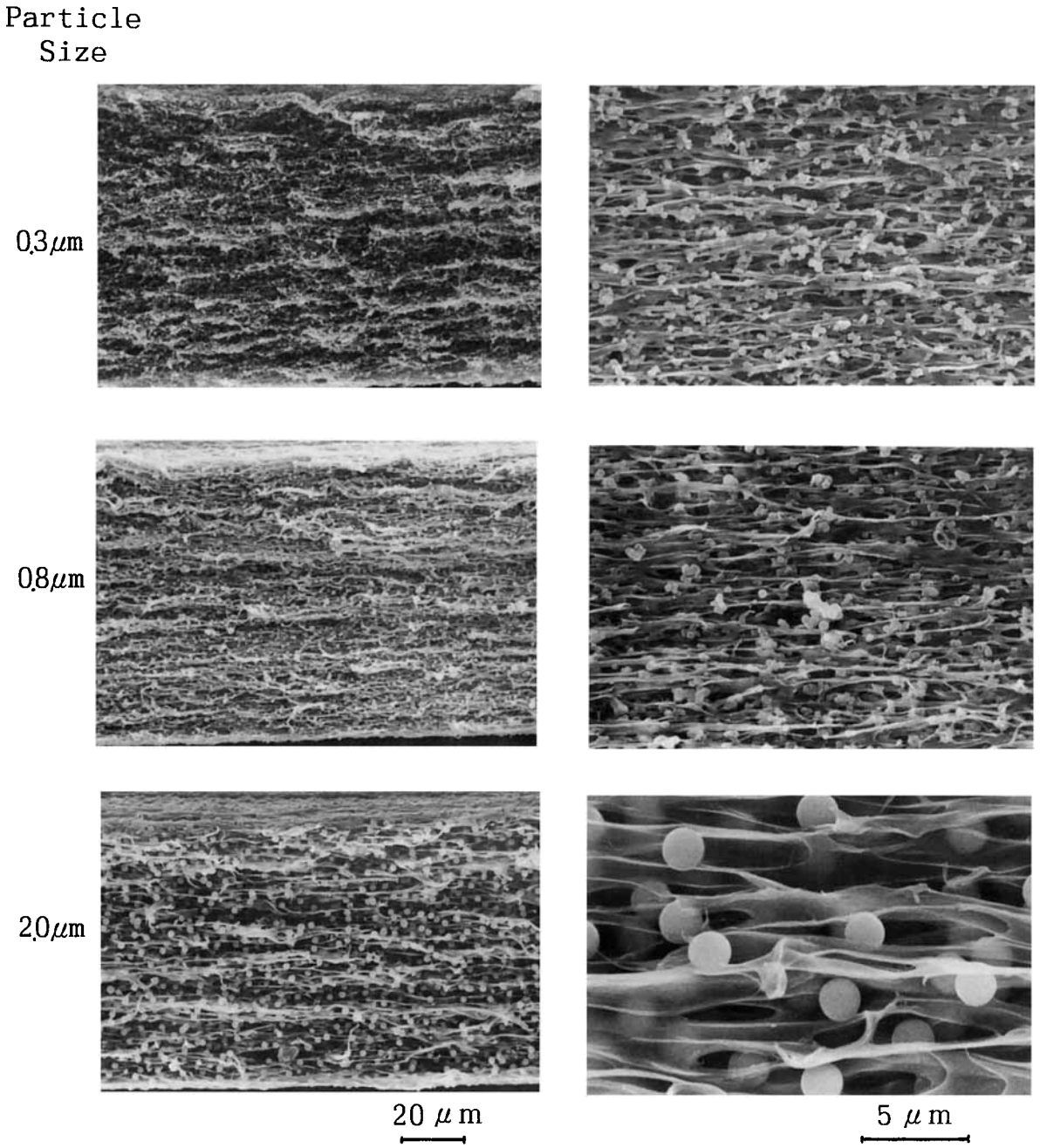

Figure 15 Scanning electron micrographs of the cross sections parallel to length direction.

the tendency in the case of the 0.3-μm particle size is different from the others similar to the case of the water flux. Its reason is still obscure.

Structure of Microporous PP Hollow Fibers

Figure 14 shows scanning electron micrographs of a microporous PP hollow fiber: the whole view, the internal and external surfaces, and the cross sections perpendicular and parallel to the length direction of the hollow fiber. No distinct difference is observed between both surfaces, showing that fine fibrous texture is formed parallel to the length direction. Also, the fine fibrous texture of the cross section parallel to the length direction is similar to those of both surfaces.

On the other hand, the cross section perpendicular to the length direction is clearly different from the others. Figure 15 shows scanning electron micrographs of the cross sections parallel to the length

direction, when the microporous PP hollow fibers were prepared by using PMSO fillers with various particle sizes. Evidently, the smaller the particle size of filler, the finer the fibrous texture of the cross section: the interconnected PP fibrils and the space between them become finer with decreasing particle size of filler.

Figure 16 shows the dependency of N_2 gas flux (J) through a microporous PP hollow fiber on pressure difference (ΔP). From the obtained linear relationship, permeability coefficient (K) can be estimated. Figure 17 shows the linear relation between permeability coefficient (K) and mean pressure ($\bar{P}$). Knudsen permeability coefficient (Ko) and Bo/η can be obtained from the intercept on the vertical axis and the slope of the linear line, respectively. Thus, tortuosity factor of pore, effective porosity, equivalent pore radius, and apparent pore number can be estimated, as shown in Table II. These values are similar to those in the case of the microporous PP sheets prepared by biaxially stretching PP sheets containing PMSO filler.[9] The detailed difference of the microstructure between the microporous PP hollow fibers and the microporous PP sheets should be investigated in the future.

SUMMARY

Microporous PP hollow fibers are prepared by stretching PP microtubes containing PMSO fillers with uniform particle sizes. Maximum pore size of the hollow fiber as a measure of its structure and the mechanical properties are controllable by adjusting the filler content, the particle size of filler, and the stretching degree. Also, the hollow fibers show permeabilities for water and N_2 gas, which are controllable as described above. Furthermore, it is elucidated by scanning electron microscopy that the hollow fibers have a fine fibrous texture of PP, in which the filler particles are dispersed.

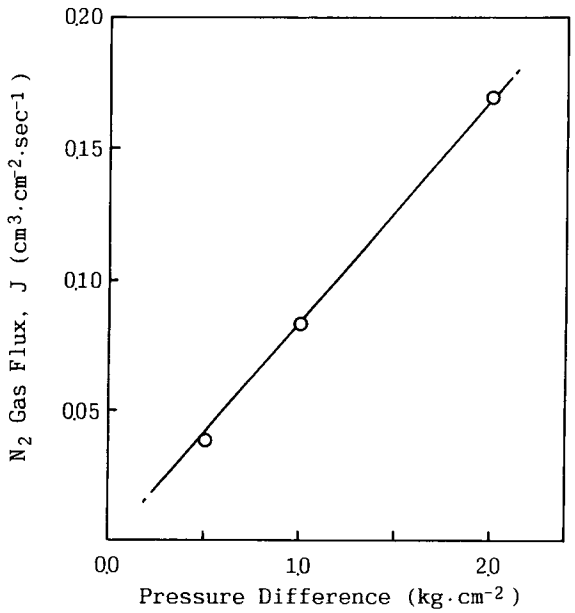

Figure 16 Relation between N_2 gas flux and pressure difference.

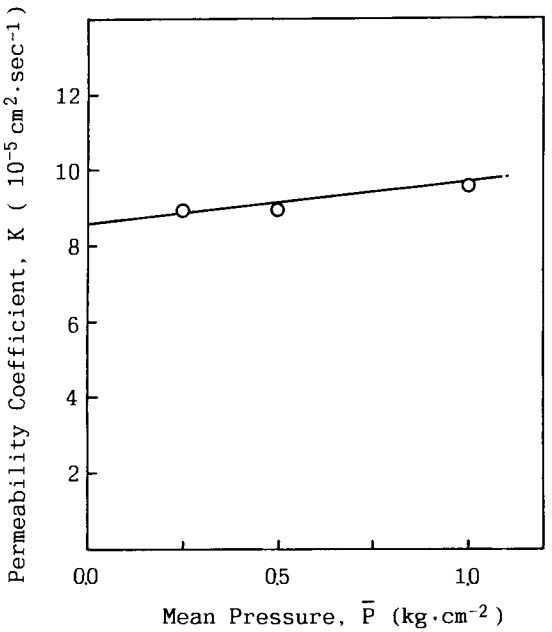

Figure 17 Relation between permeability coefficient and mean pressure.

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