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Preparation and Properties of a Hollow Fiber Consisting Mainly of Natural Mordenite

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A hollow fiber consisting mainly of a natural mordenite was spun for the first time by mixing natural mordenite with polysulfone using dry–wet spinning. The obtained hollow fiber was stable and flexible in water. The dried fiber has a pore distribution of the microfiltration membrane. The fiber can be used as a substrate for a zeolite membrane for pervaporation.

Natural mordenite (MOR) is a common and abundant zeolite in Japan. However, owing to the large particle-size distribution of natural zeolite, it is rarely used to prepare molecular separation films. Because it is difficult to sinter zeolite powders, zeolite films are usually synthesized on the surface of a porous ceramic tubular substrate and used as pervaporation (PV) and vapor permeation (VP) membranes.[1] The ceramic substrates used are microfiltration (MF) membranes having a porosity of 40–60%.[2] During the process of zeolite membrane synthesis, seed crystals for the secondary growth of the zeolite are planted into the outer surface of the substrate. The performance of the PV membrane depends on the thickness and the tightness between the membrane and the substrate.[2] Recently, Shirataki et al. reported a thin hollow fiber consisting mainly of LTA-zeolite particles, which were spun for the substrates of a LTA-zeolite membrane module.[3]

In this study, we spun hollow fibers using natural MOR powders mixed with polysulfone (PSF). We also discuss the properties of the obtained fibers. In addition, dehydration was carried out from ethanol solutions through a mordenite membrane synthesized on hollow natural MOR–PSF fibers.

A hollow natural MOR–PSF fiber was spun using dry–wet spinning.[4] The spinning slurry was prepared as follows. Natural MOR powders (Shin Tohoku Chem. Ind. Co., Ltd.) were milled in ethanol using 5 mmϕ alumina balls for 2 h and dried overnight in an oven at a temperature above 120 °C. Then, the MOR powder and a small amount of sodium dodecylbenzenesulfonate (NaDBS) were dispersed in dimethylformamide (DMF) and stirred at 35 °C. Then, PSF (Udel PSF P-1700) was added to this solution, and the resulting solution was stirred over 3 days to ensure homogeneous mixing with the MOR particles. The slurry and the inner coagulant water were spun through a tube in an orifice-type spinneret having an inner and outer diameter of 1.2 and 3.3 mm, respectively. The extrusion rates of the slurry and coagulant water were 32 and 20–32 mL min^{-1}, respectively. The air gap was 5 cm, and the temperature of the water bath was 35 °C. The obtained hollow fiber was cut and dried. The pore size distribution of the hollow fiber was measured by mercury porosimetry, and the compressive strength and the flexural strength were measured under an applied force of 50 N and 1 mm min^{-1} crosshead strength. The cross section of the fiber was observed by SEM. The MOR membrane was synthesized on the outer surface of the hollow natural MOR–PSF fiber. The MOR membrane synthesis was carried out hydrothermally at 165 °C for 24 h using a synthesis solution of Na:Si:Al = 1.75–2.3:5–6.7:1. The dehydration performance of the synthesized MOR membrane was also measured by a batch-type PV apparatus.[2]

Table 1. Conditions of spinning slurries, results of spinning, and postheating treatments of obtained hollow natural MOR–PSF fibers

Sample No.	Particle size of mordenite /μm	Slurry for spinning: Mordenite /wt %	Slurry for spinning: Polysulfone /wt %	Stirring time /d	Spinning of hollow fiber	Heating temp /°C
1	2–5	41.4	5.75	—	failed	—
2	2–5	45.7	5.92	3	OK	60
3	2–5	45.7	5.92	3	OK	500
4	2–5	43.7	5.34	3	OK	65
5	<2	44.2	5.61	1	failed	—
6	<2	44.2	5.42	3	failed	—
7	<2	44.2	8.40	4	OK	65
8	<2	38.5	10.50	5	OK	65
9	<2	24.0	24.14	4	OK	65
10	<2	16.0	31.36	2	OK	65

The obtained hollow MOR–PSF fiber was flexible and stable in the water, in spite of the high hydrophilicity of the MOR powder.

The spinning slurries, posttreatments, and the obtained samples are listed in Table 1. The concentration of NaDBS in the slurries was ca. 0.25 wt %. The hollow natural MOR–PSF fibers were successfully spun using spinning slurries consisting of 16–46 wt % MOR powder and 5.9–32 wt % PSF. When the total concentrations of PSF and MOR powders were reduced, the fiber became thin and unsuitable for forming a long hollow fiber. On the other hand, when the concentration of the MOR powder was increased to over 46 wt %, the spinneret was blocked because of the high viscosity of the spinning slurry. The mixing ratio of PSF to MOR powder was very important to ensure that the hydrophilic surfaces of the MOR particles are covered by PSF to form nanocomposites. When using fine MOR powder with particle size under 2 μm, more PSF was needed to make the hollow fiber. When the amount of PSF was too small, the hollow fiber became unstable and sometimes dispersed in the water immediately.

The dried hollow fiber had an inner and an outer diameter of 1.0–2.0 and 2.2–3.0 mm, respectively. The flexibility was lost under the dry conditions. However, if the fiber had dried at temperatures of less than 100 °C, the flexibility returned when the fiber became wet again. As shown in Figure 1, the SEM images of cross-sectioned fiber consisting of high MOR content have an isotropic structure, while the cross section of fibers which were spun using slurries of high PSF content had radial slit-like structures. The obtained hollow MOR–PSF fiber became stronger as the PSF content was increased, though the flexibility

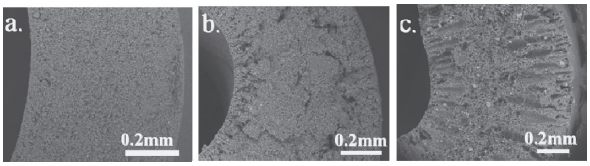

Figure 1. The cross-sectioned images of the hollow natural MOR–PSF fibers listed in Table 1. (a) Sample 4, (b) sample 7, and (c) sample 9.

Table 2. Compressive strength and flexural strength of the hollow natural MOR–PSF fibers listed in Table 1

	Sample No.					
	2	3	7	8	9	10
Compressive strength /N mm^{-2}	1.1	0.56	4.6	4.5	12.5<	12.5<
Flexural strength /N mm^{-2}	$<2.8 \times 10^{-4}$	—	1.0	1.4	5.6	—

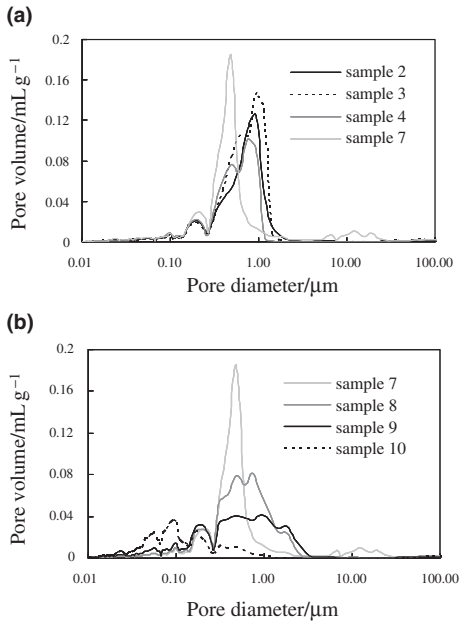

Figure 2. Pore distribution curves of the hollow natural MOR–PSF fibers listed in Table 1. (a) Difference in the curves for the hollow fibers with relatively low PSF contents. (b) Variation in the curves for the hollow fibers with increase in PSF contents.

was decreased. Because of the low-sintering effect on MOR particles, the compressive strength of the fiber was reduced after the PSF was removed by heating (Table 2).

The dried hollow MOR–PSF fibers were MF membranes with porosities of 50–60%. The pore-distribution curves of the hollow MOR–PSF fiber are compared in Figure 2. There are a few peaks in the range of 0.06–1.0 μm in the pore-distribution curves of the hollow MOR–PSF fiber. The pore volume of the peak at 0.2 μm was almost the same for samples 2, 3, 4, and 7, which suggests that the peak was derived from the interspace of the MOR crystals. When the concentration of PSF was less than 10%, the pore volume of the peaks was high in the range of 0.4 to 1.0 μm. As the PSF ratio in the spinning slurry was increased,

Table 3. Pore properties of the hollow natural MOR–PSF fibers listed in Table 1

	Sample No.						
	2	3	4	7	8	9	10
Average pore diameter/μm	0.6	0.6	0.5	0.4	0.5	0.3	0.07
Porosity/%	59	66	54	49	62	56	52

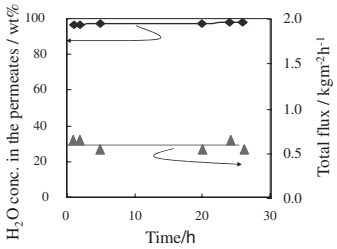

Figure 3. Dehydration performance of 90% ethanol solution at 75 °C through the MOR membrane/hollow natural MOR–PSF fiber (No. 2) composite.

the peaks in the range of 0.4 to 1.0 decreased, while the peak at 0.1 μm increased, which can be attributable to the width of the MOR crystal. In Table 3, the average pore diameter was noticeably small in sample 10, which suggests that most of the MOR crystals are isolated and embedded in the PSF matrix. The peaks in the range of 0.4 to 1.0 μm are attributed to solvents trapped by the MOR particles and released during fiber spinning and drying.

After the hydrothermal treatment, the compressive strength of the hollow natural MOR–PSF fiber was increased with the secondary growth of the mordenite layers on the outer side of the fibers. SEM images revealed that the thickness of the synthesized MOR layer was approximately 4 μm. The dehydration performances of the obtained MOR membrane/hollow natural MOR–PSF fiber composites were examined using a 90% ethanol solution at 75 °C. High dehydration performance was obtained through the MOR membrane composite using the samples 2, 3, 4, 7, 8, and 9 (Figure 3). The water selectivity was 300–10000, and the total permeation flux was 0.3–0.8 kg m^{-2} h^{-1}. The significant water selectivity was not achieved when sample 10 was used. The highest separation factor was obtained when samples 2–4, having high MOR content, were used. The permeation flux through the membrane was highest when sample 9 was used; this could be attributed to the slit-structure of sample 9. Thus, it can be expected that the cost of the dehydration module consisting of zeolite membranes is potentially reduced by using hollow natural MOR–PSF fiber instead of other ceramic substrates.

References

1 *Zeoraito no Kagaku to Oyo*, ed. by H. Tominaga, Kodansha, Tokyo, Japan, **1987**.
2 T. Nagase, Y. Kiyozumi, Y. Hasegawa, F. Mizukami, *Clay Sci.* **2006**, *12*, Suppl. 2, 100.
3 H. Shirataki, K. Aoki, Z. Wang, Jpn. Kokai Tokkyo Koho 08 43, 864, **2008**.
4 I. Cabasso, E. Klein, J. K. Smith, *J. Appl. Polym. Sci.* **1977**, *21*, 165.

