

Note

MORPHOLOGIES AND GAS SEPARATION PROPERTIES OF MELT-SPUN ASYMMETRIC POLY(4-METHYL-1-PENTENE) HOLLOW FIBER MEMBRANES*

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Abstract Poly(4-methyl-1-pentene) (PMP) hollow fiber membranes were prepared by the melt-spun and cold-stretch (MSCS) method. Scanning electronic microscopy (SEM) was used to characterize the section and surface structures of the membranes with special asymmetric structure. The preliminary results of gas permeation measurements indicated that the resultant hollow fiber membranes have the potential ability for oxygen/nitrogen separation.

Key words Poly(4-methyl-1-pentene), Asymmetric membranes, Hollow fiber membrane, Gas permeation, O₂/N₂ Separation

INTRODUCTION

Poly(4-methyl-1-pentene) (PMP) shows a desirable gas separation factor for the O₂/N₂ gas pair^[1, 2]. The potential application of a polymer as a separation membrane depends on both the possible throughput and the purity of product. This means that both the permeation rate for the gas that is transported more rapidly and the selectivity should be as large as possible. For a given polymer material such as PMP, it is a suitable choice to increase the gas permeation rate by fabricating asymmetric and/or composite membranes with a thin selective layer^[3–5].

It is well known that the melt-spun and cold-stretch (MSCS) process normally represents an ideal method for the manufacture of isotropic membranes from semi-crystalline polymers^[6], while the phase-inversion process has been further developed for the preparation of asymmetric membranes. Of all the thermoplastic polymers, semi-crystalline polyolefins have been found to be most suitable for making hollow fiber membranes. Compared with the phase inversion process, however, the MSCS process is an ecological method, since no solvents are required and no waste water or harmful by-products are evolved. Therefore, it is an interesting topic to prepare asymmetric membranes by the MSCS process^[7]. In our previous publications^[8, 9], the preparation and characterization of polypropylene (PP) and polyethylene (PE) isotropic microporous membranes by the MSCS process were carefully studied. In this note, asymmetric PMP hollow fiber membranes were prepared by the same method. The morphologies of the membranes were characterized by SEM and the preliminary results of gas separation for O₂, N₂ and CO₂ were reported.

EXPERIMENTAL

Materials

Commercial PMP resin (TPX-RT-18) produced by Petrochemical Div., Mitsui & Co Ltd., Japan was used for the preparation of hollow fibers. Its properties are listed in Table 1.

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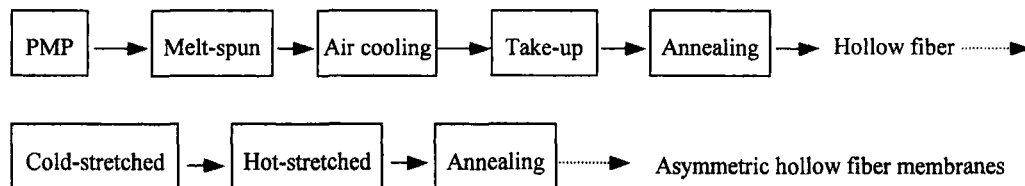
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Membrane Preparation

Scheme 1 shows the flow chart for the preparation of asymmetric PMP hollow fiber membrane by the MSCS process. The PMP granules were melt extruded and spun to form hollow fiber on a single-screw extruder with a single-hole tube-in orifice type spinneret. The resultant nascent hollow fibers were annealed for 60 min at 180°C and then stretched to a certain drawn ratio. Finally, the stretched fibers were annealed at 185°C for 10 min to set the structure and to form membranes.

Table 1. Typical properties of PMP TPX-RT-18

Appearance	Density (g/cm ³)	Melting point (°C)	T _g (°C)	MI (g/10 min at 260°C and 5 kg)
Clear transparent	0.833	240	39	26



Scheme 1. Flow chart for the preparation of PMP hollow fiber membranes with MSCS method

Structure Analysis and Properties Measurement

The structures of the inner and outer surfaces and the section of the hollow fiber membranes were examined using a SEM (Hitachi S-570). The surfaces of the samples were coated with a thin layer of gold to prevent charging prior to the SEM examinations. About ten hollow fiber membranes were bundled into U-shape and their open ends were glued together with epoxy resin to fabricate a module. The length of each fiber was about 20 cm. Then, a pure gas pressure of 0.10 MPa was applied to the outer surface of the hollow fibers at 25°C, and the amount of gas that permeated through the fiber walls was determined with a soap flowmeter. The membrane area was calculated on the basis of the outer diameters of the fibers. The gas permeation rate J was calculated according to Eq. (1)

$$J = \frac{V_{\text{gas}}}{A \times P \times t}$$

where V_{gas} is the gas volume that permeates through the membrane, A is the membrane area which is calculated on the basis of the outer diameter of the hollow fiber membrane, P is the gas pressure between both sides of the membrane, and t is the time when gas permeates through the membrane. Accordingly, the gas separation factor can be calculated with Eq. (2)

$$\alpha_j^i = \frac{J_i}{J_j}$$

where i and j denote different gases, respectively.

RESULTS AND DISCUSSION

The SEM images of the inner and outer surfaces and the section of the hollow fiber membrane (take-up speed, 300 m/min; spinning temperature, 260°C; stretching ratio, 200%; annealing temperature, 185°C) are shown in Fig. 1. As illustrated in Fig. 1(a), many pores can be observed in the cross-sectional structure of the membrane. However, the pore size distributions across the section were not uniform, especially near the outer edge. It can be seen that the porosity decreased gradually to zero from the central part to the outer edge of the hollow fiber (Fig. 1(b)). This can be demonstrated further by the SEM images of the outer and inner surface (Figs. 1(c) and 1(d)). Dense outer surface with parallel trails, which were caused by stretching, can be observed by SEM for the

membrane at a magnification of 20,000. On the other hand, however, pores between the rows of lamellar crystals can be seen on the inner surface at a magnification of 5,000. These results suggest that the MSCS process could be used to prepare PMP asymmetric hollow fiber membranes with dense outer skin layer and porous structure in radial direction. It might be described as a “skin effect”^[10] because in the preparation process, N₂ was used as the bore gas, and air at 30 °C was used to cool the outer surface of the spun hollow fibers. The N₂ supplied to the inside of the hollow fibers was swept from the surface of the spinneret and its temperature was higher than the air, which overflowed the outer surface of fibers. Therefore, a temperature gradient was formed from the outer surface to the inner surface of the fibers. As a result, the fibers acquired a structure varying along its radius.

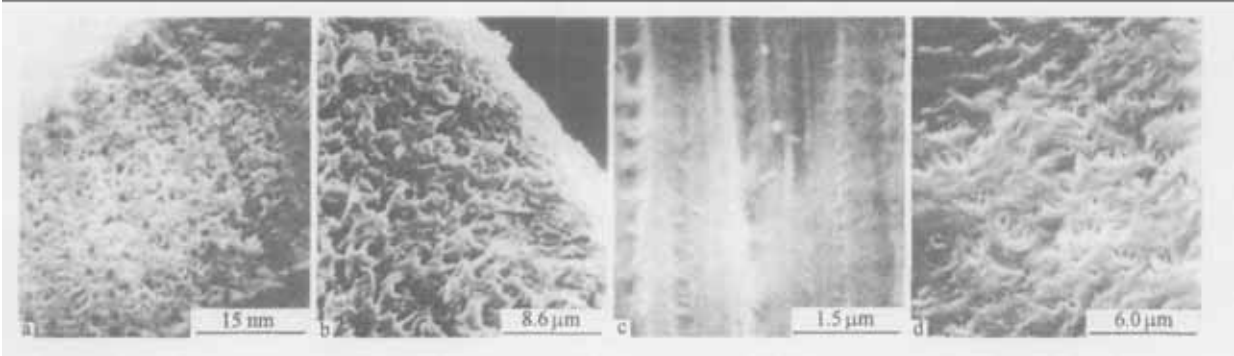


Fig. 1 SEM images of PMP asymmetric hollow fiber membrane
a) Section 1; b) Section 2; c) Outer surface; d) Inner surface

Preliminary results of gas permeation measurements indicate that the asymmetric membranes have great potential for O₂/N₂ separation (see Table 2). The separation factor and the oxygen flux of the membranes prepared in this work are 3.23 and $3.8 \times 10^{-3} \text{ m}^3/(\text{m}^2 \cdot \text{s} \cdot \text{kPa})$ at 25 °C, respectively. The membranes have good selectivity for O₂/N₂, CO₂/N₂, CO₂/O₂ gas pairs. Further work concerning the preparation, detail structure characterization and gas separation properties the asymmetric PMP hollow fiber membranes are going on in our lab.

Table 2. Typical parameters and properties of the PMP hollow fiber membrane (at 25 °C)

Inner diameter (m)	Thickness (m)	Oxygen flux (m ³ /m ² · s · kPa)	Selectivity		
			$\alpha_{\text{N}_2}^{\text{O}_2}$	$\alpha_{\text{N}_2}^{\text{CO}_2}$	$\alpha_{\text{O}_2}^{\text{CO}_2}$
280×10^{-6}	45×10^{-6}	3.8×10^{-3}	3.2	13.6	4.2

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