Preparation of Asymmetric Hollow-fiber Membrane with Ultrathin Dense Skin Layer on the Outer Surface Using Dry/Wet Phase Inversion Process

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SUMMARY: The authors have developed an asymmetric hollow-fiber membrane with a skin layer on the outer surface using a dry/wet phase inversion process with a newly synthesized aromatic fluorinated polyamide. Because the skin layer is ultrathin and has no defects, the membrane has gas selectivity in addition to higher gas flux. The membrane has excellent hemocompatibility, which is probably related to packing density of the skin layer. Authors are now clarifying the mechanism of the microstructure formation of the membrane relating to spinning conditions by the standing point of polymer physics. Generally, the microstructure of a polymeric membrane prepared by a phase inversion process is discussed using the phase diagram of the system. However, the process is so dynamic that conventional discussion based on the start and end points is not sufficient, but which path is to be chosen on the phase diagram is more important.

Introduction

Kawakami, *et al.* have reported that flat membranes prepared by a dry/wet phase inversion process with newly developed fluorinated polyimides have higher gas permeability and selectivity (CO_2/O_2, O_2/N_2, CO_2/CH_4) [1-4] and excellent hemocompatibility [4]. We are now developing hollow-fiber membrane of those polymers referring to the process for preparing the flat membranes. In this paper, the relation between the microstructure and the gas permeability of the hollow-fiber membrane is discussed relating to the spinning conditions.

Experimental

Fluorinated Polyimide

In this study, we used the 6FDA-6FAP polyimide synthesized by Kawakami, *et al.* [5] The

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molecular weight (Mw) and Mw/Mn determined by GPC were 480,000 and 2.6, respectively. Tg measured by DSC was 332 °C.

Membrane Preparation

The dry/ wet phase inversion process to prepare an asymmetric hollow-fiber membrane is represented in Fig. 1 comparing with that for a flat asymmetric membrane [1-3, 5]. The diameters of the spinning die are 400/600/800 μm from the inner to the outer, respectively.

A spinning solution consisted of the polymer (12.0 wt %), dichloromethane (5-20 wt %), 1,1,2-trichloroethane (62-83 wt %), and 1-buthanol (0-6 wt%). Methanol was used as coagulant and bore fluid.

The spinning conditions were as follows; the extrusion rate of the spinning solution at the outlet of spinning nozzle was changed from 1 to 3 ml/min, the extrusion rate of the bore fluid at the outlet of spinning nozzle was fixed at 1 ml/min, the air-gap length was changed from 0 to 50 cm and the take-up rate was changed from 4 to 10 m/min.

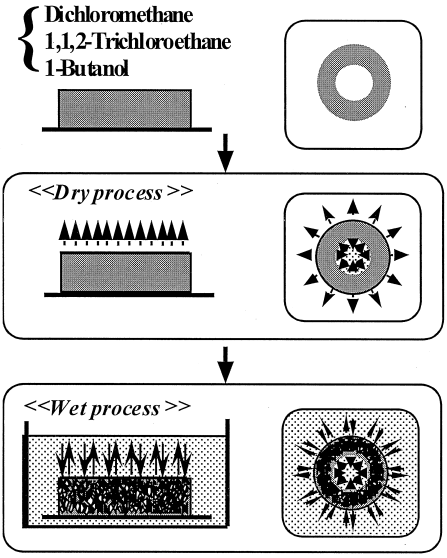

Fig. 1. Dry/wet phase inversion process.

Flat membrane as reference was prepared by casting a polymer solution onto a glass plate referring to the method presented in the previous paper [1, 5].

Gas Permeation

The permeation rate and selectivity of O_2 and N_2 for the membranes were measured at 35°C and at pressure up to 760 cmHg with high vacuum apparatus (Rika Seiki Inc., K-315N-01C).

Orientation of Polymer Chain

Orientation of the polymer chain in a hollow-fiber membrane was determined using attenuated total reflection (ATR) infrared (IR) dichroism with polarized beam following the procedure described in ref. [6].

Results and Discussion

Microstructure of Cross-section of Membrane

The microstructure of the cross-sections of the membranes observed by SEM remarkably varied with changing the spinning conditions, especially the composition of the spinning solution. All of them have asymmetric structures with dense skin layers on the outer surfaces as shown in Fig. 2. The finger-like void changes with the spinning conditions as roughly shown in Fig. 3.

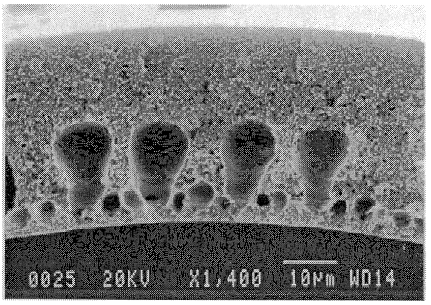

Fig. 2. Microstructure of cross-section of membrane.

Gas Transport Property

The gas permeability and selectivity of an asymmetric hollow-fiber membrane are represented in Table 1 comparing with those of flat membranes. The fact that the hollow-fiber membrane has the higher gas selectivity comparable to those of the flat membranes means that there are no defects in the dense skin layer of the hollow -fiber membrane. However, the gas fluxes of the hollow-fiber membrane are rather lower than those of the flat membranes due to the larger thickness of the dense skin layer of the hollow-fiber membrane.

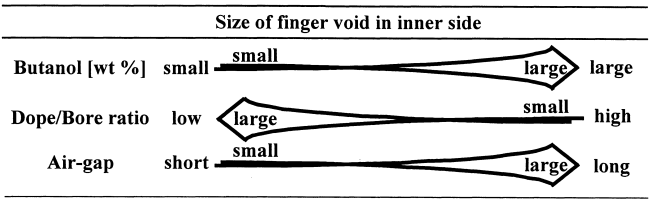

Fig. 3. Effect of spinning conditions on finger-like void formation.

Table 1. Gas transport properties of 6FDA-6FAP membranes at 35 °C and at 760 mmHg.

Membrane Type	$Q\ O_2 \times 10^{-6}$ [cm^3(STP)/cm^2/s/cmHg]	$Q\ N_2 \times 10^{-6}$ [cm^3(STP)/cm^2/s/cmHg]	Thickness [μm]	$Q\ O_2/Q N_2$ [-]
Dense flat	0.16	0.034	50	4.7
Asymmetric flat	794	150	0.01	5.3
Asymmetric hollow fiber	37.4	6.7	0.21	5.6

The 6FDA-6FAP polyimide membrane is suitable for industrial gas separation because the polymer is heat-resistance. We are now trying to reduce the thickness of the skin layer to increase the gas fluxes.

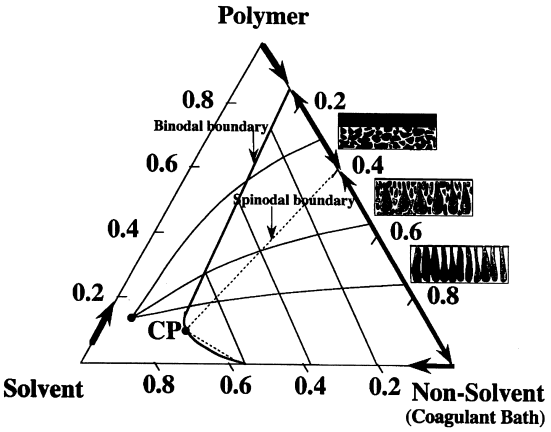

Fig. 4. Phase diagram for phase inversion process.

In addition to the gas transport property, Kawakami, *et al.* [4] have found by *in vitro* and *in vivo* experiments that 6FDA-6FAP polyimide membrane has excellent hemocompatibility. These results indicate 6FDA-6FAP hollow-fiber membrane is also suitable for artificial lung for a long-time use.

Mechanism forming defect-free dense skin layer

The process of preparing a hollow-fiber membrane is more multifactorial and complicated than that for a flat membrane. Usually, a phase inversion process is discussed using a phase diagram as shown in Fig. 4. A phase diagram represents an equilibrium state but a phase inversion process for preparing a membrane is dynamic. Furthermore, for an asymmetric membrane, spatial inhomogeneity in the microstructure formation should be also considered. For the asymmetric hollow-fiber membrane described above, we have to discuss the mechanism forming the microstructure in the membrane as a spatiotemporal process.

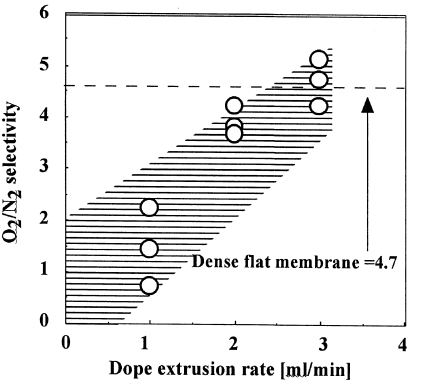

Fig. 5. Effect of shear stress in spinning die on gas selectivity.

Now, we pay attention to the result that the gas selectivity of a hollow-fiber asymmetric membrane is higher than that of a flat asymmetric membrane, which is also higher than that of a flat dense membrane. We speculate that some self-assembling mechanism works during

forming a dense skin layer of the hollow-fiber membrane. One of the primary factors is the orientation of the polymer chain caused by the shear stress in the spinning die and the drawing just under the spinning die. The gas selectivity increased with increasing the extrusion rate of a polymer solution which corresponds to the shear stress in the spinning die, as shown Fig. 5, and also increased with increasing the take-up rate which causes the drawing just under the spinning die.

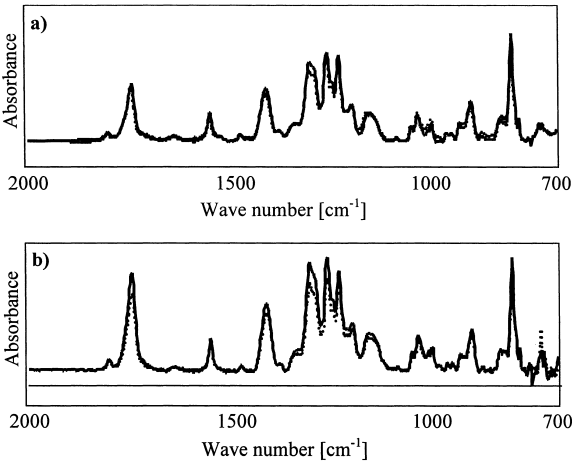

Fig. 6. ATR-IR spectra of a) dense flat membrane (—: any direction, ···: perpendicular to the direction) and b) asymmetric hollow-fiber membrane (—: the spinning direction, ···: perpendicular to the direction).

Fig. 6 is the spectra of a dense flat membrane and an asymmetric hollow-fiber membrane obtained by ATR-IR. The difference in the absorbency between parallel and perpendicular to the spinning direction for the hollow-fiber membrane is larger than that for the flat dense membrane, indicating that the polymer chain in the hollow fiber was more oriented.

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