Gas Permeation Properties of New Type Asymmetric Membranes

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SYNOPSIS

We have developed a new type of asymmetric membranes having a homogeneous hyperthin skin layer, which was used as a polyimide synthesized by 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2-bis(4-amino phenyl) hexafluoro-propane (BAAF). The skin layer thicknesses of the 6FDA–BAAF polyimide asymmetric membranes were 40–60 nm, and the porosity was $10^{-6}\%$ when a defect size was assumed as 5 nm. The permselectivity of 6FDA–BAAF polyimide asymmetric membranes after silicone coating had α of 40 for CO_2/CH_4 and a flux of 1.0 [Nm^3/m^2-h-atm] ($=3.7 \times 10^{-4}$ [$cm^3(STP)/cm^2$ s cmHg]) for CO_2, α of 4.3 for O_2/N_2 and a flux of 2.0×10^{-1} [$Nm^3/m^2/h/atm$] ($=7.1 \times 10^{-5}$ [$cm^3(STP)/cm^2$ s cmHg]) for O_2. These values were constant for large-scale manufacturing.

INTRODUCTION

Gas separation membrane systems have been interesting, and various membrane materials have been investigated within the last decade. This interest is based on the potential economic advantages[1-3] and on environmental problems,[4] since separation systems are less energy intensive than more conventional methods. We developed the organic vapor separation membranes, which consist of a polyimide supporting membrane with a solvent-resistant property and a silicone thin layer.[5,6] A new device for the recovery of organic vapor in gas mixture has been commercialized using the membrane separation process.[7] We have tried to develop a new membrane for various applications, such as clean up of natural gas or oxygen enriched membrane, etc.[8-11]

Recently, polyimides with 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) have been reported as materials exhibiting both higher gas selectivity and permeability as compared with the prior polyimides.[8-15] These homogeneous polyimide membranes, however, have still been unsatisfactory in permeability. Moreover, the mechanical strength required of these membranes have made them too large in thickness to exhibit any permeation rate that is satisfactory for practical and industrial uses. It has been well known that an asymmetric membrane is one of the successful membrane forms to give a high permeation rate and mechanical strength.[8,16-22] The development of asymmetric membranes was initiated by Loeb and Sourirajan for reverse osmosis applications about 30 years ago.[16] Basically, they used the phase-inversion method to develop integrally skinned asymmetric cellulose acetate membranes. This method has been applied for various reverse osmosis, ultrafiltration, and microfiltration membranes. Recently, it was reported that this technology can be applied to gas separation membranes.[17-23] Tai-Shung Chung et al. reported that a defect-free 6FDA-durene asymmetric hollow fiber has very thin skin layers of around 250 nm.[17] The thickness, however, is too large to give a high permeation rate for practical and industrial uses. A thickness less than 100 nm may be necessary, but it was very difficult to prepare an asymmetric membrane having such thin layers, using a conventional method.

In the present work, the permselectivity of a fluorine-containing polyimide asymmetric membrane, which has a hyperthin skin layer as reported before,[23]

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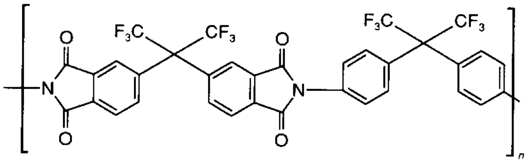
was examined for various gases. The defects of the skin layer were also simulated.

EXPERIMENTAL

Polymer Synthesis

The polyimide used in this study was prepared from 6FDA dianhydride (Hoechst AG Co., 99% purity) and 2,2-bis(4-amino phenyl) hexafluoropropane (BAAF) (Central Glass Co., LTD., > 99% purity), and preparation of the polyimide is discussed below. The polymerization reaction is performed by a two-step method. In the first step, a precursor polyamic acid solution, prepared from 6FDA and BAAF, was synthesized in a glass flask with a mixer and a nitrogen inlet tube. 6FDA and BAAF were precisely added in a 1 : 1 molar ratio and reacted for 4 h at ca. 10°C and then overnight at room temperature under a nitrogen atmosphere in *N*-methyl-2-pyrrolidone (NMP).

The second step is imidization of the polyamic acid to yield the 6FDA–BAAF polyimide (see Scheme 1). The imidization is carried out in a chemical imidization method. For the chemical imidization, acetic anhydride is added to three times the molar quantity of the aromatic diamine as a dehydrating agent; and pyridine, which is equivalent in molar quantity to acetic anhydride, was added as a catalyst. The imidizing reaction was performed overnight. The obtained polyimide was purified by dropping into water and dried overnight at 100°C and atmospheric pressure after filtration.



Scheme 1 The 6FDA–BAAF polyimide.

Preparation of the 6FDA–BAAF Asymmetric Membrane

The 6FDA–BAAF polyimide flakes were dissolved using diethylene glycol dimethyl ether (DGDE). The concentration of the solution was 18 wt %. The 6FDA–BAAF/DGDE solution was used for the membrane preparation after filtration.

The 6FDA–BAAF asymmetric membranes were prepared by casting the 6FDA–BAAF/DGDE on polyester nonwoven cloth and then were solidified in water and air-dried at 60°C. The concentration of each dope was 18 wt %. Some membranes were coated by prevulcanized silicone rubber/hexane solution (3 wt %) and dried for 5 min at 110°C.

Permeability Measurements

The measurement of steady state permeation rate for several gases were carried out by using the pressure transform method at 25°C. A membrane was set in a permeation cell, and a permeation apparatus was evacuated by a vacuum pump. Then the upstream side pressure of the membrane was 3 kgf/cm^2, and the downstream side pressure was always 10 mmHg or less. The permeation rates were determined using a Baratoron pressure transducer (Type 122A) and digital equipment with a recorder.

RESULTS AND DISCUSSION

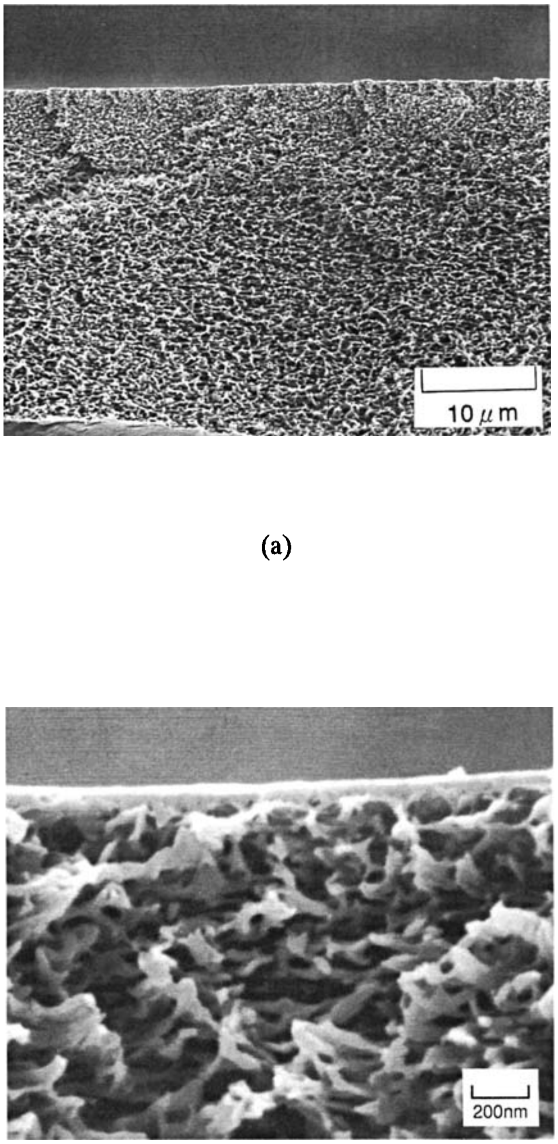
In this study, we used 6FDA–BAAF polyimide as a gas separation membrane material because this polyimide film had a high permselectivity, for example, an α of 50 for CO_2/CH_4 and a flux of 5.0×10^{-9} [cm^3(STP)cm/cm^2 sec cmHg]) for CO_2. The permeability of this homogeneous film, however, has still been unsatisfactory for practical and industrial uses. We developed the new type of asymmetric membrane, having a hyperthin skin layer less than 100 nm.[23]

Structure of the 6FDA–BAAF Asymmetric Membrane

UHR FE-SEM micrographs, illustrated in Figures 1(a) and (b), show the morphology of the cross section of the obtained 6FDA–BAAF asymmetric membranes. The 6FDA–BAAF polyimide asymmetric membranes consisted of a hyperthin skin layer and sponge-like porous matrix. The skin layer was defect-free, and the thicknesses of the membranes were 40–60 nm. The sponge-like porous matrix had finger void-free morphology. The formation mechanism of the asymmetric membrane has been reported in detail before.[23]

Simulation of Defect of the 6FDA–BAAF Asymmetric Membrane

The permselectivity of the 6FDA–BAAF asymmetric membranes had an α of 27 for CO_2/CH_4 and a flux of 1.3 [Nm^3/m^2/h/atm] (= 4.8×10^{-4} [cm^3(STP)/cm^2 s cmHg]) for CO_2 as mentioned before.[23]



(a)

(b)

Figure 1 UHR FE-SEM photographs of a cross section of the 6FDA–BAAF polyimide asymmetric membrane: (a) ×2000; (b) ×50,000.

Though 6FDA-BAAF dense films have an α of about 50 for CO_2/CH_4 ($P = 5.0 \times 10^{-9}$ [cm^3(STP)cm/cm^2 sec cmHg] for CO_2), the obtained asymmetric membranes had an α of less than 50 for CO_2/CH_4. It is thought that there are slight defects in the skin layer. The size and amount of defect were calculated using the following equation.

The defects of the membrane were assumed to be cylindrical, having a radius (R_p) and a porosity (ε). The gas flux through the defect-free part was expressed as follows:

$$Q_1 = (P/l) \times (1 - \varepsilon) \tag{1}$$

where Q_1 is volume flux through the defect free part, P is a gas permeability coefficient of the 6FDA-BAAF dense film, l is the thickness of the skin layer, and ε is porosity.

When the flow of gases through the cylindrical defect could be described by Knudsen flow, flow rate through the defect is

$$Q_2 = (4/3) \times R_p(2/\pi RTM)^{(1/2)} \Delta P/l \times \varepsilon \tag{2}$$

where Q_2 is molar flow rate, R_p is pore radius, R is gas constant, T is temperature, M is molecular weight, and ΔP is pressure. Consequently, total gas flux through the membrane is expressed as follows:

$$Q = Q_1 + Q_2 \tag{3}$$

The calculation result is shown in Figure 2. It could be calculated that the amount of defect is 10^{-6}% if the defect size is 5 nm.

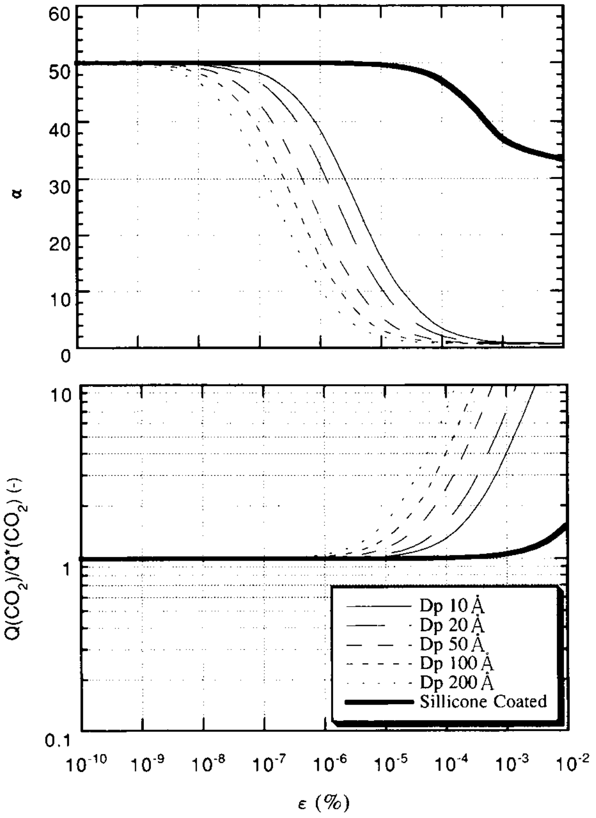


Figure 2 Simulation of the relationship between porosity at various defect sizes and permselectivity of the 6FDA–BAAF asymmetric membrane. The solid line shows the relationship after silicone coating.

Influence of Silicone Coating on Permselectivity

Gases can permeate faster through a defective part than through a dense part, but the defective part does not has an effective gas selective ability according to, for example, Knudsen flow. As the result, the total selectivity of a membrane having defects was lower than that of defect-free membrane. If defects in a membrane are filled by a polymer material, it may be effective to improve the selectivity of the asymmetric membranes.[24] The new type of asymmetric membrane developed in this study has slight defects, as mentioned above. We used silicone to fill the slight defects. As silicone rubber film has much higher gas permeability than 6FDA-BAAF polyimide film ($P_{CO_2} = 2.0 \times 10^{-7}$ [cm^3(STP)cm/cm^2 sec cmHg]), the decrease of flux caused by the filling of defects may be prevented. And because the selective ability of silicone rubber film (e.g., an α of 4 for CO_2/CH_4) was higher than the defective part, it was thought that the total selectivity of asymmetric membrane may be improved by the filling without decreasing flux drastically. The simulation result of the asymmetric membrane filled by silicone rubber was shown as a thick solid line in Figure 2. This simulation was calculated using the parallel model on the basis of the assumption that the defects were filled by silicone rubber. This result suggested that the selectivity was increased by filling silicone rubber without decreasing flux drastically. In practical terms, we examined the effect of the silicone coating on the skin layer of 6FDA-BAAF polyimide asymmetric membrane to fill the defects. The selectivity of the membrane prepared by the silicone coating was increased to around 40, and the flux was decreased slightly, as shown in Figure 3. It was confirmed that the silicone coating was an effective method to repair the defects of skin layer.

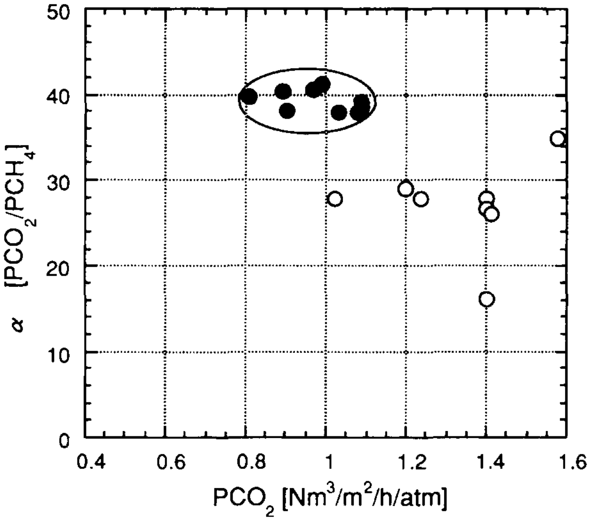


Figure 3 The influence of a silicone coating on permselectivity of the 6FDA-BAAF polyimide asymmetric membrane: ●, after silicone coating; ○, values before silicone coating.[23]

Table I Permselectivity of 6FDA–BAAF Asymmetric Membrane for Various Gases

Gas	P [Nm^3/m^2/h/atm]	α
CO_2	1.0×10^0	40 (—/CH_4) 23 (—/N_2)
CH_4	2.5×10^{-2}	—
O_2	1.8×10^{-1}	4.2 (/N_2)
N_2	4.3×10^{-2}	

The permselectivity of silicone coated 6FDA-BAAF polyimide asymmetric membrane for various gases is shown in Table I. It was confirmed that the membrane developed in this study has high permselective performance. And it was also confirmed that these values were constant for large-scale manufacturing.

CONCLUSION

The 6FDA-BAAF asymmetric membrane was developed as a new type of membrane. The skin layer thickness of the asymmetric membranes were 40–60 nm. It was calculated that the porosity was 10^{-6}–10^{-5}% if the defect size is 5 nm, and gases permeate through the defects according to Knudsen flow.

The permselectivity of 6FDA-BAAF polyimide asymmetric membranes coated by silicone had an α of 40 for CO_2/CH_4 and a flux of 1.0[Nm^3/m^2-hr-atm] (= 3.7×10^{-4} [cm^3(STP)/cm^2-sec-cmHg]) for CO_2, and α of 4.3 for O_2/N_2 and a flux of 2.0×10^{-1} [Nm^3/m^2-hr-atm] (= 7.1×10^{-5} [cm^3(STP)/cm^2 sec cmHg]) for O_2.

It is expected that the 6FDA-BAAF polyimide asymmetric membrane can be utilized for various gas separation applications at the industrial level.

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