

Plasma-Polymerized Membranes and Gas Permeability III

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Synopsis

Plasma-polymerized films of hexamethyldisiloxane were deposited onto various porous substrates having different pore sizes, and the gas permeability of these composite membranes was studied. In each membrane, permselectivity between oxygen and nitrogen was found, but the oxygen permeation rate was different with each substance tested. The minimum thickness of the plasma-polymerized film needed to plug all pores and show permselectivity is about five times the pore radius of the porous substrate. The maximum oxygen permeation rates of the permselective composite membranes are approximately proportional to the effective areas for the gas permeation and inversely proportional to the pore sizes. The composite membranes show high oxygen permeation rates in cases using porous glass hollow fibers which have small pore sizes and large surface porosity as porous substrates. In cases using polysulfone hollow fibers which have high permselectivity, the composite membranes show much higher permeability ratios of oxygen-to-nitrogen than do those of the porous glass hollow fibers.

INTRODUCTION

Polymeric materials can be formed by electric discharge from organic vapors. Since Goodman reported the glow discharge polymerization in vapor phase, this plasma polymerization has been studied by many authors.¹⁻³ The principal features of plasma polymerization are: (1) most of the organic compounds can be polymerized; (2) uniform, pinhole-free, thin polymeric films can be formed on various substrates; and (3) these films adhere well to the substrates. Studies have been made on applications of the plasma polymerization technique to reverse osmosis membranes, films for electric condensers, resist films, surface modification of polymers, and membranes for gas separation.⁴⁻¹¹

Fundamental properties required of membranes for gas separation are high permeability and high permselectivity.¹² These properties are considerably different for membrane materials. For example, polydimethylsiloxane film has a high oxygen permeability coefficient and a low oxygen-to-nitrogen permeability ratio, whereas the polycarbonate film has a low oxygen permeability coefficient and a high oxygen-to-nitrogen permeability ratio.¹³

It is well known that the permeability and selectivity of membranes depend on the chemical structures, thickness, and homogeneity of the polymeric films. We reported previously that the composite membranes consisting of a porous substrate and a pinhole-free thin film formed by plasma polymerization were recognized as having a fairly high oxygen permeability and oxygen-to-nitrogen permeability ratio.^{8,9} These organosilicic compounds were suitable as mono-

TABLE I
 Porous Substrates

Porous substrate	Material	Pore size (Å)	Surface porosity (%)
Cel	Polypropylene	400 × 2000 ^a	—
NP1000	Polycarbonate	610 ^{a, b}	9.1
NP500	Polycarbonate	230 ^{a, b}	1.5
NP300	Polycarbonate	100 ^{a, b}	0.32
G - 1	Silica	44 ^c	35
G - 2	Silica	300 ^c	35
PS	Polysulfone	—	—

Abbreviations: Cel: Celgard; NP1000 = nucleopore; G - 1 = porous glass hollow fiber; PS = porous polysulfone hollow fiber.

^a Determined from the SEM observation.

^b Pore radius.

^c Measured by the N₂ adsorption method.

mers for this purpose, and the chemical structures of the monomers influenced the permeability characteristics of composite membranes.

From our further study, it became clear that the permeability of the composite membranes was influenced not only by the monomers, but also by the porous substrates. In the present work, the nature of the porous substrates, which effected change in gas permeability, was studied using various porous substrates.

EXPERIMENTAL

Materials

An organosilicic compound used for plasma polymerization was hexamethyldisiloxane (M₂, Nakarai Chemical Co. Ltd.) It was used without further purification.

Various porous films used as the porous substrates of composite membranes are shown in Table I. NP series and Cel films are commercially available. NP films have circular pores, and Cel has rectangular pores. The porous glass hollow fibers with a pore radius of 44 Å were prepared as follows. Hollow fibers were spun by the melt-spinning method from sodium-boro-silicate glass which was composed of 65 wt% of SiO₂, 30 wt% of B₂O₃, and 5 wt% of Na₂O. Their outer diameter was 250 μm and the thickness was 15 μm. The fibers were heated to 500°C for 16 h to separate the glass into two phases, SiO₂ phase and B₂O₃-Na₂O phase. After cooling the fibers to room temperature, about 1000 fibers were exposed to the plasma of CF₄-O₂ mixed gases (the pressure was 0.23 Torr, radio frequency power was 100 W) for 20 min in order to etch the surface layer of the fiber in which the B₂O₃-Na₂O phase hardly developed. The B₂O₃-Na₂O phase was leached out from the fibers in 1-N hydrochloric acid at 98°C for 3 h, and subsequently washed in boiling water for several hours. The fibers were taken out and air-dried, and soaked in 0.5-N sodium hydroxide solution at 30°C for 8 min to remove the residual B₂O₃. The fibers were washed with water and air dried. Subsequently, they were heated at 500°C for 30 min. In this manner, porous glass hollow fibers composed of silicon dioxide were obtained. The pore radius was 44 Å, which was measured

with the N_2 adsorption method. Porous glass hollow fibers with a pore radius of 300 Å were prepared in a manner similar to that described above, except that the composition of the starting glass was 65 wt% of SiO_2 , 28 wt% of B_2O_3 , and 7 wt% of Na_2O , and the conditions of the heat treatment for the phase separation were 120 h at 550°C. Porous polysulfone hollow fibers were prepared by conventional spinning techniques. Dimethylformamide solution of polysulfone resin (Aldrich Co. Ltd.) was made to flow from an outer nozzle and water was flowed through an inner nozzle, and the polymer solution and the water were immersed in water. The resin was gelled in the anisotropic form and the hollow fibers were thus prepared.

Plasma Polymerization

The apparatus and experimental procedures for plasma polymerization were the same as those reported previously in detail.^{8,9} The system is constructed of a Pyrex glass chamber of the bell jar type, a monomer inlet, a vacuum pump, a Pirani gauge, and a radio frequency power supply of 13.56 MHz with a matching network. In order to deposit plasma-polymerized film of almost equal thickness on each kind of substrate, the substrates were placed on the wall of the bell jar-type chamber as shown in Fig. 1; three kinds of NP film and a glass slide were placed side by side in 9 lines on the Cel film [Fig. 1(B)], and these substrates were placed on the wall [Fig. 1(A)]. Each kind of substrate was also placed on the sample stage. The hollow fiber-type composite membranes were set as follows: Several pieces of the hollow fibers about 10 cm long were placed on a metallic wire frame, and both ends of the fibers were adhered on the frame with adhesive tape to prevent contact between

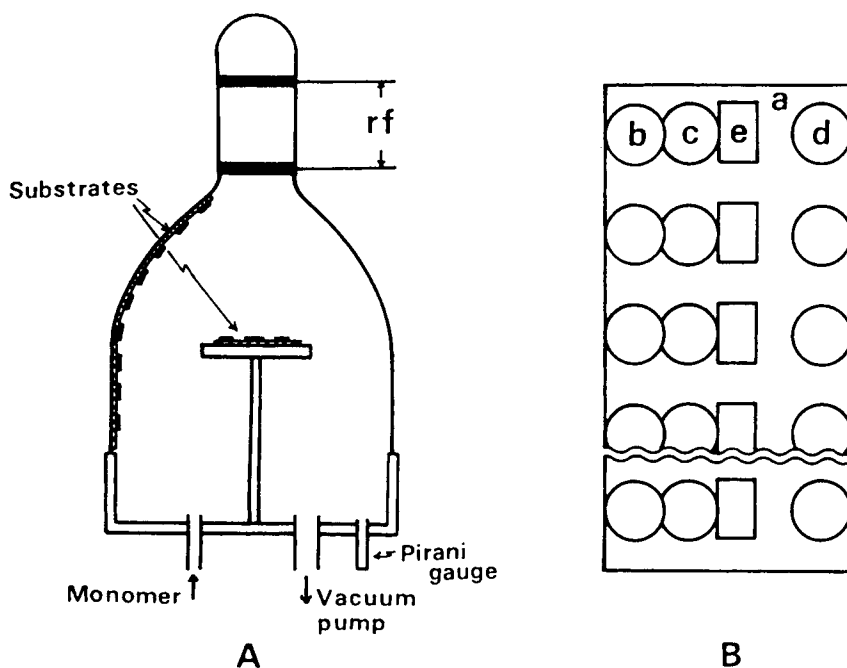


Fig. 1. Schematic diagrams of the apparatus for the plasma polymerization (A) and the porous substrates set on the wall (B): (a) Cel, (b) NP1000, (c) NP500, (d) NP300, (e) a glass slide.

fibers. The metal frame was placed on the sample stage keeping the fibers from contacting the stage. The system was evacuated to 0.01 Torr by the rotary vacuum pump. Vapor of M_2 was introduced into the chamber. Through this process, the substances were controlled with a pressure of 0.2 Torr by the appropriate opening of a needle valve in accordance with the evacuating speed of the pump. Under this condition, a radio frequency electric power of 50 W was supplied to continue plasma polymerization for certain periods of time.

Measurement of Gas Permeability

Gas permeability of the flat-sheet-type composite membranes was measured as follows. Measurements were performed at 25°C by the partition method on a Yanako GTR 10s. A test cell containing a membrane and a measuring tube for collecting the gas permeated through the membrane, were evacuated to a pressure of 0.01 Torr before each run. Atmospheric air was introduced to one side of the membrane and the gas which permeated through the membrane was collected in the measuring tube for a few minutes. The collected gas was carried to a gas chromatographic (GC) analyzer, and volumes of oxygen and nitrogen gases were determined. GC analysis was carried out on a Yanako G180. The permeation rate R_x was calculated using the expression $R_x = v / s \cdot t \cdot \Delta P_x$, where v is the volume of the permeated gas, s is the area of the membrane, t is the collecting time, and ΔP_x is the partial pressure difference of gases between the membrane.

Gas permeability of hollow fiber-type composite membranes were measured as follows. One end of the fiber was sealed and the other was inserted into a flexible tube and sealed with epoxy resin. The outside of the hollow fiber was exposed to atmospheric air and the inside of the fiber was evacuated through the flexible tube with a rotary vacuum pump. After the system was isolated from the vacuum pump, the gas which permeated through the membrane was collected in the measuring tube for varying periods of time. The collected gas was carried to the GC analyzer and the volumes of O_2 and N_2 were determined as mentioned above. This measurement was performed twice, at two sampling times (5 and 10 s). The permeation rate was calculated from the difference in volumes of the permeating gases (v) and in the sampling times (t) between the two measurements.

Measurement of Thickness

A plasma-polymerized film was deposited on a glass slide and the thickness of the film was determined by using the multibeam interferometry method.

RESULTS AND DISCUSSION

In plasma polymerization, polymerization time and the positions of the porous substrates in the chamber were changed in order to vary thickness of the plasma-polymerized films. Composite membranes were prepared from M_2 as the monomer and various flat-sheet-type porous films, NP300, NP500, NP1000, and Cel. Measurements were made of the oxygen permeation rate (R_{O_2}) expressed in terms of cm^3 (STP)/ $cm^2 \cdot s \cdot cmHg$ and oxygen-to-nitrogen permeability ratios (R_{O_2}/R_{N_2}) of these composite membranes.

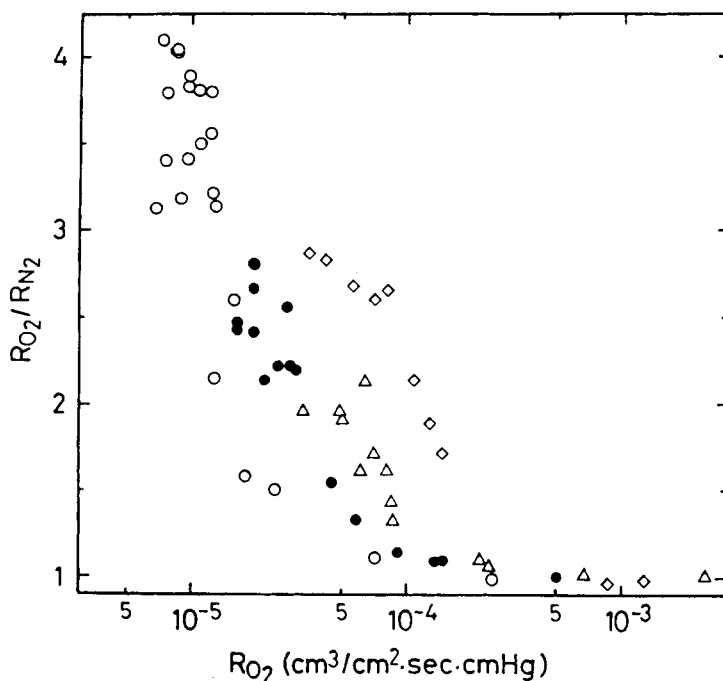


Fig. 2. Gas permeability of the composite membranes prepared from various porous films: (\diamond) Cel; (Δ) NP1000; (\bullet) NP500; (\circ) NP300.

Figure 2 shows the relationship between R_{O_2} and R_{O_2}/R_{N_2} of the composite membranes prepared under various conditions. For each kind of substrate, a sigmoid-like relationship is observed between these two parameters for gas permeability. This behavior is related to the plugging of the pores on the surface of the substrates by the plasma polymer. When the plasma-polymerized films are too thin to plug the pores, the composite membranes do not show permselectivity. When the films become thick enough to plug the pores, permselectivity appears and the R_{O_2}/R_{N_2} values rise rapidly with a slight decrease of R_{O_2} . In this region where the R_{O_2}/R_{N_2} values increase rapidly, the plasma film has the minimum thickness required to plug all pores and for the membranes to show permselectivity. Therefore, the R_{O_2} value in this region is important to evaluate the gas permeability characteristics of the plasma polymers. The values of R_{O_2}/R_{N_2} increase at different regions of R_{O_2} for different porous films, and the value of R_{O_2} of Cel is about one magnitude larger than that of NP300. In our previous paper, we proposed that gas permeability of composite membranes is influenced by the monomers used for plasma polymerization.⁹ These results suggest that gas permeability of composite membranes is influenced not only by monomers but also by porous films used for substrates.

To determine the factors in the porous substrates which affect the gas permeability of the composite membranes, the thickness of the plasma films, which is known to affect the gas permeability rate, was measured. The thickness of the plasma-polymerized films varied with the positions where the films were deposited, however, the thickness was found to be almost uniform

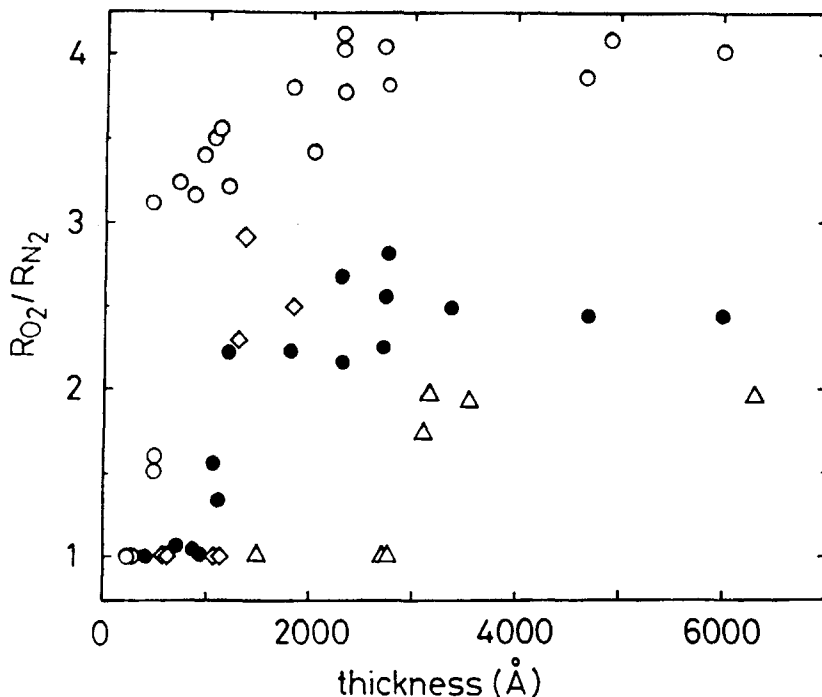


Fig. 3. Relationship between the thickness of the plasma-polymerized films and the R_{O_2}/R_{N_2} value of the composite membrane: (\diamond) Cel; (Δ) NP1000; (\bullet) NP500; (\circ) NP300.

in the direction of the circumference of the bell jar-type reactor by observing the interference colors of the films. Therefore, in order to deposit plasma films of the same thickness on each kind of substrate, the substrates were placed in the chamber as shown in Figure 1. Film deposition was made on the glass slide and the porous substrates under these conditions.

Thickness was determined with the former sample and gas permeability was determined with the latter samples. Figure 3 shows the relationship between thickness of plasma-polymerized films and R_{O_2}/R_{N_2} of composite membranes prepared from flat-sheet-type porous films. The value of R_{O_2}/R_{N_2} increases drastically at different thicknesses for each porous film. These results indicate that the thickness of the plasma-polymerized films required to plug all pores of porous films varies with the pore sizes. For each kind of substrate, this thickness corresponds with the thickness at which the R_{O_2}/R_{N_2} value increases rapidly (Fig. 2), because both of the thicknesses are the minimum value required for the composite membrane to show permselectivity. When the data in Figure 3 are plotted, with the thickness where the R_{O_2}/R_{N_2} value increases as ordinate and the pore radius of the porous substrate used as abscissa, a proportional relationship is obtained between these two values as shown in Figure 4. It is found that a thickness of the plasma film larger than the pore radius of the porous substrate by a factor of about 5 is required to plug all of the pores and for the membrane to show permselectivity. In a case of rectangular pores, as with Cel, the length of the shorter side is a dominant factor.

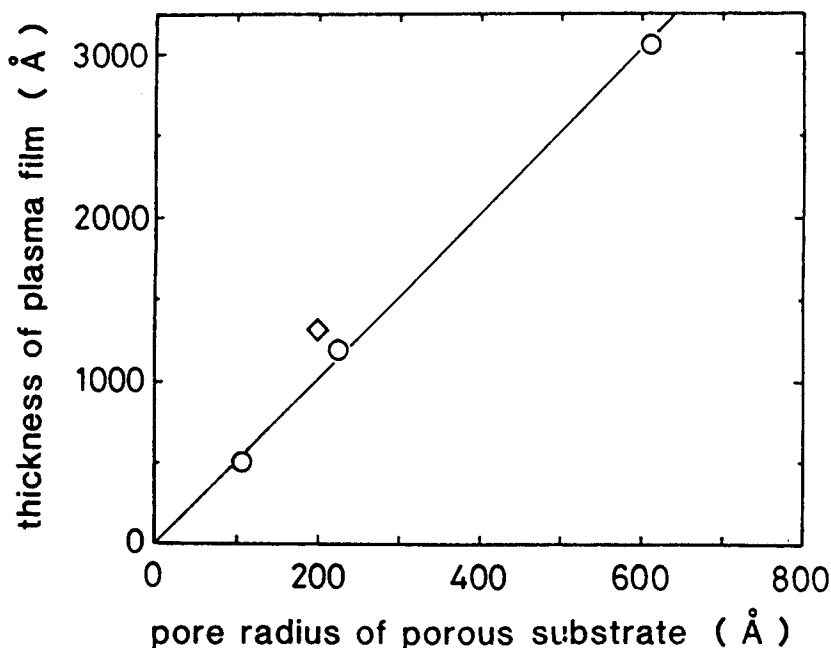


Fig. 4. Relationship between pore radii of the porous substrates and thickness of the plasma-polymerized films required to plug all pores: (○) NP films; (◇) Cel, in this case a half length of the shorter side of the rectangular pore is adopted as the pore radius.

There is a possibility that the surface layer of the substrate is affected by the plasma, and the surface structure, pore size, and surface porosity, are changed. However, the NP film has cylindrical pores, not a skin layer as in anisotropic membranes, which is apt to be affected by the plasma, and a proportional relationship is observed between the thickness of the plasma film and the pore radius of the NP film in Figure 4. Therefore, it is considered that the surface structure of the substrate is not changed due to the plasma in this study.

It is well known that the permeation rate is inversely proportional to the film thickness. Therefore, the permeation rate increases with decreased thickness. The corrected value of R_{O_2} by the thickness of the plasma film was calculated from the R_{O_2} value and the thickness at which the R_{O_2}/R_{N_2} increased rapidly in Figures 2 and 3, respectively. The R_{O_2} value and the corrected value were shown in Table II. Despite using the same monomer, the corrected values vary more widely than the uncorrected values. It is found that in addition to the thickness of the plasma polymer there are other factors which affect the gas permeability of composite membranes.

Composite membranes in this work can be divided into two areas by gas permeation type; one area over the pore where gas permeates only through plasma-polymerized films and another area where gas must permeate through both plasma-polymerized films and the nonporous part of porous films. Polycarbonate resin which is a material of the NP films has a higher oxygen-to-nitrogen permeability ratio (about 4), but about two orders lower oxygen permeability coefficient than that of the silicone resin. The NP film with a

TABLE II
Correction on the R_{O_2} Value by the Factors Which Affect Gas Permeability

Porous substrate	R_{O_2} ^a	Thickness [Å]	R_{O_2} corrected by thickness ^b	Effective area [%]	R_{O_2} corrected by thickness and effective area ^b
NP 1000	6.5×10^{-5}	3100	2.0×10^{-9}	53	3.8×10^{-9}
NP 500	3.5×10^{-5}	1200	4.2×10^{-10}	11	3.8×10^{-9}
NP 300	1.7×10^{-5}	500	8.5×10^{-11}	2.5	3.4×10^{-9}
Cel	1.3×10^{-4}	1300	1.7×10^{-9}	—	—

^aThe R_{O_2} value at the R_{O_2}/R_{N_2} of 2, in $\text{cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$.

^bIn $\text{cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$.

thickness of 5 μm is much thicker than the plasma film with a thickness of several thousand angstroms. It is considered that plasma-polymerized films placed over the pores contribute to gas permeation, however, covering other places plays only a minor role in gas permeation, because the porous film material disturbs gas permeation. Only part of the composite membrane is effective in gas permeation, and to determine an oxygen permeability coefficient of the plasma polymer the R_{O_2} value must be corrected not only by the thickness, but also by the effective area. The effective area of each composite membrane was determined by reiterating the calculation of the diffusion equation with a computer under conditions where the ratio of plasma film thickness to pore radii was 5:1 and gas permeation through the nonporous part of the substrate was negligible in comparison with that through only the plasma polymer.* For each kind of composite membrane, the R_{O_2} value in Table II was corrected by the thickness of the plasma film and the effective area; multiplied by the thickness and divided by the effective area. These corrected values and the effective areas are also shown in Table II. The R_{O_2} values are approximately equal, irrespective of the kind of substrate. It is found that the maximum R_{O_2} value of the permselective composite membrane is directly proportional to the effective area and inversely so to the pore size of the porous substrate. A gas permeability coefficient of the plasma polymer must be calculated not only by thickness, but also by the effective area, though it seems correct to calculate it from the R_{O_2} value and the thickness.

When the effective area is small and/or the porous substrate has a skin layer, gas permeation through the nonporous part makes a greater contribution to the overall gas permeation. As a result, for NP films, the maximum values of R_{O_2}/R_{N_2} increase with the decreasing effective area. In Figure 3, the R_{O_2}/R_{N_2} values of the membrane prepared from NP300 increase gradually in the range of 500–2000 Å in thickness. These increases are attributed to the large contribution of gas permeation through the nonporous part whose material has higher permselectivity than does the silicone resin.

*If the plasma polymerized film is much thicker, the effective area comes close to 100%. The more detailed report of this calculation will be presented elsewhere.

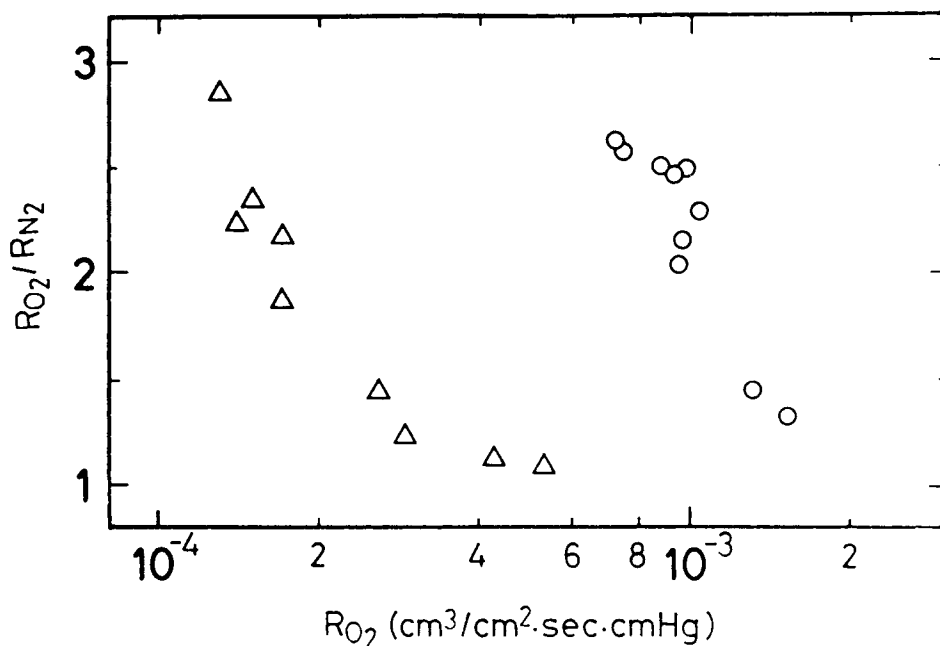


Fig. 5. Gas permeability of the composite membranes prepared from the porous glass hollow fibers: (○) G-1, $r = 44 \text{ \AA}$; (△) G-2, $r = 300 \text{ \AA}$.

In conclusion, the prerequisites for porous substrates required to obtain highly permeable composite membrane are:

1. The pore size is small (to make the plasma-polymerized films thinner).
2. The surface porosity is large (to enlarge the effective area for gas permeation).
3. The porous substrate is made from a highly permeable and permselective material or has a thin surface layer (to make the porous substrate participate in the gas permeation).

Two kinds of porous glass hollow fibers, which satisfied prerequisites 1 and 2, possessing relatively large surface porosity (35%), and small pore radii (44 \AA and 300 \AA , respectively), were used as the porous substrates. Figure 5 shows the gas permeability characteristics between R_{O_2} and R_{O_2}/R_{N_2} of composite membranes prepared from the glass hollow fibers. It is found that the R_{O_2} value obtained from the 44 \AA pore radius fiber is about 7 times larger than that of the 300 \AA pore radius fiber where the R_{O_2}/R_{N_2} value increases rapidly with a slight decrease of the R_{O_2} value in Figure 5. These results substantiate the fact that the maximum values of R_{O_2} of the permselective composite membranes are inversely proportional to the pore radii of the porous substrates used. Highly permeable composite membranes can be obtained when small pores and large surface porosity substrates are used. In the case of porous glass, gas permeation through the nonporous part, glass, must be negligible. The effective area of 60% was obtained by the computer simulation.

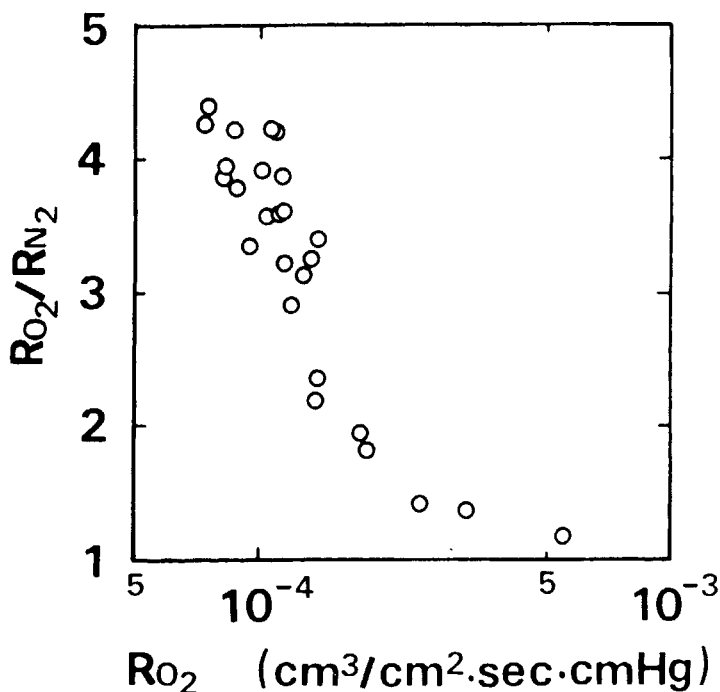


Fig. 6. Gas permeability of the composite membranes prepared from the porous polysulfone hollow fibers.

The thickness of the plasma film was estimated by using the relationship in Figure 4. From these values, the oxygen permeability coefficient of the plasma-polymerized M_2 of 3.7×10^{-9} cm³ (STP) · cm/cm² · s · cmHg was obtained. R_{O_2}/R_{N_2} of plasma-polymerized M_2 is 2.5 ~ 2.6. In previous papers, we described the chemical structure of the plasma-polymerized M_2 as being similar to that of the polydimethylsiloxane.⁸ It is well known that polydimethylsiloxane resin is the most permeable polymeric material for common gas such as O₂ and N₂, and its O₂ permeability coefficient is $3 \sim 6 \times 10^{-8}$ cm³ (STP) · cm/cm² · s · cmHg and the R_{O_2}/R_{N_2} value is about 1.9. The oxygen permeability coefficient of plasma-polymerized M_2 obtained in this study, is one magnitude lower than that of the polydimethylsiloxane resin, and the R_{O_2}/R_{N_2} of plasma-polymerized M_2 is higher than that of the polydimethylsiloxane resin. These results suggest the presence of crosslinked structures in the plasma-polymerized M_2 .

Polysulfone hollow fibers were used as porous substrates which satisfy prerequisite 3. The R_{O_2}/R_{N_2} of polysulfone resin is 5.4, a high value*. The polysulfone hollow fiber in the anisotropic form has a skin layer on the surface. The skin layer is thin and the surface porosity is very small.¹⁴ The relationship between R_{O_2} and R_{O_2}/R_{N_2} of composite membranes is shown in

*The oxygen permeability coefficient was 3.8×10^{-11} cm³(STP) · cm/cm² · s · cmHg. This value was determined from measurements on a dense film.

Figure 6. The R_{O_2}/R_{N_2} of the composite membranes prepared from the polysulfone hollow fibers shows a high value, 4.2, and R_{O_2} is about 1×10^{-4} cm^3 (STP)/ $\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$. The high value of R_{O_2}/R_{N_2} of the composite membrane using the polysulfone hollow fiber is attributed to the large contribution of the gas permeation through the nonporous part of the polysulfone fiber, and to being closer to that of the polysulfone resin.

CONCLUSION

Composite membranes were prepared from plasma-polymerized films and various porous substrates. The thickness of the plasma-polymerized films required to plug all pores is 5 times as large as the pore radius. Gas permeability characteristics of composite membranes are different for each porous film. Oxygen permeation rates are approximately proportional to the effective area for the gas permeation and inversely related to the thickness of the plasma-polymerized films and pore sizes. The O_2 permeability coefficients must be calculated by these two parameters, because the effective area is the total area in cases where films are simply placed on the porous substrate, but the plasma-polymerized films adhere well to the substrates, therefore, the effective area must become small if the nonporous part of porous substrates is hardly permeable. From these studies, proven methods of establishing composite membranes permeability have been described. Using porous glass fibers as substrates, highly permeable composite membranes were obtained, and using polysulfone hollow fibers, highly permselective membranes were obtained.

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