

Plasma Polymerized Membranes and Gas Permeability. I

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Synopsis

Gas permeability of composite membrane prepared by plasma polymerization of various organic compounds was studied. In the membrane, a pinhole-free polymeric thin film was formed on a porous substrate. This film below 0.2 μm in thickness had sufficient mechanical strength for gas separation. The composite membranes were recognized to have high permeability and high permselectivity. Especially, the membranes prepared from hexamethyldisiloxane showed high permeation rate for oxygen, and those prepared from 1-hexene or cyclohexene showed high permselectivity between oxygen and nitrogen. Chemical structure of plasma-polymerized film prepared from hexamethyldisiloxane was similar to that of dimethylpolysiloxane with a crosslinking of the polymer. The high permeability and high permselectivity of this film is considered to be due to its structure as mentioned above.

INTRODUCTION

Many polymeric membranes and their synthetic methods so far have been studied by various authors from different points of view.¹⁻⁵ Fundamental properties required for membranes for gas separation are high permeability and high permselectivity. These properties are affected by chemical structure and thickness of the membranes. A pinhole-free thin membrane made up of high permselective material will be suitable for gas separation.

A polymeric material can be deposited on a substrate placed in the plasma or glow discharge of an organic vapor.⁶⁻¹¹ The reaction product will be in the form of powder, thin film, oil, or a combination of these, depending on the plasma polymerization conditions and the kinds of organic compounds. The films produced by these processes are usually insoluble and pinhole-free and adhere well to the substrate. Plasma polymerization technique is considered as a unique method for preparation of thin polymeric films.

In the present work, the gas permeability of plasma polymerized membranes was studied. In order to make highly permeable membranes, a composite membrane comprising a porous substrate and a homogeneous thin film thereon was designed. This homogeneous thin film was prepared by plasma polymerization.

EXPERIMENTAL

Materials. The porous substrate used was a porous polypropylene membrane (Cellgard) with 20 μm thickness and rectangular pores of 2000 \AA \times 200 \AA in their maximum size.

Organic compounds used for plasma polymerization were hexamethyldisiloxane, triethoxyvinylsilane, 1-hexene, and cyclohexene (Wako Pure Chem. Ind.) of extra pure grade, and they were used without further purification.

Plasma System. A schematic diagram of the apparatus is shown in Figure 1. A Pyrex glass chamber of a bell jar type having a diameter of 20 cm and a height of 60 cm was evacuated from the bottom by a rotary vacuum pump via a cold trap. Pressure in the chamber was monitored by a Pirani gage during the plasma polymerization process. The raw material was reserved in an egg-shaped flask so that the vapor of the raw material was gently supplied from the bottom of the chamber via the needle valve. Plasma polymerization was initiated by loading high-frequency electric power of 13.56 MHz to a electrode wound around top of the chamber.

Procedure of Plasma Polymerization. After closing the needle valve for the raw material, the chamber was evacuated by the rotary vacuum pump until the Pirani vacuum gage indicated the pressure of 0.01 Torr. An organic vapor was introduced into the chamber, and the pressure was controlled at 0.2 Torr by appropriate opening of the needle valve in accordance with the evacuating speed of the rotary vacuum pump. Under this condition the radio frequency electric power of 50 W at 13.56 MHz was supplied to continue plasma polymerization for a certain period. Porous substrates were placed at various positions in the chamber as denoted by 1, 2, 3(1), 3(2), and 3(3) in Figure 1.

IR Measurement. Infrared (IR) spectra for each sample were obtained on a Jasco DS-701G infrared spectrophotometer by the ATR method.

SEM Observation. The microstructure of composite membranes was observed under a Hitachi S-450 Scanning Electron Microscope. The sample was coated with evaporated gold using a Eico IB-3 ion coater to a thickness of about 200 Å.

Measurement of Gas Permeability. Permeability measurements were performed at 25°C by the partition method on a Yanako GTR 10S. A test

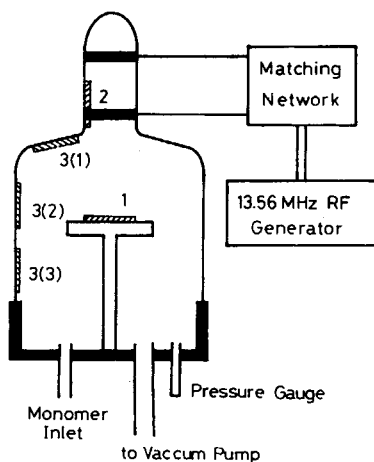


Fig. 1. A schematic diagram of the apparatus for plasma polymerization: 1, sample stage; 2, head of chamber; 3 (1), shoulder of chamber; 3 (2), top of side wall; 3 (3), bottom of side wall.

cell containing a membrane and a measuring tube in which the gas permeated through membrane was collected were evacuated to pressure of 0.01 Torr before each run. After the system was isolated from a vacuum pump, atmospheric air was introduced to one side of the membrane and the gas permeated through the membrane was collected in a measuring tube for a few minutes. Subsequently, a carrier gas (He) stream was passed through the measuring tube, and the collected gas was carried to a gas chromatographic (GC) analyzer. GC analysis was carried out on a Yanako G180 instrument with a column of Molecular Sieve 5 A for separation of oxygen and nitrogen gases and a thermal conductivity detector for determination of the volume of each gases. Permeability rate P_x was calculated from the expression $P_x = v/S \times t \times \Delta p_x$ where v is the volume of permeated gas, S the area of the membrane, t the collecting time, and Δp_x the partial pressure of gas between membrane.

RESULTS AND DISCUSSION

IR Spectra

Figure 2 shows IR spectra of plasma polymerized membranes formed on a porous substrate. Symbols a, b, c, and d denote IR spectra of membranes prepared from hexamethyldisiloxane, triethoxyvinylsilane, 1-hexene, and cyclohexene, respectively. The characteristic absorption of Figure 2 was similar to that of raw material,¹² as indentified by absorption at 1255 cm^{-1} (δ_s , CH_3 in SiCH_3), $1100\text{--}1000\text{ cm}^{-1}$ (ν_{as} , SiOSi), 840 cm^{-1} and 750 cm^{-1} [ρ , CH_3 in $\text{Si}(\text{CH}_3)_3$].¹³ Absorption band at 800 cm^{-1} which is assigned to stretch

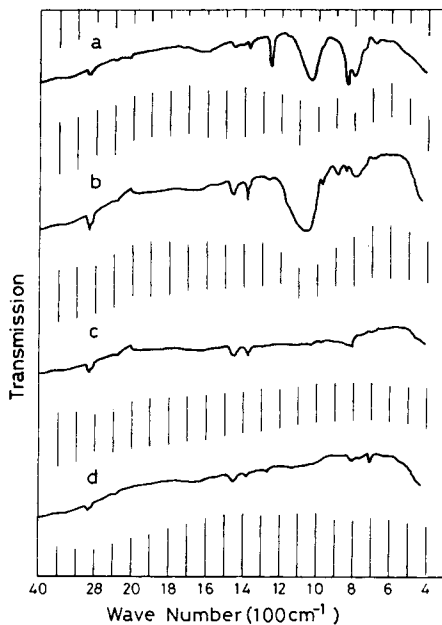


Fig. 2. IR spectra of plasma polymerized membranes formed on porous polypropylene: (a) hexamethyldisiloxane; (b) triethoxyvinylsilane; (c) 1-hexene; (d) cyclohexene.

vibration of Si—C linkage in dimethylsiloxane was apparently seen. These results suggest that at least two species of siloxane structure such as trimethylsiloxane and dimethylsiloxane exist in plasma-polymerized films prepared from hexamethyldisiloxane.

In Figure 2(b), absorption bands at $1100\text{--}1000\text{ cm}^{-1}$ and 800 cm^{-1} were seen, but those at 1255 cm^{-1} , 840 cm^{-1} , and 750 cm^{-1} were weak or not seen. This implies that siloxane bonding participates in forming a polymeric film, and Si atom of this siloxane structure does not bind methyl group. Decrease in absorption intensity at 1600 cm^{-1} and 960 cm^{-1} , which are assigned to stretch vibration of $\text{CH}=\text{CH}$ and deformation vibration of C—H in $=\text{CH—}$, respectively, indicates consumption of the vinyl group in the raw material during the plasma polymerization process.

In Figure 2(c) and 2(d), the absorption spectra of polymerized membranes are similar to that of substrate, polypropylene. This suggests that plasma polymerized films from 1-hexene and cyclohexene are composed of hydrocarbon having a high molecular weight.

Microstructure of Composite Membranes

Figure 3 shows typical electron micrographs of composite membranes. From the micrograph of the cross section, a homogeneous plasma polymerized film with thickness of about $0.2\text{ }\mu\text{m}$ is found to be formed on a porous substrate. From the micrographs of the membrane surfaces, it is clear that the polymer is formed homogeneously.

Gas Permeability

Permeability data of the composite membranes prepared from various organic compounds are presented in Table I. Here, P_{O_2} and P_{N_2} denote permeation rates of the membranes for oxygen and nitrogen, respectively, and are expressed in terms of $\text{cm}^3\text{ (STP)/cm}^2 \cdot \text{s} \cdot \text{cm Hg}$. The permeability ratio for oxygen and nitrogen ($P_{\text{O}_2}/P_{\text{N}_2}$) of any composite membranes was over 2. Especially, the permeability ratio of the membranes prepared from 1-hexene and cyclohexene were over 3.

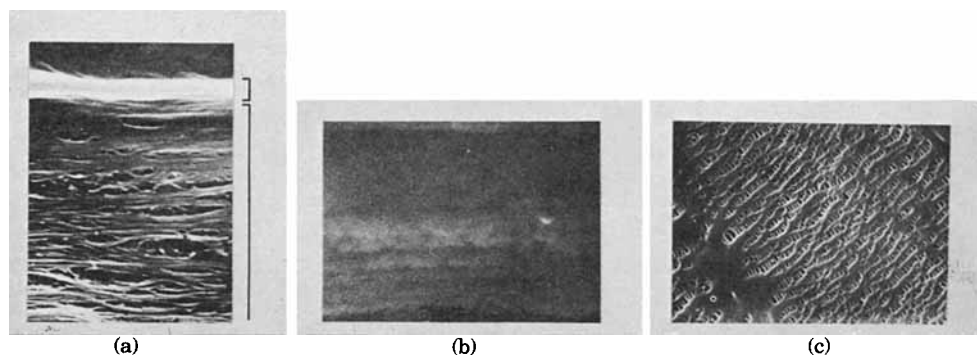


Fig. 3. Scanning electron micrographs of composite membrane: (a) cross section of membrane; top bracket marks polymer film, bottom bracket marks porous substrate. Bar = $1\text{ }\mu\text{m}$. (b) surface of plasma polymerized membrane. (c) surface of porous substrate. Bar = $1\text{ }\mu\text{m}$.

TABLE I
Gas Permeability of Plasma Polymerized Membranes Prepared from Various Organic Compounds

Sample no.	Monomer	Plasma polymerization conditions					Permeation rate ^a		
		Pressure (Torr)	rf power (W)	Time (min)	Position	P_{O_2}	P_{N_2}	P_{O_2}/P_{N_2}	
1	Hexamethyldi-siloxane	0.2	50	10	1	1.5×10^{-4}	6.5×10^{-5}	2.3	
2		0.2	50	20	3(1)	1.0×10^{-4}	4.0×10^{-5}	2.6	
3		0.2	50	30	1	1.2×10^{-4}	4.5×10^{-5}	2.6	
4	Triethoxyvinyl-silane	0.2	50	30	1	4.4×10^{-5}	2.0×10^{-5}	2.3	
5		0.2	50	30	3(2)	7.0×10^{-5}	2.8×10^{-5}	2.5	
6	1-Hexene	0.2	50	30	3(1)	7.2×10^{-6}	2.7×10^{-6}	2.7	
7		0.2	50	60	3(2)	8.1×10^{-6}	2.4×10^{-6}	3.4	
8		0.2	50	60	2	7.4×10^{-6}	2.5×10^{-6}	3.0	
9	Cyclohexene	0.2	50	15	2	5.4×10^{-6}	2.0×10^{-6}	2.8	
10		0.2	50	15	2	6.1×10^{-6}	1.8×10^{-6}	3.4	
	Membrane ^b					6.2×10^{-6}	3.2×10^{-6}	2.0	

^a cm³ (STP)/cm² · s · cm Hg.

^b dimethylpolysiloxane (thickness 100 μm).

Table I also shows the permeability data of dimethylpolysiloxane membrane* with a thickness of 100 μm as a reference, which is said to be the highest permeability coefficients among the polymeric membranes on the market but to be difficult to fabricate thin film. The composite membranes prepared by plasma polymerization of any organic compounds show higher oxygen permeation rates than the reference membrane. This means that plasma polymerization technique enable us to prepare a pinhole-free thin film.

The composite membranes prepared from hexamethyldisiloxane showed 20 times higher oxygen permeation rates than the dimethylpolysiloxane membrane with a thickness of 100 μm . The oxygen permeation rate of this membrane was the highest of all plasma polymerized membranes. This desirable property may be derived from resemblance in the chemical structure between plasma polymerized film from hexamethyldisiloxane and dimethylpolysiloxane. The permeability ratio ($P_{\text{O}_2}/P_{\text{N}_2}$) of this membrane is about 2.5, and this value is higher than that of the reference membrane. The high permeability ratio of the plasma polymerized membranes suggests the presence of a crosslinked structure.

CONCLUSION

Composite membranes comprising a porous substrate and a pinhole-free thin film formed thereon by plasma polymerization were prepared. Permeability and permselectivity of these membranes were superior to the membrane made from dimethylpolysiloxane by a conventional method. Especially, the composite membrane prepared from hexamethyldisiloxane showed 20 times higher permeation rate for oxygen than the dimethylpolysiloxane membrane with thickness of 100 μm . The former also showed higher permselectivity than the latter. These desirable properties of gas separation will be derived from the reduced thickness and the chemical structure of plasma-polymerized film. This film with thickness below 0.2 μm formed on a porous substrate has sufficient mechanical strengths for gas separation. IR spectra show that the chemical structure of this film resembles dimethylpolysiloxane which shows the highest permeation rates for oxygen. The crosslinked structure of this plasma-polymerized film contributes to high permselectivity. From the facts described above, we can conclude that plasma polymerization technique is useful for preparing the pinhole-free thin film.

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* It is well known that dimethylpolysiloxane is the most permeable polymeric material for common gas such as O_2 and N_2 .¹⁴

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