Plasma Deposition of Vinyl Monomers onto Poly(4-methyl-1-pentene)/Poly(dimethyl siloxane) Blend Membrane for Enrichment of Oxygen From Air

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ABSTRACT: An oxygen enriched membrane with improved O_2-to-N_2 selectivity was prepared by plasma deposition vinyl monomers onto poly(4-methyl-1-pentene)(TPX)/poly(dimethylsiloxane) (PDMS) blend membrane. The effects of deposition time, supply power, and kinds of monomers on the gas separation performance of membranes were studied. The monomers used in this study included methyl methacrylate (MMA), vinyl acetate (VAc), 2-hydroxy-ethyl methacrylate (HEMA), and ethyl acrylate (EA). The structure of the modified membrane was confirmed by FT-IR, SEM, and X-ray diffraction. The crystallinity of the plasma modified membrane was higher than that of the unmodified membrane. Pressure-normalized O_2 flux and O_2-to-N_2 selectivity through a TPX/PDMS blend membrane plasma coated with vinyl acetate (PVAc-p-TPX/PDMS) at 10 W—20 min, were 0.81×10^{-6} cm^3 cm^{-2}-s^{-1}-cmHg^{-1} and 5.16, respectively. O_2-to-N_2 selectivity and pressure-normalized O_2 flux were higher than that of the pure TPX membrane.
       KEY WORDS   Gas Separation Membrane / Poly(4-methyl-1-pentene) /
Plasma Deposition / Oxygen Enrichment / Vinyl Monomer /

It is well-known that the plasma surface treatment of polymeric films can be utilized to change surface energy.[1] A coating of plasma-polymerized ultrathin film permanently changes the surface energy of a substrate without altering bulk properties of the material.[2-4] Generally, plasma polymers are crosslinked and thus are thermally stable and insoluble in organic solvents.

Gas separation by membrane, such as oxygen enrichment from air, is increasingly important due to its inherent energy efficiency. Hachisuka et al.[5] reported the influence of the sub-T_g annealing of the poly(vinylidene cyanide-co-vinyl acetate) membranes on their permeabilities of oxygen and nitrogen. Inagaki et al.[6] investigated the perme-

ation of gases through a hexafluoropropene/methane mixtures-grafted substrate by plasma polymerization. Several studies have treated substrates with plasma polymerization for gas separation.[7-9] Poly(4-methyl-1-pentene) (TPX) membranes with higher gas permeability and selectivity of oxygen to nitrogen were developed by Teijin Co. and Mitsui Co.[10,11] Vinylpyridine was grafted onto TPX membrane for gas separation.[12] But little work has been done to quantify the amounts of available functional groups produced on substrate surfaces.

The purpose of this study was to improve the gas separation performance of TPX membrane by plasma deposition modification. Various vinyl monomers were grafted onto the

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TPX/PDMS blend membrane to form a composite membrane. The effects of plasma deposition conditions, such as supply power and deposition time, on the performance of oxygen enrichment from air were investigated. The gas separation performance of the above composite membranes was assessed. In order to further characterize these plasma polymerized films, several surface analysis techniques including FT-IR, SEM, and X-ray diffraction were used.

EXPERIMENTAL

Materials

Poly(4-methyl-1-pentene) (TPX, MX-002) and poly(dimethyl siloxane) (PDMS, MW 17000) were supplied by Mitsui Co. and Polyscience Inc., respectively. Cyclohexene supplied by Merck Co. was used as a casting solvent. Methyl methacrylate, vinyl acetate, 2-hydroxyethyl methacrylate, and ethyl acetate made by Merck Co. was used as the plasma grafted monomers. All the above chemicals are reagent grade. Air of 99.9% purity was used for all gas permeation measurement in this study.

Membrane Preparation

The membrane was prepared from a casting solution of TPX blended with PDMS in cyclohexene. The casting solution is 5% weight concentration and TPX to PDMS is 9 to 1 weight ratio. The solution was agitated and milled at 65°C for 30 min. The substrate was formed by casting the solution onto a glass plate to predetermined thickness by using Gardner knife. The glass plate was heated for 1 h at 90°C in a well-circulated oven. Then the glass plate with the membrane were immersed in 4°C water for 40 min. The membrane was then peeled off and dried in vacuum for 24 h to remove solvent residue. Membrane thickness was in the range of 30—40 μm.

Plasma Treatment

A bell jar type plasma deposition system, as mentioned in a previous paper,[13] was used in this study. The system was pumped down to less than 80 Pa before the vinyl monomers (VAc, MMA, HEMA, and EA) were introduced into the reactor and it was allowed to equilibrate at a pressure of 133 Pa for MMA, VAc, and EA and at a pressure of 100 Pa for HEMA. The plasma was then ignited for 20 min at 5—30 W for MMA, VAc, and EA and for 1 h at 1—20 W for HEMA with a frequency of 13.56 MHz.

Gas Permeation Measurement

The permeability of membranes was determined by Yanaco GTR-10 gas permeability analysis. The pressure-normalized flux was determined by the following equation:

$$P/l = q/[(p_1 - p_2) \times A \times t]$$

where P/l is the pressure-normalized flux [$cm^3(STP) cm^{-2}$-s^{-1}-$cmHg^{-1}$], q/t is the volumetric flow rate of gas permeate [$cm^3(STP)$ s^{-1}], l is the membrane thickness (cm), p_1 and p_2 are the pressure (cmHg) on the high pressure side and low pressure side of the membrane, respectively, and A is the effective membrane area (cm^2).

Structure–Property Measurements

The structure of the prepared membranes was examined by a Hitachi S570 scanning electron microscope (SEM). The samples were coated with gold for SEM inspection. WAXD scans were generated by a Shimadzu XD-5 diffractometer operating with monochromatized copper radiation. FT-IR spectra was obtained from a JASCO FT/IR-7000.

RESULTS AND DISCUSSION

Influence of Deposition Time on the Gas Permeation Process

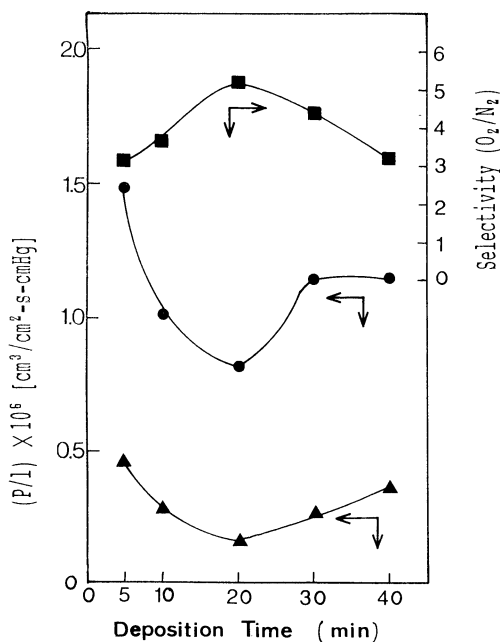In order to study the effects of the deposition time on the plasma modified membrane, the

Figure 1. Effects of deposition time on gas flux and selectivity for PVAc–p-TPX/PDMS membrane. Supply power: 10 W. (●), pressure-normalized flux of O_2; (▲), pressure-normalized flux of N_2; (■): O_2-to-N_2 selectivity.
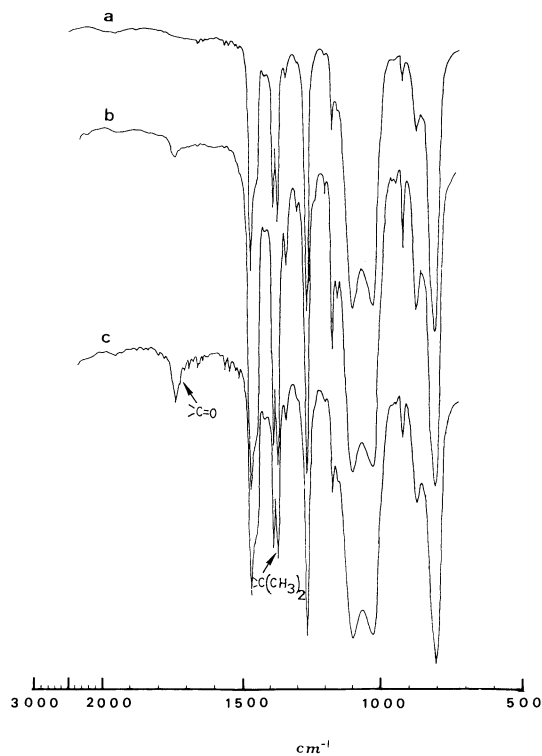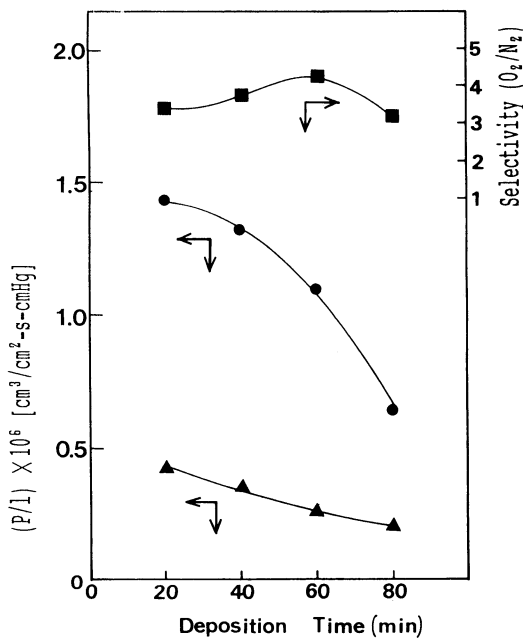

Figure 2. Effects of deposition time on gas flux and selectivity for PHEMA–p-TPX/PDMS membrane. Supply power: 1 W. (●), pressure-normalized flux of O_2; (▲), pressure-normalized flux of N_2; (■), O_2-to-N_2 selectivity.

Figure 3. FT-IR spectra for deposition condition: 10 W—20 min. (a) unmodified TPX membrane, (b) PHEMA–p-TPX/PDMS membrane, (c) PMMA–p-TPX/PDMS membrane, (d) PVAc–p-TPX/PDMS membrane, and (e) PEA–p-TPX/PDMS membrane.
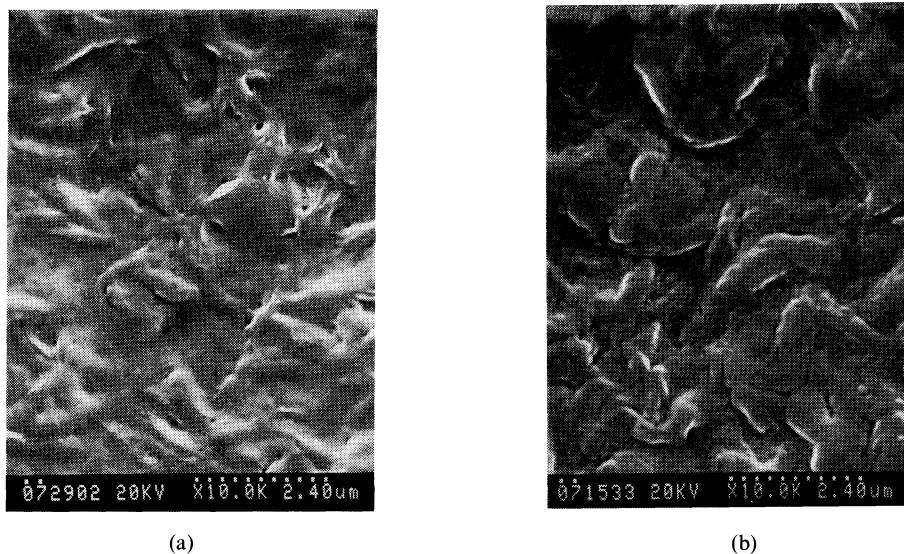
(a)

(b)

Figure 4.

deposition time was varied from 5 min to 40 min at a supply power of 10 W for the PVAc–p-TPX/PDMS membrane. As shown in Figure 1, the pressure-normalized flux of O_2 and N_2 decreases to a minimum value at 20 min deposition time and then increases as the deposition time is further increased. An opposite phenomenon of O_2 to N_2 selectivity was noted at the same time. This phenomenon might be due to the fact that an increase in deposition time may enhance membrane thickness due to an increase in the deposited amount of PVAc. For a deposit time longer than 20 min, the etching effect plays a more important role, resulting in selectivity decrease. As shown in Figure 2, the pressure-normalized flux of O_2 and N_2 decreased and the selectivity of O_2 to N_2 increased with increasing deposition time for PHEMA–p-TPX/PDMS membrane at a fixed supply power of 1 W. At 60 min, the selectivity of O_2 to N_2 reached maximum and then decreased as deposition time increased further due to the etching effect. From the above results, the proper deposition times for PVAc–p-TPX/PDMS and PHEMA–p-TPX/PDMS membranes are 20 min and 60 min, respectively.

Table I. Relative absorbance of FT-IR spectra for various monomer plasma deposited membranes at different supply powers[a]

Supply power	Relative absorbance		
	A_{1742}	A_{1736}	A_{1736}
W	A_{1369}	A_{1369}	A_{1369}
	VAc	MMA	EA
0	0	0	0
5	0.101	0.300	0.337
10	0.222	0.324	0.371
20	0.102	0.250	0.309
30	0.080	0.190	0.206

[a] Deposition time, 20 min. Substrare, TPX/PDMS (9/1) membranes.

Characterization of Grafting Polymer

The FT-IR spectra of the substrate membrane (a), PHEMA–p-TPX/PDMS membrane (b), PMMA–p-TPX/PDMS membrane (c), PVAc–p-TPX/PDMS membrane (d), PEA–p-TPX/PDMS membrane(s) are shown in Figure 3. The peak at 1736—1742 cm^{-1} was due to $C=O$ stretching[14] in the monomers of HEMA, MMA, VAc, and EA, and it was not observed in the spectrum of the substrate membrane. Therefore, plasma modified membranes were
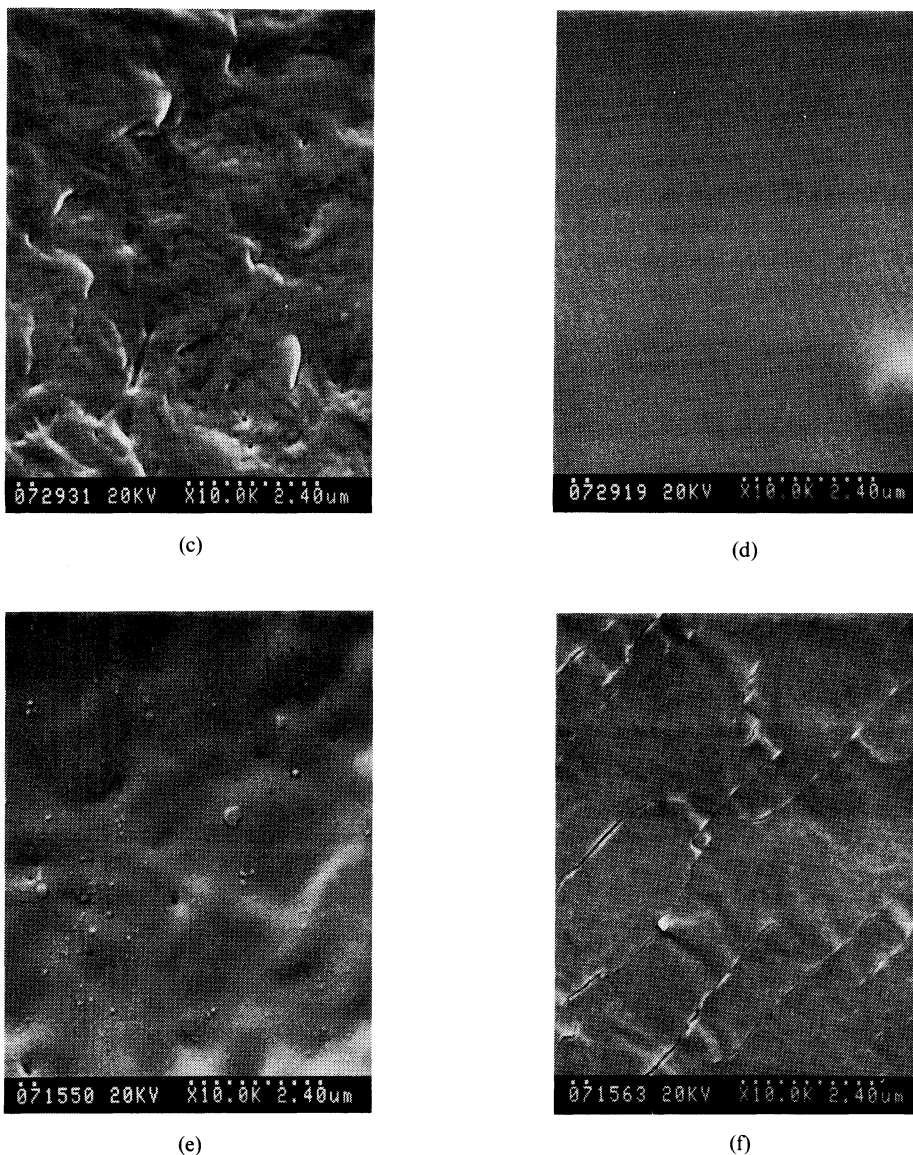
(c)

(d)

(e)

(f)

Figure 4. SEM (10000 ×) of membrane surface. (a) unmodified TPX membrane, (b) PMMA–*p*-TPX/PDMS membrane (10 W—20 min), (c) PVAc–*p*-TPX/PDMS membrane (10 W—20 min), (d) PEA–*p*-TPX/PDMS membrane (10 W—20 min), (e) PHEMA–*p*-TPX/PDMS membrane (3 W—1 h), and (f) PHEMA–*p*-TPX/PDMS membrane (20 W—1 h).

successfully synthesized.

As shown in Table I, the absorbance ratios of $C=O$ bond to $C(CH_3)_2$ bond for the various modified membranes increased as the supply power increased from 5 to 10 W. However, they decreased as the supply power further increased from 10 to 30 W because of the effect etching process became dominant during deposition.

Morphologies of the Plasma Modified Membranes

The surface morphologies of the plasma

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modified membrane using SEM micrographes are illustrated in Figure 4(b)—(e), and are different from that of the substrate membrane shown in Figure 4(a). As the supply power increased to 20 W for 1 h microcracks occurred on the surface as illustrated in Figure 4(f).

Figure 5(a)—(d) illustrate SEM micrographs of the surface morphology of the PEA–p-TPX/PDMS membrane at four differ- ent supply powers. For the supply power of 10 W, as illustrated in Figure 5(b), the surface density is higher than that of the supply power of 5 W as shown in Figure 5(a). However, as the supply power increased further etching and microcracks started to become dominant, resulting in a rough surface morphology as shown in Figure 5(c)—(d).
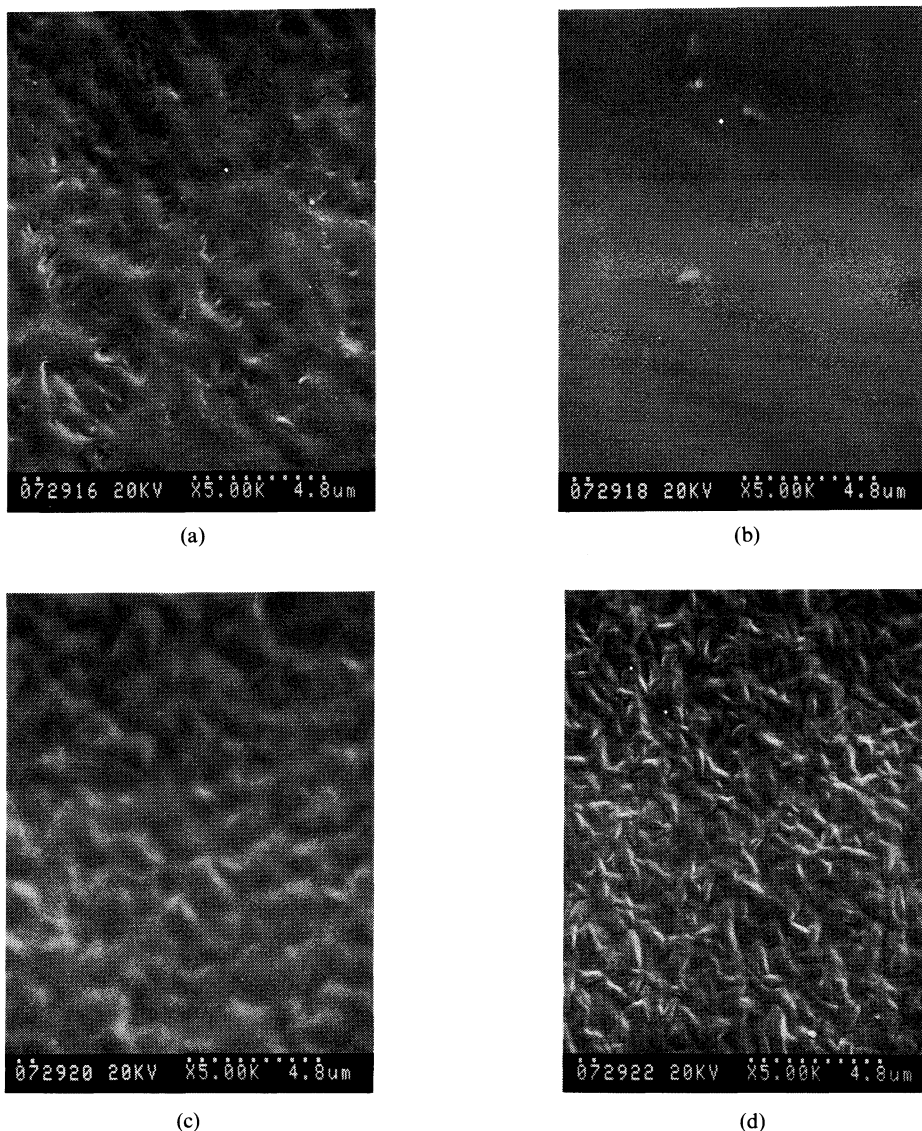

(a)

(b)

(c)

(d)

Figure 5. SEM (5000 ×) of membrane surface for the PEA–p-TPX/PDMS membrane. Deposition time: 20 min. (a) 5 W, (b) 10 W, (c) 20 W, and (d) 30 W.

Effect of Plasma Deposited Condition on Membrane Performance

In order to study the effects of a plasma deposition conditions on the modified membrane, plasma supply power was varied from 5 W to 30 W at a fixed deposition time of 20 min for PMMA–p-TPX/PDMS, PVAc–p-TPX/PDMS, and PEA–p-TPX/PDMS membranes. Plasma supply power was chosen in the range of 1—20 W at a fixed deposition time of 60 min for PHEMA–p-TPX/PDMS membranes. The effects of supply power on the selectivity of O_2-to-N_2 and pressure-normalized flux of O_2 and N_2 for the PVAc–p-TPX/PDMS membranes, PHEMA–p-TPX/PDMS membranes, and PMMA–p-TPX/PDMS membranes are shown in Figures 6, 7, and 8, respectively. Those values reached a minimum at 10 W, and then increased as the supply power increased, as shown in Figure 6. However, the result of O_2-to-N_2 selectivity is just opposite that of the pressure-normalized flux.

As the supply power increased, the pressure-

Figure 7. Effects of supply power on gas flux and selectivity for the PHEMA–p-TPX/PDMS membrane. Deposition time: 1 h. (●), pressure-normalized flux of O_2; (▲), pressure-normalized flux of N_2 (■), O_2-to-N_2 selectivity.
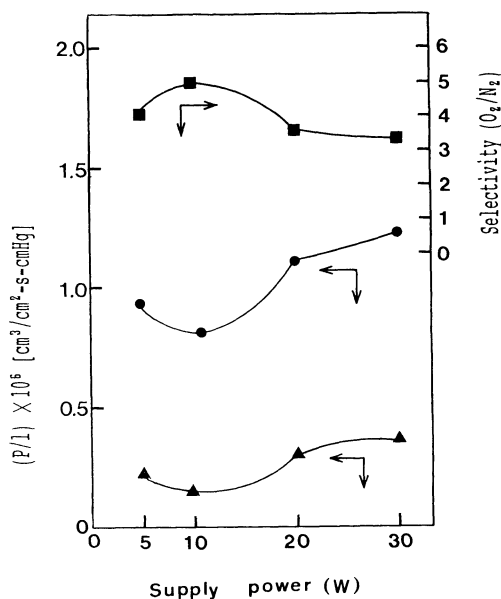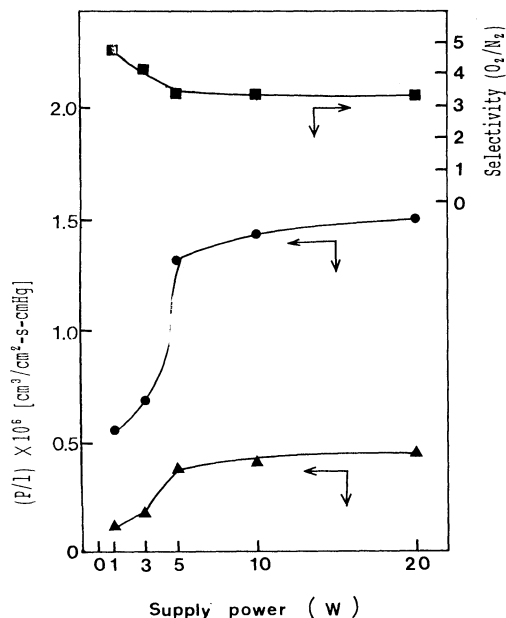

Figure 6. Effects of supply power on gas flux and selectivity for the PVAc–p-TPX/PDMS membrane. Deposition time: 20 min. (●), pressure-normalized flux of O_2; (▲), pressure-normalized flux of N_2; (■), O_2-to-N_2 selectivity.
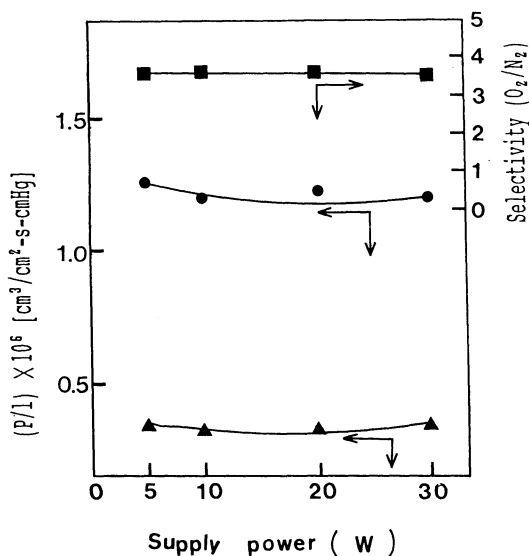

Figure 8. Effects of supply power on gas flux and selectivity for the PMMA–p-TPX/PDMS membrane. Deposition time: 20 min. (●), pressure-normalized flux of O_2; (▲), pressure-normalized flux of N_2; (■), O_2-to-N_2 selectivity.

normalized flux of O_2 and N_2 increased and O_2-to-N_2 selectivity decreased for PHEMA–p-TPX/PDMS membranes, as shown in Figure 7. In other words, the surface of the membrane would etch seriously with increase of the supply power. As mentioned earlier, the depositing effect played an important role for the supply power of 1 W, and microcracks were formed on the membrane surface at a supply power over 20 W. The result obtained from EA plasma deposited membrane was similar to that from HEMA plasma deposited membrane.

For PMMA–p-TPX/PDMS membrane, the pressure-normalized flux of O_2 and N_2 decreased and the O_2-to-N_2 selectivity increased with increase of supply power, as shown in Figure 8. These results might be due to the fact that the plasma deposition layer of

PMMA increases with supply power.

The crystallinity of the plasma modified membranes was higher than that of the unmodified TPX membrane, as shown in Figure 9. Results of X-ray diffraction studies on these modified membranes are shown in Figure 10(a)—(c), for the substrate with PMMA–p-TPX/PDMS, PEA–p-TPX/PDMS, PHEMA–p-TPX/PDMS, and PVAc–p-TPX/PDMS membranes, respectively. After modification, a crystallization peak at $2\theta = 16.8$ (MMA, EA, HEMA, and VAc) ($d = 5.27$) was formed due to depositing various vinyl monomers onto the substrate surface. A decrease of the gas pressure-normalized flux and increase of selectivity due to increase of the crystallinity was similar to the results of the PC–copolyester blend membrane.[16,17]
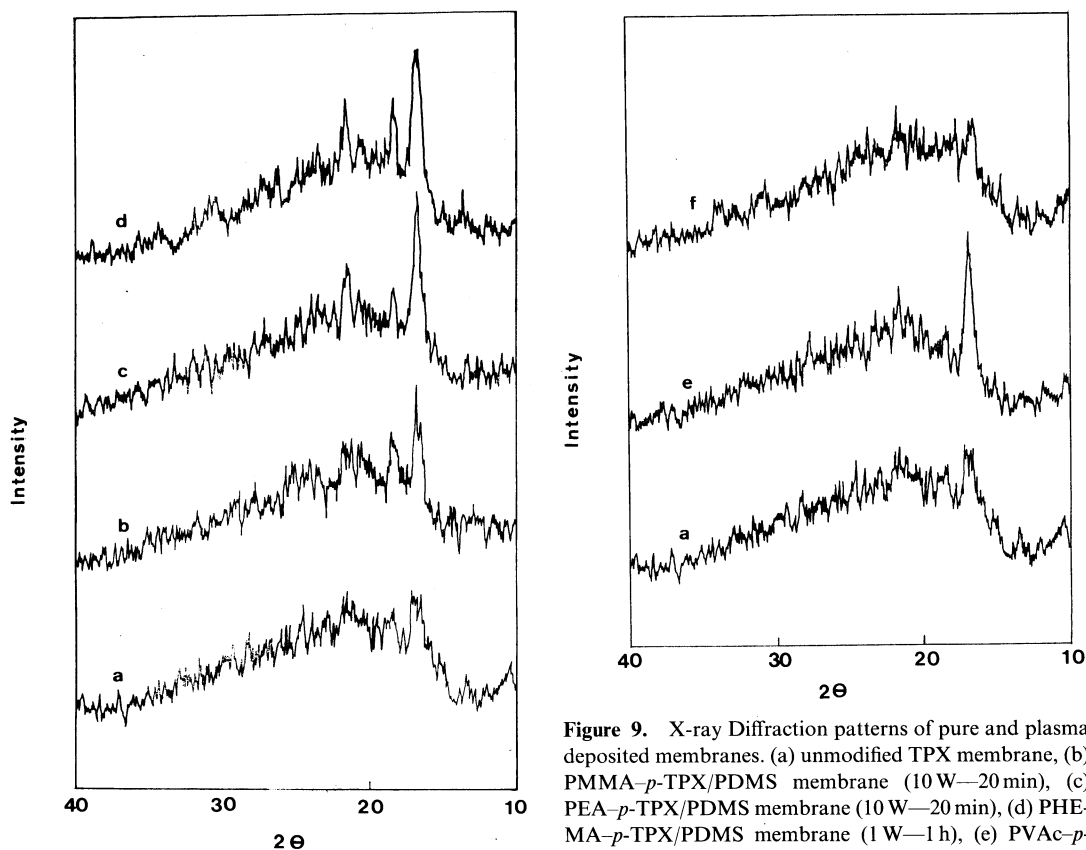

Figure 9.   X-ray Diffraction patterns of pure and plasma deposited membranes. (a) unmodified TPX membrane, (b) PMMA–p-TPX/PDMS membrane (10 W—20 min), (c) PEA–p-TPX/PDMS membrane (10 W—20 min), (d) PHEMA–p-TPX/PDMS membrane (1 W—1 h), (e) PVAc–p-TPX/PDMS membrane (10 W—20 min), and (f) PVAc–p-TPX/PDMS membrane (30 W—20 min).

Table II. Comparison of pressure-normalized O_2 flux and O_2-to-N_2 selectivity for various membranes

Membranes	Pressure-normalized O_2 flux	Selectivity	Reference
	(GPU)[a]	O_2-to-N_2	
TPX (23 μm)	—	3.49	Teijin Co.[18]
TPX	0.54	4.15	Mitsui Co.[6]
TPX/PDMS (9/1)	1.37	3.0	This study
PVAc–p-TPX/PDMS (10 W—20 min)	0.81	5.16	This study
PMMA–p-TPX/PDMS (10 W—20 min)	1.24	3.68	This study
PEA–p-TPX/PDMS (10 W—20 min)	1.05	3.70	This study
PHEMA–p-TPX/PDMS (1 W—1 h)	0.51	4.79	This study

[a] $GPU = 1 \times 10^{-6} cm^3 (STP) cm^{-2}$-$s^{-1}$-$cmHg^{-1}$.

The requirements of a good oxygen enrichment membrane are high pressure-normalized flux, high O_2-to-N_2 selectivity, and good mechanical strength. The pressure-normalized flux of the plasma modified TPX/PDMS blend membrane are better than those of the pure TPX membrane. In addition, compared with the unmodified TPX/PDMS blend membrane, the plasma deposited TPX/PDMS membrane shows improved O_2-to-N_2 selectivity. For an example, the pressure-normalized O_2 flux and the O_2-to-N_2 selectivity for PVAc–p-TPX/PDMS membrane at 10 W—20 min deposited conditions are 0.81 $cm^3 cm^{-2}$-s^{-1}-$cmHg^{-1}$ and 5.16, respectively. A tensile strength of 1.12 MPa, and a 1.43% elongation at break for a PVAc–p-TPX/PDMS blend membrane were obtained by ASTM D-628 and D-822 Instron Analysis.

Comparison with the Results of Previous Works

Table II shows a comparison of the pressure-normalized O_2 flux and O_2-to-N_2 selectivity for various membranes by other authors with those of this study. Teijin Co. has many patents on TPX membranes in which the O_2-to-N_2 selectivity are in the range of 2.9—3.49, *e.g.*, the O_2-to-N_2 selectivity of 3.49 was obtained for 23 μm thickness membrane.[18] Mitsui Co. has a patent for TPX membrane with a pressure-normalized flux of 0.54 cm^3 $(STP) cm^{-2}$-s^{-1}-$cmHg^{-1}$ and O_2-to-N_2 select-

ivity $= 4.15$.[11] A comparison of pressure-normalized O_2 flux and O_2-to-N_2 selectivity for various types TPX membrane is shown in Table II. It shows that the pressure-normalized flux of TPX/PDMS blend membrane is higher than that of the pure TPX membrane, due to higher gas permeability of PDMS. In addition, the pressure-normalized O_2 flux of plasma modified TPX/PDMS membrane is higher than that of the pure TPX membrane, but lower than that of the unmodified TPX/PDMS blend membrane. These phenomena may be due to the fact that the grafted polymer layer was formed on the surface of the TPX/PDMS blend membrane. Hirotsu *et al.*[19] indicate that the vinyl monomer of HEMA is a high reactivity monomer by using plasma-grafted polymerization. Thus, the pressure-normalized O_2 flux of the plasma modified TPX/PDMS blend membrane are higher than those of pure TPX membrane except PHEMA–p-TPX/PDMS membrane.

CONCLUSIONS

Throughout this study, pressure normalized fluxes of TPX membranes improved by PDMS blended with TPX. Furthermore, a composite membrane prepared *via* a plasma deposition process was obtained. O_2-to-N_2 selectivities and crystallinity of some plasma modified membranes were higher than that of the pure

TPX membrane. In this study, the best results were obtained with a PVAc–*p*-TPX/PDMS membrane made *via* a 10 W—20 min plasma deposition. The pressure-normalized O_2 flux and the O_2-to-N_2 selectivity of this membrane were $0.81 \times 10^{-6} \, \text{cm}^3 \, \text{cm}^{-2}\text{-s}^{-1}\text{-cmHg}^{-1}$ and 5.16, respectively.

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