Korean J. Chem. Eng., **17**(2), 143-148 (2000)

Preparation and Gas Separation Properties of Asymmetric Polysulfone Membranes by a Dual Bath Method

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(Received 7 December 1998 • accepted 10 January 2000)

Abstract–Defect-free skinned asymmetric gas separation membranes were prepared by a dual bath coagulation method that is a wet/wet phase inversion technique. The membranes were cast from a polysulfone/N,N-dimethylacetamide solution. In two sequent nonsolvent baths, the first bath using iso-propanol (IPA) leads to the formation of a dense skin top layer and the second bath using water makes the actual polymer precipitation. The top skin layer thickness was governed by changing the immersion time of the first IPA bath. We suggest that the growth rate of the skin layer is to be determined by a diffusion process.

Key words: Defect-free Asymmetric Membrane, Dual Bath Method, Wet/Wet Phase Inversion Technique

INTRODUCTION

The method for preparing asymmetric membranes except for thin film composite process coating on the membrane surface is by liquid-liquid phase separation process. In both asymmetric and composite membranes the hydrodynamic resistance is largely determined by the thin dense top layer. This top layer must avoid defects because a few defects can significantly reduce the selectivity without having much influence on the flux.

It is very difficult to make an ultrathin and defect-free top layer from a glassy polymer by enhancing flux. However, two phase inversion methods such as the dual method [van't Hof et al., 1992] and the evaporation method [Pinnau and Koros, 1991] can be used to prepare a defect-free asymmetric membrane. These processes include dry phase separation, dry/wet phase separation, and wet/wet phase separation.

A dry/wet phase separation process can be used to form ultrathin and defect-free asymmetric membranes by using several glassy polymers [Pesek and Koros, 1993; van't Hof et al., 1992]. The evaporation process is dry step requiring loss of a volatile solvent from a casting solution containing a less volatile nonsolvent component. The selective loss of the volatile solvent makes unstable the top skin layer region of the nascent membrane. Interfacial dry phase separation can be observed by the almost instantaneous onset of turbidity in this top skin layer region. The nascent membrane is then immersed in a nonsolvent coagulant that is a wet-phase separation step. In this quench step, the bulk of the membrane structure is formed and the remaining solvents and nonsolvents are extracted.

A wet/wet phase separation process is that membranes are formed by contacting polymer solution with two nonsolvent baths in series. The first bath is used to obtain a concentrated layer of polymer at the interface. This step makes ultrathin skin top layer similar to the evaporation step of dry/wet phase separation process. On the other hand, the second bath is responsible for the actual coagulation to be precipitated. The choice of nonsolvents for the bath strongly depends upon the type of solvent to be dissolved in the polymer solution. At the first bath, a ultrathin interfacial layer according to a high polymer concentration is formed. This step is the delayed liquid-liquid phase separation process to make a dense skin top layer. Although this results in a densified top layer, it usually contains defects and has no gas separation properties. Therefore this step requires a precise technique to make an ultrathin and defect-free skin top layer. The polymer concentration in the sublayer as supporter has hardly changed when the phase separation process starts, and a relatively open substructure like sponge-type structure is formed. At the second bath, the substructure is made as a precipitation process. This step is an instantaneous phase separation process.

It is very hard to make asymmetric membrane having defect-free top layer by a wet/wet method to use a glassy polymer such as polysulfone. Also, because of difficult preparation of asymmetric membrane, the composite membrane coating on the membrane surface is mainly used. It is not easy find articles of asymmetric polysulfone membrane prepared by a wet/wet method. The objective of this study is to prepare asymmetric polysulfone membrane with defect-free top layer by a wet/wet membrane. The gas separation properties of asymmetric polysulfone membranes were made by wet/wet phase inversion processes. It is demonstrated that optimized wet/wet phase inversion processes generate ultrathin and defect-free skinned asymmetric membranes. The structure of asymmetric polysulfone membranes made by dual bath method has been illustrated from scanning electron microscopy (SEM). The effect of gas permeability and selectivity with immersion time of IPA first bath, temperature and pressure was examined.

EXPERIMENTAL

1. Materials

Polysulfone (Udel P-3500) polymer was kindly supplied by

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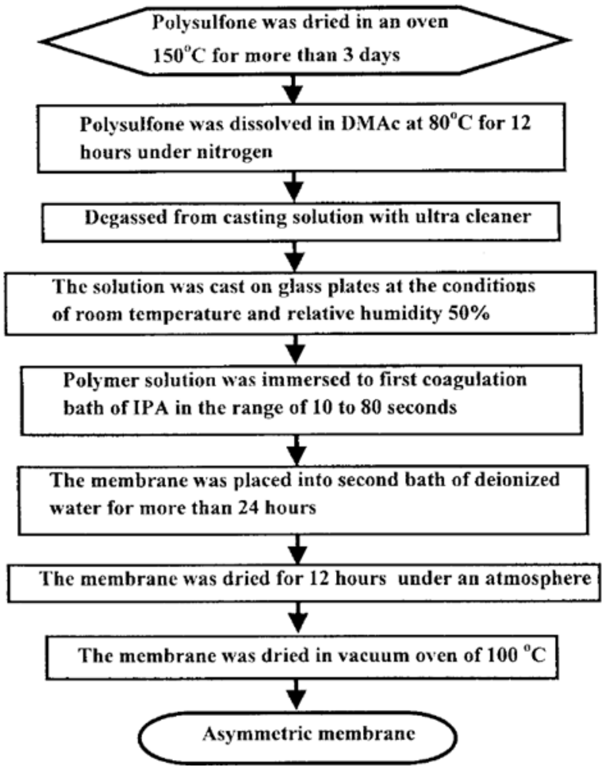

Fig. 1. Preparation of an asymmetric polysulfone membrane.

Sunkyung Co. Ltd. in Korea. Polysulfone is an amorphous hydrophobic polymer which has a glass transition temperature of 185 °C. N,N-dimethylacetamide (DMAc), purchased from Aldrich Co., was used as the casting solvent and its boiling temperature is 165.2 °C. Also, iso-propanol and deionized water were used as nonsolvents.

2. Preparation of Membranes

Fig. 1 shows the procedure of the preparation of asymmetric membrane. Membranes were made from 26 wt% polysulfone and 74 wt% DMAc. The polysulfone which is the polymer was dried in an oven (150 °C) for more than 3 days to remove absorbed water vapor before use. The polymer was then completely dissolved in DMAc at 80 °C for 12 hrs under nitrogen. It was degassed from casting solution with ultra cleaner. The membranes were cast on glass plates to a thickness of 250 μm at the conditions of room temperature and relative humidity 50%. Immediately after casting, the membranes were immersed in the first coagulation bath of iso-propanol in the range of 10 to 90 seconds, and then the membranes were placed into a second bath of deionized water for more than 1 day for the solvent to come out. After being dried for 12 hrs the membranes were dried for 3 days in vacuum oven of 100 °C.

3. Gas Permeability Measurements

The material of the permeability cell is stainless steel and the effective membrane area is 12.46 cm^2. The schematic diagram of the apparatus of gas permeability measurement is given in Fig. 2. Pure gas such as oxygen and nitrogen to be permeated was fed into upstream side, while downstream side was filled with the same gas at atmosphere. Permeability measurements for oxygen and nitrogen were made by the variable volume method. The experiment

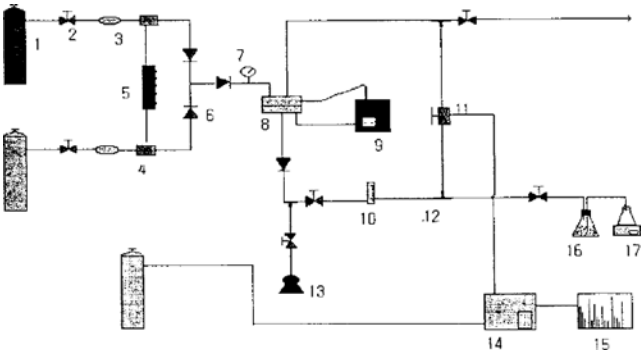

Fig. 2. Experimental apparatus for permeability measurement.

1. Gas bombe
2. On-off valve
3. Filter
4. MFC
5. Readout
6. Check valve
7. Pressure gauge
8. Cell
9. Temperature reader
10. Flower meter
11. Three-way valve
12. Tee
13. Vacuum pump
14. Gas chromatography
15. Recorder
16. Flask
17. Digital balance

was carried out with the upstream pressure in the range of 2-10 bar. The gas flux, J, can be expressed as P/*l*, and P/*l* is determined by the following equation:

$$\frac{P}{l}=\frac{1}{(\Delta P)}\left(\frac{q/t}{A}\right) \tag{1}$$

$$P=D\times S \tag{2}$$

$$\theta=l^2/(6D) \tag{3}$$

where P/*l* represents the gas flow to be permeated, q/t is the volumetric flow rate of gas permeation, *l* is skin layer thickness of membrane, ΔP is the pressure difference on the high and low pressure sides of the membrane and A is the effective membrane area. The gas permeation fluxes are reported in gas permeation units. P, D and S are permeability, diffusivity and solubility, respectively. Also, θ represents time lag.

RESULTS AND DISCUSSION

1. Morphology of Asymmetric Polysulfone Membranes

The membrane prepared by the dual bath system depends on the two types of phase separation processes in polymer-solvent-nonsolvent system. Membranes are formed by contacting a polymer solution with two successive nonsolvent baths. One is the delayed phase separation process, the other is instantaneous phase separation process. In this process, because the diffusional process starts at the interface between cast film and first bath, the change in composition of polymer occurs in the outermost region, upper part, of the film. Hence, the first IPA bath is used to obtained a concentrated layer of polymer at the interface. In case of immersing to a second water bath, the polymer concentration in the sublayer as supporter cannot be significantly changed. Therefore, this step gives an open and porous structure like sponge-type. Finally, the polymer is actually precipitated. Table 1 shows the permeance and selectivity for asymmetric polysulfone membrane with immersion

Table 1. Permeance and selectivity of asymmetric polysulfone membranes

Immersion time	T (°C) / P (bar)	25		30		35		40		45	
		O_2 permeance[a] $(P/L)_{O2}$	Selectivity (O_2/N_2)	O_2 permeance[a] $(P/L)_{O2}$	Selectivity (O_2/N_2)	O_2 permeance[a] $(P/L)_{O2}$	Selectivity (O_2/N_2)	O_2 permeance[a] $(P/L)_{O2}$	Selectivity (O_2/N_2)	O_2 permeance[a] $(P/L)_{O2}$	Selectivity (O_2/N_2)
10s	2.00	5.34	1.07	6.27	1.05	6.75	1.07	9.12	1.33	10.83	1.03
	4.00	5.52	1.05	6.06	1.06	6.66	1.07	8.88	1.05	10.38	1.07
	6.00	5.70	1.16	7.41	1.04	8.07	1.07	9.57	1.04	10.74	1.04
	8.00	5.94	1.06	7.71	1.07	8.10	1.05	9.69	1.03	10.83	1.05
	10.00	5.94	1.03	7.62	1.01	8.40	1.07	6.32	1.04	11.34	1.02
30s	2.00	3.51	1.77	4.17	1.64	4.77	1.52	7.35	1.38	8.49	1.38
	4.00	3.48	1.55	3.72	1.54	4.38	1.48	7.11	1.28	8.10	1.28
	6.00	3.33	1.54	4.11	1.47	4.89	1.37	7.29	1.11	9.00	1.11
	8.00	3.33	1.54	4.59	1.32	5.13	1.24	8.07	1.02	9.12	1.02
	10.00	3.41	1.50	4.47	1.25	5.16	1.21	7.98	0.98	9.36	0.98
50s	2.00	3.33	1.87	4.14	1.75	4.62	1.68	6.99	1.57	8.22	1.48
	4.00	3.36	1.78	3.64	1.68	4.11	1.59	6.93	1.46	7.89	1.35
	6.00	3.30	1.72	4.29	1.58	4.71	1.49	6.99	1.37	8.28	1.25
	8.00	3.27	1.63	7.47	1.52	5.19	1.46	7.35	1.37	8.16	1.19
	10.00	3.36	1.56	4.89	1.38	5.31	1.31	7.38	1.25	9.12	1.13
60s	2.00	2.30	3.38	2.65	3.14	2.77	2.98	2.90	2.53	3.16	2.10
	4.00	2.62	3.18	2.69	3.14	2.91	2.95	3.09	2.52	3.27	2.10
	6.00	2.20	2.84	2.52	3.10	2.65	2.94	2.61	2.52	3.01	2.10
	8.00	2.14	2.89	2.42	3.10	2.61	2.94	2.69	2.50	2.92	2.18
	10.00	2.05	2.89	2.31	3.10	2.50	2.94	2.57	2.50	2.92	2.18
70s	2.00	1.35	5.00	1.62	4.75	2.04	4.55	2.43	4.38	2.82	4.18
	4.00	1.32	5.00	1.71	4.75	1.83	4.36	2.55	4.38	3.00	4.08
	6.00	1.74	4.30	1.83	4.09	2.19	3.90	2.46	4.00	2.97	3.93
	8.00	1.68	4.30	1.83	3.92	2.19	3.73	2.67	3.62	2.88	3.40
	10.00	1.59	4.30	1.74	3.60	2.04	3.67	2.58	3.20	2.58	3.41
80s	2.00	1.02	6.00	1.19	5.42	1.49	4.54	1.62	4.42	2.05	3.48
	4.00	1.07	6.00	1.25	5.24	1.52	4.54	1.70	4.42	2.10	3.42
	6.00	1.02	5.00	1.14	5.24	1.43	4.38	1.59	4.44	1.95	3.40
	8.00	0.98	5.00	1.17	5.24	1.36	4.38	1.52	4.40	1.87	3.40
	10.00	0.93	5.00	1.12	5.24	1.31	4.38	1.46	4.40	1.79	3.40

[a] 10^{-6} $cm^3(STP)/cmHg{\cdot}sec{\cdot}cm^2$

time, temperature and pressure.

Fig. 3(a) represents an SEM photograph for the structure of the membrane immersed only in a water bath for 24 hrs without immersion into an IPA bath. In this case, the membrane has no distinctive skin layer, the oxygen permeance of the membrane was 30×10^{-6} $cm^3(STP)/cmHg\text{-}sec\text{-}cm^2$ at 4.0 bar and the selectivity for O_2/N_2 was 0.95, indicating that gas transport was predominantly determined by pore flow. This result demonstrates that the skin layers of the membranes made by wet phase inversion were highly defective. The reason is that the liquid-liquid phase separation is instantaneous since solvent DMAc present in polymer solution rapidly contacts with water which is very polar. As shown in Fig. 3(a) the cross-section of a membrane consists of a sponge-like substructure containing the macrovoids.

Fig. 3(b) to (g) represent SEM photographs of the cross-sectional view of the membranes immersed in the second water bath for 24 hrs after being immersed in the first IPA bath up to 10, 30, 50, 60, 70 and 80 sec. These results are the structures of membranes with increasing immersion time. The skin layer thickness increased up to about 2, 5, 7, 11, 12 and 13 μm according as immersion times increased up to 10, 30, 50, 60, 70 and 80 sec. Hence, the skin layer thickness is governed by changing the immersion time of the first IPA bath.

Fig. 3(b) to (d) represent the cross-section of a membrane after 10, 30 and 50 sec diffusional processes at the film/bath interface. It is interesting to note that the sublayer (bottom layer) obtained by instantaneous phase separation shows the structure such as the type of sponge containing microvoids. However, the top region represents the ultrathin skin layer supported by highly porous substructure. This result indicates that the structure of the skin layer is a microphase separation process, which is a delayed phase separation process. The oxygen permeabilities of the membranes were 5.52×10^{-6}, 3.48×10^{-6} and 3.36×10^{-6} $cm^3(STP)/cmHg\text{-}sec\text{-}cm^2$ at 4.0 bar and 25 °C, and the selectivities for O_2/N_2 were 1.05, 1.55 and 1.78, respectively. The fact that the oxygen selectivities were nearly 1.0 suggested the small microvoids will exist to the skin

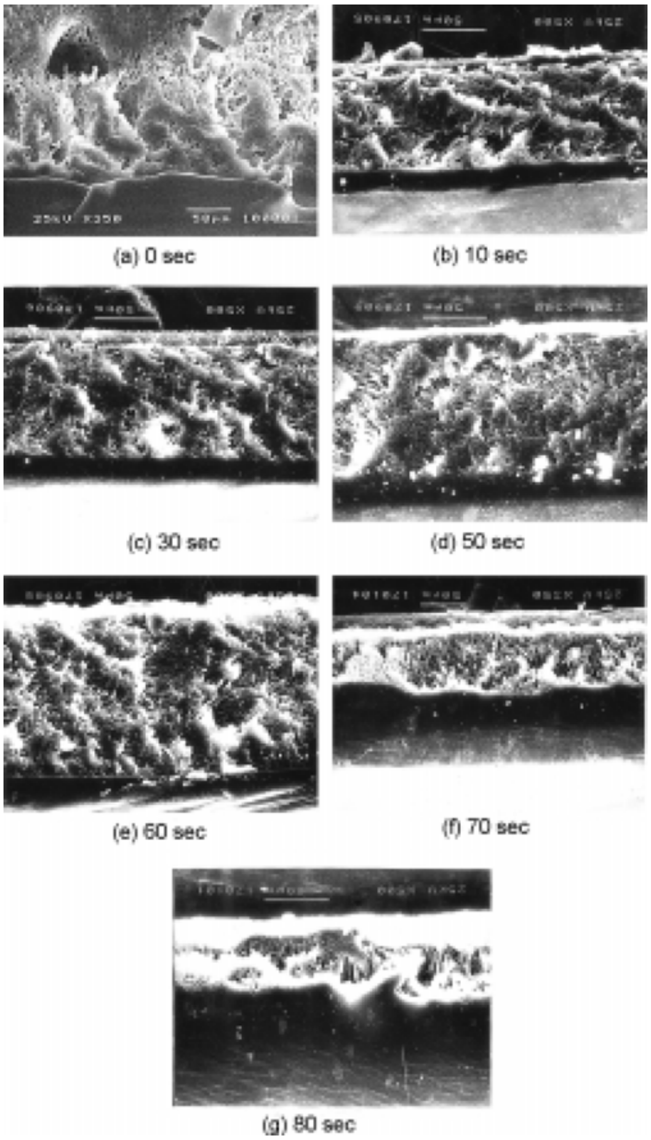
(a) 0 sec
(b) 10 sec
(c) 30 sec
(d) 50 sec
(e) 60 sec
(f) 70 sec
(g) 80 sec

Fig. 3. SEM photographs of the cross sectional views: (a) immersed only in a water bath, (b)-(g) immersed in second water bath for 24 hrs after immersed into first IPA bath.

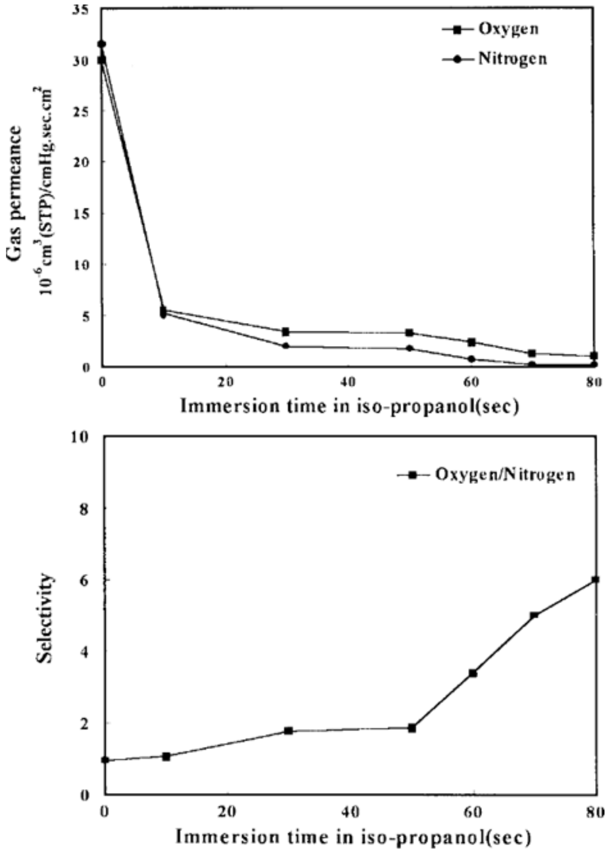

Fig. 4. Effect of immersion time in IPA on the gas separation characteristics of polysulfone at 25 °C, 4 bar (Note: permeability of oxygen and nitrogen for dense polysulfone membrane is 10.6×10^{-6} and 1.71×10^{-6} cm^3 (STP)cm/cmHg-sec-cm^2; selectivity is 6.2).

layer. These phenomena might be due to the fact that the particles of the nodules can not develop in the skin layer. This might be caused by variations in the residence time in the first bath.

Membranes immersed to the first IPA bath during 60, 70 and 80 sec as shown in Fig. 3(e) to (g) showed a substantial increase in oxygen selectivities. In particular, a selectivity of oxygen of a membrane immersed to the first IPA bath during 80 sec is up to 6.0. But the oxygen permeability of a membrane is decreased up to 1.07×10^{-6} cm^3(STP)/cmHg-sec-cm^2 at 4.0 bar. In this study, in case of immersing to first IPA bath during 90 sec or more, the oxygen permeability showed very low number, that is, 1.06×10^{-10} cm^3(STP)/cmHg-sec-cm^2, and the selectivity is 6.2 [Pinnau and Koros, 1991]. It might be due to the fact that the skin layer of a membrane is very thick and dense. As shown in Fig. 3 membranes with higher oxygen selectivities can be prepared by the dual bath method, and we can confirm that the gas flux strongly depends upon the combination of nonsolvents. By combining the IPA of the first bath and water of the second bath, the highest flux can be obtained. The high flux is due to the fact that residual IPA is rapidly removed from the film surface. The reason is the low density of IPA and the poor miscibility of IPA and water. The relatively short contact time with the first nonsolvent results in an ultrathin top layer and a good flux. But it must preceded the dual bath procedure to be avoided defects in membranes.

2. Effect of Gas Permeability and Selectivity with Immersion Time

Fig. 4(a) and (b) show the effects of oxygen and nitrogen permeabilities and selectivity with immersion times of 0, 10, 30, 50, 60, 70 and 80 sec in IPA bath at 25 °C, 4 bar. The oxygen permeability decreases and oxygen selectivity increases with increasing immersion time. The reason is that the resistance of gas permeance increases with an increase of the thickness of skin layer. Particularly, when the immersion time was over 60 sec, the selectivity was more than 3.38. It is assumed that it is the very definite pore structure which excludes the larger nitrogen molecule to a greater extent than the smaller oxygen molecule. Hence, separation is determined by the selective diffusion of oxygen to nitrogen rather than specific interaction.

3. Effect of Gas Permeability and Selectivity with Temperature

Fig. 5(a) and (b) indicate the effect of oxygen permeability and

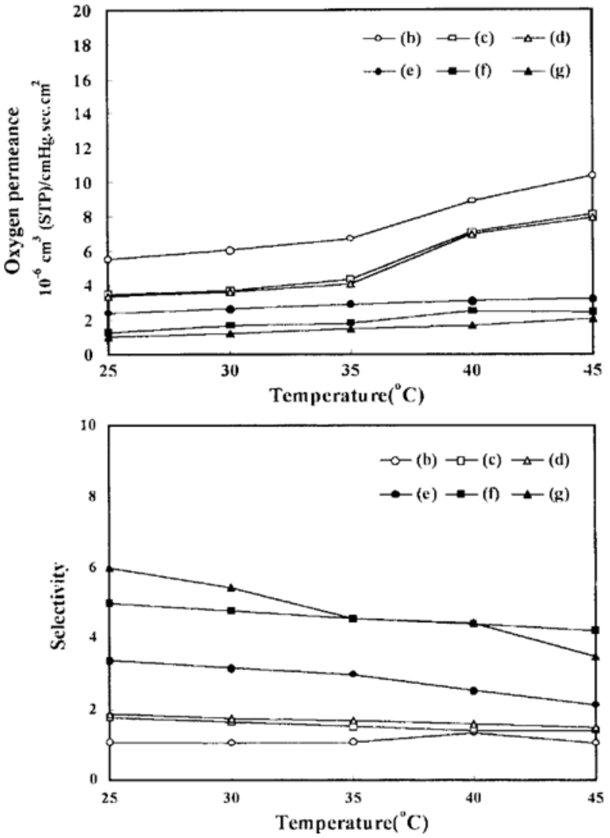

Fig. 5. Effect of temperature on the gas separation characteristics of polysulfone after immersed to IPA during (b) 10 sec, (c) 30 sec, (d) 50 sec, (e) 60 sec, (f) 70 sec and (g) 80 sec.

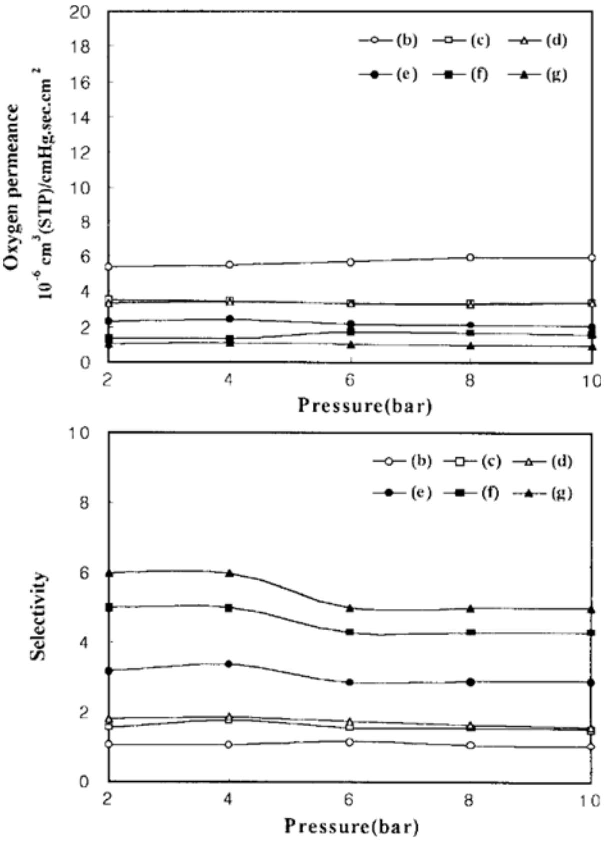

Fig. 6. Effect of pressure on the gas separation characteristics of polysulfone after being immersed to IPA during (b) 10 sec, (c) 30 sec, (d) 50 sec, (e) 60 sec, (f) 70 sec and (g) 80 sec.

selectivity with increasing temperature in immersion time. With increasing temperature in the range of 25-45 °C, considered here, the oxygen permeability of the membrane increases gradually, while the selectivity of the membrane decreases slightly. The increase of oxygen permeability might be due to the increase of diffusion by movement of gas molecules with increasing temperature. Particularly, the large increase of oxygen permeability in the range of 10, 30 and 50 sec of immersion time seems that micropores or defects within the skin layer of the polymer are formed. In the case that the immersion time is 60, 70, 80 sec of immersion time, the segment movement of polymer is slow with increasing the skin layer. These results indicate that free volume within the skin layer is decreased with increasing immersion time. The decrease of free volume means an increase of intermolecular and intramolecular polymer chain packing density.

4. Effect of Oxygen Permeability and Selectivity with Pressure

Fig. 6(a) and (b) represent the effect of oxygen permeability and selectivity with increasing pressure (2-10 bar) of upstream side in immersion time. The oxygen permeability with increased pressure is nearly constant. As shown by this result, this mechanism is governed by diffusion process. The reason is that the oxygen permeability only depends on the change of temperature, but not the change of pressure.

5. Effect of Flux with Permeating Time

Table 2 shows gas separation properties of polysulfone membranes with immersion time (60, 70 and 80 sec). The gas separation properties of Table 2 were calculated from Eqs. (1)-(3). The skin layer thickness, *l*, is approximately measured from SEM photographs. Also, Fig. 7 indicates the cumulative gas flux to be permeated with immersion time. As mentioned above, oxygen permeability increased with increasing temperature, and was nearly constant with increasing pressure. Hence, we can suggest following Henry's law that permeability (P) is equal to diffusivity (D) times solubility (S). By extrapolating from flux vs. permeating time, we can find out time lag (θ). The time lags were approximately 0, 0, 0, 180, 300 and 420 sec with immersion time (10, 30, 50, 60, 70 and 80 sec). The time lag increased as immersion

Table 2. Coefficients of diffusivity and solubility of asymmetric polysulfone membranes

Time (sec)	*l* (μm)	θ (min)	q/t (cm^3/min)	ΔP (bar)	P×10^{-10} [cm^3(STP)/cm^2cmHg·sec]	D×10^{-10} (cm^2/sec)	S (cm^3/cm^3·cmHg)
60	11	3	0.54	4	26.0	11	2.36
70	12	5	0.29	4	15.3	8	1.91
80	13	7	0.24	4	13.7	6	2.28

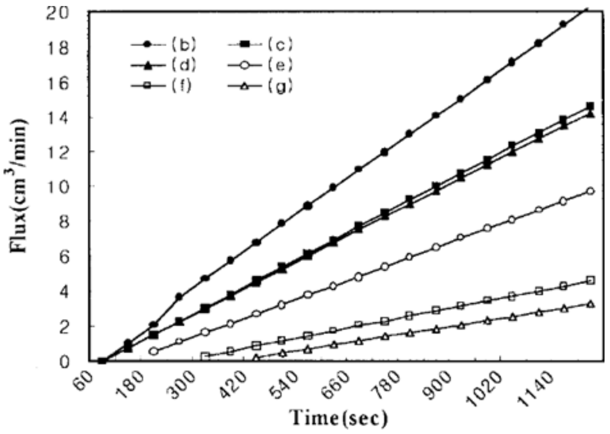

Fig. 7. Effect of flux with permeating time at 25 °C, 4 bar.

time increased. This means that the gas flux is inversely proportional to the skin layer thickness. After steady state, the relationship between gas flux and permeating time shows to be linear. We suggest that the growth rate of the skin layer is to be determined by a diffusion process.

CONCLUSIONS

A wet/wet phase separation process in combination with two series nonsolvent bath was used to prepare ultrathin and defect-free asymmetric polysulfone membranes for gas separations. The skin layer thickness was determined by changing the immersion time of the first IPA bath. The skin layer thickness increased from about 2 μm to about 13 μm as immersion times increased from 10 sec to 80 sec. The time lag increased as immersion time increased. Hence, the growth rate of the skin layer is to be governed by a diffusional process. The oxygen permeability decreased as the skin layer increased. A selectivity of oxygen of a membrane immersed to first IPA bath during 80 sec obtained up to about 6.0.

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