Preparation of Polyethyleneglycol (PEG) and Cellulose Acetate (CA) Blend Membranes and Their Gas Permeabilities

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SYNOPSIS

Miscible blend membranes containing 10 wt % PEG of low molecular weight 200, 600, 2000, and 6000, and 10 wt %, 20 wt %, 30 wt %, 40 wt %, 50 wt %, and 60 wt % of molecular weight 20,000 were prepared to investigate the effect of PEG on gas permeabilities and selectivities for CO_2 over N_2 and CH_4. The permeabilities of CO_2, H_2, O_2, CH_4, and N_2 were measured at temperatures from 30 to 80°C and pressures from 20 cmHg to 76 cmHg using a manometric permeation apparatus. It was determined that the blend membrane, which contained 10% PEG 20,000, exhibited higher permeability for CO_2 and higher permselectivity for CO_2 over N_2 and CH_4 than those of the membranes that contained 10% PEG of the molecular weight ranging from 200 to 6000. The high PEG 20,000 content blend membranes showed remarkable permeation properties such that the permeability coefficients of CO_2 and the ideal separation factors for CO_2 over N_2 reached above 200 barrer and 22, respectively, at 70°C and 20 cmHg. Based on the data of gas permeability coefficients, time lags, and characterization of the membranes, it is proposed that the apparent solubility coefficients of all CA and PEG blend membranes for CO_2 were lower than those of the CA membrane. However, almost all of the blend membranes containing PEG 20,000 showed higher apparent diffusivity coefficients for CO_2, resulting in higher permeability coefficients of CO_2 than those of the CA membrane. It is attributed to the high diffusivity selectivities of CA and PEG 20,000 blend membranes that their ideal separation factors for CO_2 over N_2 were higher than those of the CA membrane in the temperature range from 50 to 80°C, even though the ideal separation factors of all CA and PEG blend membranes for CO_2 over CH_4 became lower than those of the CA membrane over nearly the full temperature range from 30 to 80°C. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

General public awareness concerning the so-called atmospheric greenhouse effect attributed to CO_2 has created the need to devise environmentally friendly and energy efficient technology for the removal of CO_2 from industrial waste gas streams. Polymeric gas separation membranes are candidates for the separation task, though industrial waste gases are often at high temperature and low pressure.[1]

Polymer blends have been the focus of extensive gas membrane separation research in the last two decades. That the blending of polymers can result in properties not found in a single polymer has attracted considerable attention, and the number of polymer pairs that form miscible blends has increased dramatically. Polymer–polymer interaction can strongly influence not only the gas sorption and transport properties of blends but also their mechanical properties.[2-4]

As is known, Cellulose Acetate (CA) is one of the membrane materials applied to the separation of CO_2 from natural gas. It is inexpensive and highly qualified for the preparation of membranes. The ideal separation factors of CA membranes for CO_2

over N_2 can reach relatively high values of about 25 ∼ 30 at about 30°C. However, the permeability coefficients of CA membranes for CO_2 only reach 5 ∼ 6 barrer under the same conditions and are not satisfactory.[5,6] It has been reported that PEG can dissolve substantial amounts of sour gases,[7] and the diffusivity of large penetrants such as CO_2 and CH_4 in PEG may be high, considering its flexible main chain.[8,9] It was also reported that the membranes of copolymers in which —O—C— linkage polyethers were copolymerized with polyimides exhibited not only high permeability coefficients of about 100 barrer for CO_2 but also very high ideal separation factors of about 50 ∼ 70 for CO_2 over N_2 at 35°C.[6] The addition of PEG 6000 to polytrimethylsilylpropyne (PMSP) increased its ideal separation factors for CO_2 over N_2 up to about 25 at 35°C.[10,11]

The purpose of this study was to examine (1) if the solubility of CO_2 in membranes containing PEG could be enhanced, and (2) the effect of PEG on the improvement in permeability coefficients for CO_2 and the ideal separation factors for CO_2 over N_2 through the blending of PEG with CA, in order to develop a new kind of membrane with high permeability coefficients for CO_2 and high ideal separation factors for CO_2 over N_2.

THEORETICAL

One can generally characterize the permeation of penetrants through polymer membranes for gas separations using a permeability coefficient, P, which is generally defined as a normalized flux as in eq. (1):

$$P = \frac{Q}{(p_2 - p_1)/l} \qquad (1)$$

where p_2 and p_1 are the upstream and downstream pressures of the gas penetrating a membrane of thickness l. Q is the steady-state flux of the gas for one-dimensional Fickian diffusion.

Permeation is universally described as a solution-diffusion process in terms of the sorption and transport coefficients for the individual polymer and gas. Therefore, the permeability coefficient can be expressed as a product of an average diffusion coefficient and a solubility coefficient as follows:

$$P = D \cdot S \qquad (2)$$

The solubility coefficient, S, is thermodynamic in nature and is determined (1) by the inherent con-

densibility of the penetrant, (2) by polymer–penetrant interactions, and (3) by the amount of excess volume existing in glassy polymer. The average diffusion coefficient, D, is a kinetic term, which is a measure of the mobility of the penetrant between the upstream and downstream conditions in the membrane; it is determined by the packing and motion of the polymer segments and by the size of the penetrant molecule. For membranes of the materials such as crystalline polyethylene[12] and glassy polysulfone,[12] polycarbonate,[12,13] polyimide,[14–16] polypyrrolanes,[17] and poly(4-vinylpyridine-co-styrene)[18] or rubbery–glassy blend polymers,[19] the apparent diffusivity coefficients, D, had been obtained by eq. (3):

$$D = \frac{l^2}{6\theta} \qquad (3)$$

where l is the membrane thickness and q is the time lag. In our study, eq. (3) was also employed to obtain the apparent diffusivity coefficients, D. Thus, the apparent solubility coefficient, S, can be estimated from the permeability coefficient, p, and the apparent diffusivity coefficient, D, using eq. (4):

$$S = P/D \qquad (4)$$

$$\alpha_{A/B} = \frac{[Y_A/Y_B]}{X_A/X_B]} \qquad (5)$$

When the downstream pressure is negligible, as in the present work, the gas separation factor, $\alpha_{A/B}$, defined by eq. (5), can be related to the ratio of the pure gas permeability coefficients of penetrants A and B. This can be represented by eq. (2), as shown by eqs. (6) and (7), if the two penetrants do not interact strongly with each other:

$$\alpha^*_{A/B} = \frac{P_A}{P_B} \qquad (6)$$

$$\alpha^*_{A/B} = \left(\frac{S_A}{S_B}\right)\left(\frac{D_A}{D_B}\right) \qquad (7)$$

where X_A, X_B, and Y_A, Y_B are the mol fractions of components A and B at the upstream and downstream sides of the membrane, respectively.

The ideal separation factor, $\alpha^*_{A/B}$, provides a measure of the intrinsic permselectivity of a membrane material for a mixture of penetrants A and B. Without strong gas–polymer interactions, the separation factor, $\alpha_{A/B}$, for mixed gases, can be approximated as $\alpha^*_{A/B}$ within 10% using the ratio of

Table I Permeabilities and Permselectivities of CA and Its Blend Membranes Containing PEG at 35°C and 20 cmHg

	$P^a_{CO_2}$	PN_2	PCH_4	PO_2	PH_2	DCO_2^b	SCO_2^c	$\alpha^d CO_2/N_2$	$\alpha CO_2/CH_4$
CA	5.96	0.231	0.205	1.05	14.9	0.560	106	25.8	29.2
CA + 10%PEG200	4.92	0.918	1.14	1.46	22.2	0.475	104	5.36	4.31
CA + 10%PEG600	5.72	0.418	0.831	1.22	14.8	0.639	89.5	13.7	6.88
CA + 10%PEG2000	6.30	0.452	0.549	1.10	13.8	0.723	80.4	13.9	11.5
CA + 10%PEG6000	6.16	0.194	0.247	—	10.9	0.929	66.3	31.7	25.0
CA + 10%PEG20000	7.49	0.207	0.248	0.993	11.4	1.00	74.6	36.2	30.3

[a] Permeability coefficient; Barrer.
[b] Apparent diffusivity coefficient for CO_2; $\times 10^8$ (cm^2/s).
[c] Apparent solubility coefficient for CO_2; $\times 10^3$ [$cm^3(STP)/cm^3 \cdot cmHg$].
[d] Ideal separation factor.

the permeability coefficients for the pure gases A and B.[6,20]

As shown in eq. (7), one can also conveniently consider the overall selectivity to have two components, a solubility and a diffusivity contribution, where D_A/D_B is the diffusivity selectivity, and S_A/S_B is the solubility selectivity. Clearly, if we can increase the diffusivity or the solubility of a desired gas by altering the structure of the polymer, the permeability of the gas will increase proportionately. Similarly, to improve the permselectivity of one gas over another, one must increase either the diffusivity selectivity, the solubility selectivity, or both.

EXPERIMENTAL

Preparation of Membranes

CA and PEG used to prepare membranes for the gas permeation measurements were obtained from Junsei Chemical Co. The method of dissolution-re-precipitation was employed in the purification of CA in which CA was dissolved in tetrahydrofuran and then the solution was poured into methanol. The CA and PEG blend membranes used for this study were prepared by casting a 1% CA and PEG solution, in which the solvent was a mixture of 40% dichloromethane and 60% tetrahydrofuran, onto a flat-bottomed Petri dish in a glass bell-type vessel at room temperature. The solvent was allowed to evaporate slowly over a period of about 5 to 7 days, and the membranes were then dried under vacuum. The thickness of the dry membranes ranged from 35 to 100 μm, depending on the weight of the casting solution.

Gases

The gases employed for the gas permeation measurements were obtained from Keihin Koatsu Gas Co., and their purity was at least 99.5 mol %.

Permeability Measurements

The experimental method used in this study was an adaptation of the vacuum gas transmission technique using an apparatus equipped with an RSK K-315-N pressure transducer. The permeability coefficients were calculated from the slopes of time–pressure curves in the steady state. The apparent diffusivity coefficients for CO_2 were determined by the time-lag method, and the apparent solubility coefficients for CO_2 were calculated using eq. (4).

The Measurement of Membrane Characterization

The membrane density was determined by its weight and volume. The glass transition temperature, T_g, and the melting peak temperature, T_{mp}, were measured by differential scanning calorimetry at a heating rate of 20°C/min. The d-spacing was measured by wide-angle x-ray diffraction (WAXD) using Bragg's equation shown as follows:

$$\lambda = 2\, d \sin \theta \; (Cu\text{-}K\alpha, \lambda = 1.54 \text{ Å}) \qquad (8)$$

RESULTS AND DISCUSSIONS

Permeability and Selectivity of Blend Membranes Containing Different Molecular Weight PEGs

Table I lists the pemeability coefficients of carbon dioxide, PCO_2, nitrogen, PN_2, oxygen, PO_2, hydrogen,

P_{H_2}, and methane, P_{CH_4}, and the apparent solubility coefficients and apparent diffusivity coefficients of CO_2, S_{CO_2}, and D_{CO_2}, for CA and 10% PEG 200, 600, 2000, 6000, 20,000 blend membranes at 35°C and 20 cmHg. A comparison was made of the effects of different molecular weights of PEG in the blend membranes on the permeability coefficients of CO_2 and the ideal separation factors for CO_2 over N_2 and CH_4. The blend membrane containing 10% PEG 20,000 exhibited the highest permeability for CO_2 and selectivity for CO_2 over N_2 and CH_4 compared to the other blend membranes listed in Table I. The apparent diffusivity coefficients of CO_2 for almost all of the blend membranes were higher than that for the CA membrane although the apparent solubility coefficients of CO_2 for the former were lower than those for the latter as shown in Table I. Therefore, it is suggested that CA and PEG 20,000 blend membranes should be the most promising for improved permeability of CO_2 and selectivity for CO_2 over N_2 and CH_4 relative to the others listed in Table I. Although the apparent solubility coefficient of CO_2 for the membrane containing 10% PEG 20,000 was lower than those for the membranes containing low molecular weight PEG, the apparent diffusivity coefficient of CO_2 for the former was higher than those for the latter, which resulted in the highest CO_2 permeability for the former. Because of the relatively high permeabilities of N_2 and CH_4 for the membranes containing 10% low molecular weight PEG, their ideal separation factors for CO_2 over N_2 and CH_4 were very low compared to those of the membrane containing 10% PEG 20,000. One may infer that higher molecular weight PEG caused denser intersegmental chain packing in the blend membranes because there is an obvious tendency for the permeability coefficients of almost all gases except CO_2 to decrease with increased PEG molecular weight in the blend membranes. Therefore, we focused on the results of the permeability and selectivity for CO_2 of the blend membranes conaining PEG 20,000 and their structures.
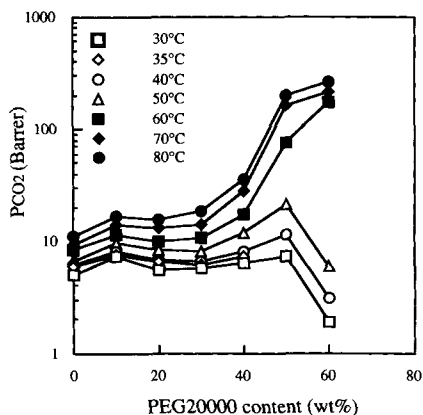
Permeation of CO_2

Figure 1 shows an Arrhenius plot of the permeability coefficients of CO_2 for CA and its blend membranes containing PEG 20,000 from 10 to 60%. The blending of PEG 20,000 in the membranes increased the permeability coefficients of CO_2 over the full temperature range except for the membrane containing 60% PEG 20,000. The PEG 20,000 should play a dominant role in gas permeation, and its permeability coefficients of CO_2 were the lowest
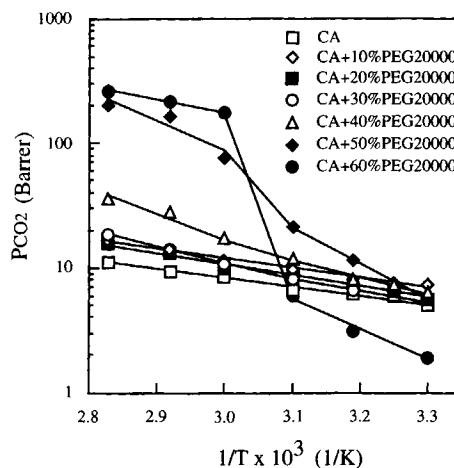
Figure 1 Temperature dependence of permeability coefficients for CO_2 at 20 cmHg.

at temperatures below 50°C, as shown in Figure 1, due to its high crystallinity. The relationships between P_{CO_2} and $1/T$ for CA and its blend membranes containing 10% and 20% PEG 20,000 were linear as were those for the common polymers. However, instead of straight lines, those for the other blend membranes were broken lines, which were different from the relationship between the permeability coefficient and $1/T$ for general polymers and bent further upward with higher content of PEG 20,000 in the membranes at temperatures from about 50 to 60°C. It is obvious that the higher the content of PEG 20,000 in the blend membranes, the greater was the increment in permeability coefficients for CO_2 with increasing temperature. The permeability coefficients of CO_2 for the blend membranes containing 60% PEG 20,000 reached over 200 barrer as the temperature reached 70°C. These break points in the Arrehnius plots in permeability suggest an abrupt increase in the mobility of CO_2 molecules, depending on the increase in the segmental motion in these blend membranes, which likely results from the influence of PEG 20,000 melting. Figure 2 clearly shows that the high content of PEG 20,000 led to an outstanding effect on the enhancement of CO_2 permeability for the blend membranes containing 40, 50, and 60% PEG 20,000 in the range of high temperatures from about 60°C, which is about the beginning of the melting temperature of PEG 20,000. However, the effect was not obvious and there were little differences in the permeability coefficients of CO_2 for the blend membranes containing 10, 20, and 30% PEG 20,000 at these experimental temperatures. There were maximum peak values in Figure 2 at the point of 50% PEG 20,000 content at temperatures below

Figure 2   Permeability coefficients of CO_2 as a function of PEG 20,000 content at 20 cmHg.

50°C. Thus, it is proposed that an increment in PEG 20,000 content that is higher than 50% will not act effectively in improving CO_2 permeability until the temperature reaches the PEG 20,000 melting point due to the dominance of PEG 20,000 crystallinity in the membrane.

Figures 3 and 4 show the temperature dependences of apparent diffusivity coefficients and apparent solubility coefficients for CO_2. As seen from Figure 3, the apparent diffusivity coefficients of CO_2 for the blend membranes were increased by the blending of PEG 20,000. They became high with increased PEG 20,000 content, but their differences were small for the blend membranes, which contained 10, 20, and 30% PEG 20,000, and there are also broken lines for the blend membranes containing 40% and 50% PEG 20,000 in Figure 3 like the lines shown in Figure 1, which were different from the relationship between the diffusivity coefficient and $1/T$ for general polymers. On the contrary, as shown in Figure 4, the apparent solubility coefficients of CO_2 were decreased due to the existence of PEG 20,0000 in the blend membranes, and the higher the PEG 20,000 contents were, the lower they became. All lines shown in Figure 4 are linear and nearly parallel, though the differences in the apparent solubility coefficients of CO_2 are relatively small as Figures 1 and 3 show for the blend membranes containing 10, 20, and 30% PEG 20,000.

Based on the above analysis, it is proposed that the increment in apparent diffusivity coefficients of CO_2 contributed to the improvement in CO_2 permeability coefficients for the blend membranes, and the contribution became very obvious for the blend membranes with high PEG 20,000 content at high temperatures, as shown in Figure 2.
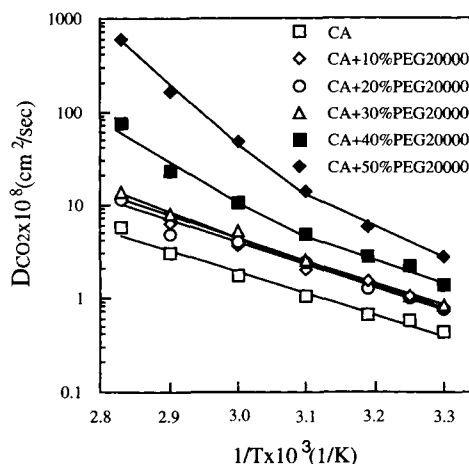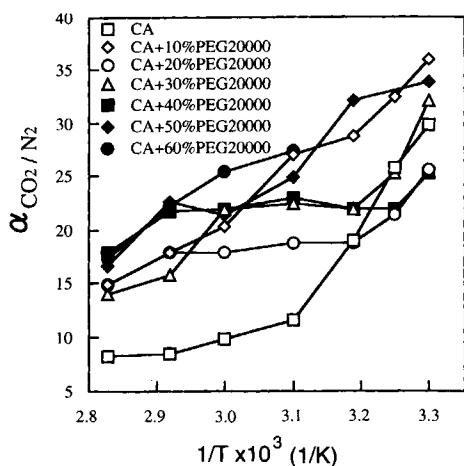

Figure 3   Temperature dependence of apparent diffusivity coefficients for CO_2 at 20 cmHg.

Permselectivity for CO_2 over N_2 and CH_4

Figures 5 and 6 show the temperature dependence of ideal separation factors of CO_2 over N_2 and CH_4, $\alpha CO_2/N_2$ and $\alpha CO_2/CH_4$, respectively. Although the $\alpha CO_2/N_2$ value for the blend membrane containing 10% PEG 20,000 was relatively higher than those of the CA membrane shown in Figure 5 at temperatures below about 50°C, the other blend membranes containing 20 or 30% PEG 20,000 did not exhibit higher selectivity for CO_2 over N_2 than those for the CA membrane at those temperatures. The $\alpha CO_2/N_2$ values for all the CA and its blend membranes shown in Figure 5 decreased as did those of general polymeric membranes with increasing temperature. However, the blend membranes showed strong restraint of the decline in $\alpha CO_2/N_2$
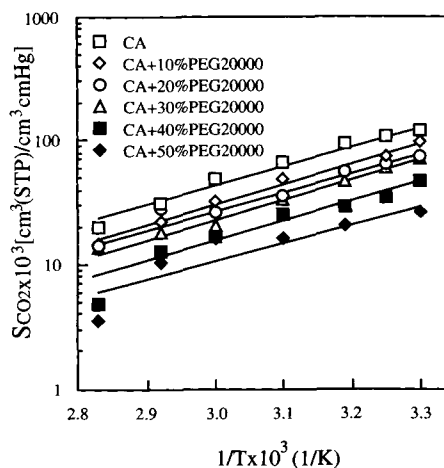
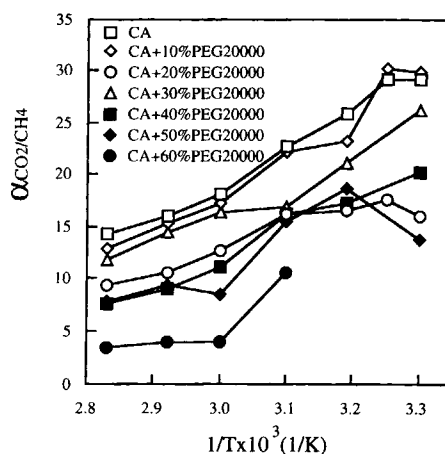
Figure 4   Temperature dependence of apparent solubility coefficients for CO_2 at 20 cmHg.

Figure 5 Temperature dependence of ideal separation factors $\alpha(P_{CO_2}/P_{N_2})$ at 20 cmHg.

Figure 6 Temperature dependence of ideal separation factors $\alpha(P_{CO_2}/P_{CH_4})$ at 20 cmHg.

as the temperature increased, especially for the blend membranes containing 40, 50, and 60% PEG 20,000 at temperatures from about 50 to 80°C, while the $\alpha CO_2/N_2$ value of the CA membrane distinctly decreased, as shown in Figure 5. Because for any polymeric membrane, the function of solubility selectivity in permselectivity for gas separation should be minor at high temperatures, according to the permeation behavior of CO_2, it can be suggested that the selectivity properties of the blend membranes for CO_2 over N_2 may mainly correspond to the improvement in diffusivity selectivity for CO_2 over N_2 to some extent. Due to its low melting point, PEG 20,000 should be able to exert a distinctive effect on the apparent diffusion of CO_2 with increasing temperature, as can be seen from Figures 1 and 3, especially for the blend membranes containing 40, 50, and 60% PEG 20,000. Because of its crystallinity, the existence of PEG 20,000 in the blend membranes was not able to exert sufficient effect on the improvement in the apparent diffusivity of CO_2 and the $\alpha CO_2/N_2$ at temperatures from 30 to 50°C, as can be seen from Figures 3 and 5.

Comparatively, the $\alpha CO_2/CH_4$ values of almost all the blend membranes shown in Figure 6 were lower than those of the CA membrane at these experimental conditions. The effects of PEG 20,000 on the decrease in $\alpha CO_2/CH_4$ and the restraint of the decline in $\alpha CO_2/N_2$ with increasing temperature may be explained that, because of its flexible main chain, PEG 20,000 allowed large penetrants such as CO_2 and CH_4 to diffuse easily, resulting in the improvement in P_{CO_2} and P_{CH_4}. As the temperature increased, especially from 50 to 80°C, the PEG 20,000 molecules gradually became free to have

an effect on the increase in the diffusion of CO_2 and CH_4.

Structural Properties of the Blend Membranes

Table II lists the pressure dependence of P_{CO_2}, S_{CO_2}, D_{CO_2} for CA and the blend membranes. As was the case with the CA membrane, the S_{CO_2} of the blend membranes tended to decrease while their D_{CO_2} slightly increased with increasing pressure. Therefore, it can be said that the blend membranes containing PEG 20,000 possessed the same structural properties as a glass polymeric membrane such as the CA membrane as can be seen from Figure 7 in which the pressure dependence of P_{CO_2} was plotted.

Figure 8 shows the temperature dependence of the permeability coefficients of hydrogen, P_{H_2}. The reduction in P_{H_2} for the blend membranes with increasing PEG 20,000 content indicated that the vol-
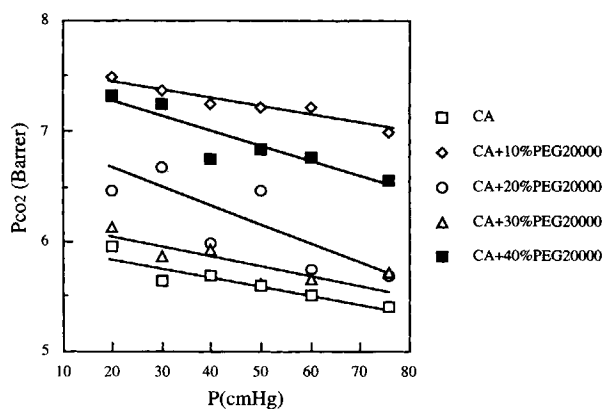
Figure 7 Pressure dependence of permeability coefficients for CO_2 at 35°C.

Table II   Pressure Dependence of the P, θ, D, S of Blend Membranes of PEG 20,000 and CA for CO_2 at 35°C

p cmHg	PEG%	0	10	20	30	40
20	P[a]	5.96	7.49	6.46	6.13	7.32
	θ[b]	681.2	365.3	423.5	264.3	178.5
	D[c]	0.5602	1.004	0.9987	1.014	2.102
	S[d]	106.4	74.63	64.66	60.42	34.84
30	P	5.64	7.36	6.67	5.87	7.24
	θ	690.5	339.7	345.9	237.7	190.3
	D	0.5526	1.079	1.223	1.127	1.972
	S	102.1	68.20	54.59	52.11	36.71
40	P	5.69	7.25	5.98	5.93	6.75
	θ	677.0	335.6	406.0	245.8	194.1
	D	0.5637	1.092	1.042	1.090	1.933
	S	100.9	66.35	57.43	54.40	34.92
50	P	5.60	7.21	6.47	5.61	6.84
	θ	640.1	311.6	328.3	241.9	200.6
	D	0.5965	1.177	1.288	1.108	1.870
	S	93.88	61.29	50.25	50.61	36.58
60	P	5.51	7.21	5.74	5.66	6.77
	θ	630.9	320.5	382.5	238.5	220.1
	D	0.6048	1.144	1.106	1.124	1.705
	S	91.16	63.06	51.89	50.39	39.73
76	P	5.40	6.99	5.68	5.72	6.56
	θ	622.3	301.6	356.2	217.5	179.0
	D	0.6133	1.215	1.187	1.232	2.097
	S	88.10	57.51	47.85	46.42	31.31

[a] P, Permeability coefficient, Barrer.
[b] θ, Time lag, S.
[c] D, Apparent diffusivity coefficient for CO_2; $\times 10^8$ (cm^2/s).
[d] S, Apparent solubility coefficient for CO_2; $\times 10^3$ [$cm^3(STP)/cm^3 \cdot cmHg$].

ume of microvoids in the membranes should become less than that in the CA membrane. This is thought to be in accordance with the densities and d-spacing of the membranes shown in Table III, which lists the characteristics of the membranes at room temperature. Therefore, the decreasing apparent solubility coefficients of CO_2 may mainly result from the reduction in the free volume or the Langmuir sorption of CO_2 in the blend membranes. According to these structural properties, it can consequently be suggested that the flexible main chain of PEG 20,000 should be the main contributor to the increase in the permeability coefficients of CO_2 for the blend membranes.

As shown in Table III, two glass transition temperatures for the blend membranes except for the membrane containing 10% PEG 20,000, indicated microphase separation in the membranes; the gases permeated through the CA glass phase and the PEG rubber phase at the same time, although the blend membranes were well distributed and transparent. The CA phase weakened the crystallinity of the PEG

20,000 in the formation of the blend membranes and provided mechanical strength and heat resistance. The melting peak temperatures should be the proper explanation for those broken lines shown in Figures
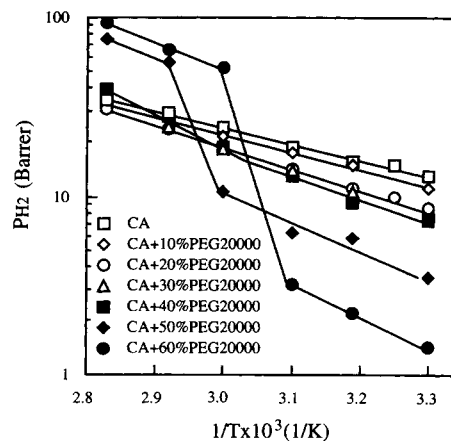
Figure 8 Temperature dependence of permeability coefficients for H_2 at 20 cmHg.

Table III   Characterization of Cellulose Acetate(CA) and Its Blend Membranes Containing PEG20000 Membranes

	Density[a]	d-spacing[b]	T_{g1}[c]	T_{g2}[c]	Tmp[d]
CA	1.300	5.2	185.5	—	—
CA + 10%PEG20000	1.302	5.0	183.7	—	56.8
CA + 20%PEG20000	1.324	4.8	191.2	−54.1	62.4
CA + 30%PEG20000	1.338	4.9	192.0	−55.6	62.6
CA + 40%PEG20000	1.340	4.6	197.0	−51.4	66.1

[a] Determined by volume and weight. Unit: g/cm^3.
[b] Determined by wide-angle x-ray diffraction (WAXD) using Bragg's equation; $\lambda = 2d\sin\theta$. Unit: Å.
[c] Glass transition temperature, determined by DSC at heating rate of 20°C/min. Unit: °C.
[d] The temperature of melting peak of blend membranes; Unit: °C.

1, 3, and 8, which had been thought to be the results from the effect of the low melting temperature of PEG 20,000. Penetrants should easily permeate through the PEG phase, which should have become liquid in the blend membranes at temperatures from about 60 to 80°C. For the low PEG 20,000 content in the blend membrane containing 10% PEG 20,000, its density and d-spacing were almost the same as those of the CA membrane, so that it should be the best distributed and the freest of the crystallinity of PEG 20,000 among the blend membranes. The PEG 20,000 is thought to freely increase the apparent diffusion of CO_2 and result in the relatively high $\alpha CO_2/N_2$ at room temperature compared with the other blend membranes, as can be seen in Figure 5.

CONCLUSIONS

Well-distributed transparent CA and PEG blend membranes were successfully prepared with a mixed solvent of 40% dichloromethane and 60% tetrahydrofuran. The blend membranes containing PEG 20,000 were proposed to be the most promising for improving the permeability of CO_2 and the selectivity for CO_2 over N_2 of all the blend membranes containing PEG 200, 600, 2000, 6000, and 20,000. In our study, the results are quite contrary to those of Kuehne and Friedlander,[7] which showed a high solubility of sour gas in PEG. Though the apparent solubility coefficients of CO_2 were decreased by the blending of PEG 20,000, the increased apparent diffusivity coefficients of CO_2 resulted in improvement in the permeability coefficients of CO_2 for the blend membranes. They were strikingly enhanced at high temperatures for the blend membranes with high PEG 20,000 content compared with the CA membrane, though this was not the case for the blend membranes containing 10, 20, and 30% PEG 20,000.

In addition to its influence on the permeability of CO_2, the existence of PEG 20,000 in the CA blend membranes also clearly restrained the decline in their $\alpha CO_2/N_2$ values with increasing temperature but caused their $\alpha CO_2/CH_4$ values to decrease substantially at all experimental temperatures. The characterization of the membranes suggested that microphase separation occurred and the intersegmental chain packing was densified, which may result in the decreasing apparent solubility of CO_2 in the blend membranes containing PEG 20,000 at temperatures below 50°C. Therefore, the theory that the flexible main chain of PEG 20,000 allowed large penetrants such as CO_2 and CH_4 to diffuse easily through the blend membranes was proposed to be the explanation for the main tenancy of high $\alpha CO_2/N_2$ values at high temperatures resulting from their high diffusivity selectivity for CO_2 over N_2. However, their $\alpha CO_2/CH_4$ values were decreased by the blending of PEG 20,000 in the membranes.

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