Gas Permeation Properties of a Composite Membrane Filled with Poly(ethylene oxide) into a Porous Membrane

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ABSTRACT: The permeability coefficients of O_2, N_2, and CO_2 gases at 25°C were examined for composite membranes that were prepared by filling poly(ethylene oxide)(PEO) with different molecular weights into a porous membrane. The permeability coefficients of O_2, N_2, and CO_2 were $2 \times 10^{-10} - 4 \times 10^{-10}$, $5 \times 10^{-11} - 9.5 \times 10^{-11}$, and $6 \times 10^{-10} - 1 \times 10^{-9}$ (cm^3 STPcm/cm^2 s cmHg), respectively. The higher permeability coefficients of CO_2 are explained in terms of high solubility of CO_2 in filled PEO. The permeability coefficient of CO_2 was affected by the degree of crystallinity of PEO in the composite. On the other hand, there was little effect of crystallinity on O_2 and N_2 permeability coefficients. Some probable relationships between selectivities of O_2 to N_2 and CO_2 to N_2 and the degree of crystallinity of PEO were observed. The CO_2 gas permeability coefficients of the composite membrane for PEO50000 ($M_w = 5 \times 10^4$) showed a marked change due to melting or crystallization of PEO. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2733–2738, 1999

Key words: gas permeability; selectivity; crystallinity; composite membrane; poly(ethylene oxide)

INTRODUCTION

Gas permeation properties of polymer blends with poly(ethylene oxide)(PEO) have been extensively investigated.[1,2] In general, the polymer blend membranes with PEO exhibit high CO_2 permeability, as CO_2 is highly soluble in PEO. It is reported that PEO in polymer blends with nitrocellulose acts as a plasticizer and enhances CO_2 permeability.[1] On the contrary, the CO_2 diffusivity and CO_2 permeability for a polymer blend of poly (maleic acid-*co*-styrene) with PEO were lowered because hydrogen bonds can be formed between the two polymer chains.[2] It is found that the CO_2 permeability coefficient is controllable in a certain range using a polymer blend with PEO as one component. Using the parallel and series transport models,[3] the gas permeation behavior of polymer blends is usually explainable, but is sometimes very complex and at a probably qualitative explanation level.[4,5] Moreover, unfortunately, the gas permeation properties of PEO itself are scarcely clear.

In this study, composite membranes using a porous polypropylene (PP) filled with PEO, in which pores of a fixed size (200 × 2000 Å) are uniformly distributed, were prepared. The objective of our work is to know the change of morphology of PEO polymer in the pore and its effect on the permeability of PEO. Varying molecular weights of PEO were used, and we examined the gas permeation and separation properties of these

composite membranes from the standpoint of the structure of PEO. The effect of molecular weight of PEO, packing fraction in the pore, and melting of crystalline PEO on the gas permeation properties of the composite membranes are discussed.

EXPERIMENTAL

Materials

A porous polypropylene membrane treated with a very small amount of surfactant (38% porosity), which was generously supplied from Daicel Chemical Industries Ltd., was used in this study. PEOs with various molecular weights were purchased from Wako Pure Chemical Industries Ltd., and used without further purification. The composite membranes were prepared by two different methods. The first was the method of immersing the porous PP membrane into the melt of PEOs at 80°C for an hour, and under vacuum to get rid of air bubbles in a pore. After quick cooling to room temperature, the PEO on the surface of the composite membrane was removed by detaching the surface, and then the composite membrane was kept at room temperature under vacuum. The packing fraction of the prepared composite membrane was estimated from a weight fraction of the prepared membrane, and it was assumed that the packing fraction of the membrane prepared by the first method was equal to unity. The second method was that of immersing the porous PP membrane into a PEO–benzene solution with different concentrations for 24 h at 50°C to change the packing fraction of PEO. When PEO solidified at room temperature, after taking it out from the solution, the PEO on the surface of the composite membrane was removed by detaching the surface, and the composite membrane was dried at room temperature for 24 h under vacuum. The composite membranes prepared in such a way were weighed to evaluate the packing fraction. Abbreviations used for the prepared composite membrane are as follows: PEO X-Y; X is the molecular weight of used PEO and Y is the concentration (wt %) of PEO–benzene solution when the composite membrane is prepared by the second method.

O_2, N_2, and CO_2 gases used in this study were at least 99.9% purity, and were used without further purification.

Method

Differential scanning calorimetry (DSC) measurements were carried out using a Perkin–Elmer DSC 7. DSC thermograms of the composite membrane of approximately 5 mg were obtained at the heating rate of 10°C/min from 25 to 100°C under circulating dry N_2. The degree of crystallinity of PEO filler was evaluated using the observed enthalpy of melting and the reference value of the enthalpy of melting of perfect crystal (213.4 J/g).[6]

The measurements of the gas permeability coefficients at 25–60°C were performed according to the following procedure. The composite membrane mounted in a permeation cell (the permeable area is 1.887 cm^2) was degassed for 24 h at 10^{-4} mmHg in a permeation apparatus. The downstream side of the membrane was evacuated to about 10^{-4} mmHg. Permeate gas was introduced into the upstream side (100–500 cmHg), and the permeate pressure at the downstream side was monitored using a MKS-Baratron pressure transducer (227AA). The permeability coefficient was evaluated from the steady-state gas permeation rate obtained experimentally.

RESULTS AND DISCUSSION

Degree of Crystallinity of PEO in the Composite Membrane

DSC measurements were made for the composite membranes prepared by the first method, and the degree of crystallinity of PEO in the composite membrane was calculated by the observed enthalpy of melting using the following equation:

$$\chi_c = \frac{\Delta H}{\Delta H_c} \qquad (1)$$

where χ_c, ΔH, and ΔH_c are the degree of crystallinity, the observed enthalpy of melting for PEO in the composite membrane, and the enthalpy of melting of 100% crystalline PEO, respectively. The value of ΔH_c was used here as the reference value of 213.4 J / g.[6] The values of χ_c are shown in Table I. The χ_c of pure PEO was increased with the molecular weight of PEO, and the highest was for molecular weights of 3000 or 7500. When the molecular the weight of PEO is more than 3000, the χ_c of pure PEO saturates to 85–86%. This is a general trend of crystalline polymers. There is a limitation of χ_c because of chain folding, the presence of lattice defects, and void et al.[7] PEOs with lower molecular weight cannot exhibit high χ_c because of the effect of the chain end groups. The

Table I   Crystallinity of Pure PEO and PEO in a Porous Membrane

	Crystallinity (%)	
M_w	Pure PEO	PEO in a Porous Membrane
1000	66	39
2000	82	74
3000	86	77
7500	86	77
10,000	85	71
20,000	85	73
50,000	85	61

χ_c of the PEO in the composite membrane is lower than that of the pure PEO. In other words, there is a probable tendency that the size of the PEO crystal in a pore (200 × 2000 Å) is reduced compared to that of the PEO crystal formed in a free space.

Permeation Properties

O_2, N_2, and CO_2 permeability coefficients of the composite membranes were examined at 25°C from the standpoint of the effect of the PEO component. Figures 1–3 show the pressure dependence of the respective permeability coefficients of O_2, N_2, and CO_2 for composite membranes prepared by the first method. The permeation properties of these composite membranes are affected by the PEO component and, judging from the value of the permeability coefficient and its pressure dependence, these composite membranes are considered to be not porous but fundamentally dense. It is important to consider the permeation of each component of PP and PEO of the composite membrane. Because the component of the PP

Table II   Selectivity of O_2 to N_2 and CO_2 to N_2 at 30 cmHg for PEO1000, PEO2000, PEO7500, PEO20000, and PEO50000

Sample	P_{O_2}/P_{N_2}	P_{CO_2}/P_{N_2}
PEO1000	5.3	16
PEO2000	4.3	14
PEO7500	3.3	9.8
PEO20000	2.7	7.9
PEO50000	4.0	26

Figure 1   Pressure dependence of permeability coefficient of O_2 for PEO1000 (○), PEO2000 (●), PEO7500 (□), PEO20000 (■), and PEO50000 (△) at 25°C.

has the same effect on the permeation properties of the composite membrane, the change in permeability is particularly affected by the PEO component. It is necessary to examine the degree of crystallinity of the PEO component, as the crystalline part can cause no permeation at all. There might not be any clear relationship between permeability coefficients of O_2 and N_2 and the degree of crystallinity of PEO, as can be seen from Figures 1 and 2 and Table I. It is noted, however, that there are some probable relationships between the permeability coefficient of CO_2 and the degree of crystallinity of the PEO from Figure 3 and Table I. PEO1000 and PEO50000 composite

Figure 2   Pressure dependence of permeability coefficient of N_2 for PEO1000 (○), PEO2000 (●), PEO7500 (□), PEO20000 (■), and PEO50000 (△) at 25°C.

Figure 3 Pressure dependence of permeability coefficient of CO_2 for PEO1000 (○), PEO2000 (●), PEO7500 (□), PEO20000 (■), and PEO50000 (△) at 25°C.

Figure 4 Pressure dependence of permeability coefficient of O_2 for PEO1000 (○), PEO1000-50 (●), and PEO1000-75 (△) at 25°C.

membranes exhibit higher permeability coefficient than the other composite membranes. This corresponds to the lower degree of crystallinity of PEO1000 and PEO50000. It seems strange that there is not a relationship for O_2 and N_2 gas permeation, but only for CO_2 gas permeation. The permeabilities in this system are expected to be affected by the PEO component. The obtained results show that the PEO component influences CO_2 permeability. There are probable explanations such as high CO_2 solubility of the PEO component.

Table III shows selectivity at 30 cmHg of O_2 to N_2 and CO_2 to N_2 of the composite membranes prepared by the first method. There are also similar relationships between selectivity of O_2 to N_2 and CO_2 to N_2 and the degree of crystallinity of PEO. This corresponds to the fact that the permeability coefficient of CO_2 is higher than that of N_2, and is affected by the degree of crystallinity of the PEO. Assuming that gas permeation, through pores partly filled in the composite membranes, is a Knudsen flow, selectivity of O_2 to N_2 is about 1,

because the permeability varies inversely as the square root of the molecular weight in such a system. Selectivity of O_2 to N_2 of the composite membranes studied here is higher than 1, as seen in Table III. It is confirmed that these membranes are not porous.

Figures 4–6 show the pressure dependence of permeability coefficient at 25°C of O_2, N_2, and CO_2 of the composite membranes prepared by the second method. Table III shows selectivity of O_2 to N_2 and CO_2 to N_2 at 30 cmHg for the composite membranes prepared by the second method. There is a remarkable effect on O_2, N_2, and CO_2 permeability coefficients, i.e., an enhancement of

Table III   Selectivity of O_2 to N_2 and CO_2 to N_2 at 30 cmHg for PEO1000, PEO1000-75, and PEO1000-50

Sample	$\bar{P}_{O_2}/\bar{P}_{N_2}$	$\bar{P}_{CO_2}/\bar{P}_{N_2}$
PEO1000	5.3	16
PEO1000-75	3.2	6.3
PEO1000-50	1.1	0.83

Figure 5 Pressure dependence of permeability coefficient of N_2 for PEO1000 (○), PEO1000-50 (●), and PEO1000-75 (□) at 25°C.

permeability coefficient by such a membrane preparation method. As the concentration in solution increases, packing fraction is increased and as a result, it is observed that O_2, N_2, and CO_2 permeability coefficients decrease. There is a slightly increasing tendency of O_2, N_2, and CO_2 permeability coefficients of PEO1000-50 (packing fraction: 55%) and PEO1000-75 (packing fraction: 70%) as gas pressure increases. PEO1000-75 exhibits higher permeability coefficient of O_2, N_2, and CO_2 than PEO1000, and also permeability coefficients of O_2 and N_2 increase much more remarkably than those of CO_2. This shows that compared with PEO1000, gas permeation of PEO1000-75 might be affected by smaller pore component in the partly filled composite membrane. The CO_2 permeability coefficient of PEO1000-50 is lower than the O_2 and N_2 permeability coefficients, and selectivities of O_2 to N_2 and CO_2 to N_2 are, respectively, about 1 and 0.8. As these selectivities vary inversely as the root of the molecular weight according to the Knudsen flow, it is considered that gas permeation of PEO1000-50 exhibits the Knudsen flow. The composite membrane prepared by the second method could provide a porous membrane that is composed of pore filled partly with PEO.

From the facts discussed above, it was found that the PEO component in the composite membrane affects the permeability of the composite membranes. Therefore, it is expected that the permeability of the composite membranes might vary considerably by melting of the PEO crystal-

Figure 6 Pressure dependence of permeability coefficient of CO_2 for PEO1000 (○), PEO1000-50 (●), and PEO1000-75 (□) at 25°C.

Figure 7 Temperature dependence of permeability coefficient of CO_2 for PEO50000 at $p = 10$ cmHg.

line part in the temperature range of 25–60°C, although there is also a very slight change of permeability coefficient of the PP membrane itself. Figure 7 shows the Arrhenius type temperature dependence of the permeability coefficients at 10 cmHg of CO_2 for PEO50000. The permeability coefficients of CO_2 increased with temperature, and varied remarkably at temperatures near 40°C. Namely, temperature dependence of permeability coefficients showed an inflection point around 40°C, which demonstrates the beginning of melting of PEO crystals in the composite membrane. Similarly, one could observe the abrupt change with crystallization of PEO in the cooling process. From the results of DSC thermograms, it was found that PEO in the pores of PEO50000 begins to melt near 40°C, and has a melting point of 53°C. Therefore, it is considered that such a remarkable increase of permeability coefficient is due to the melting of the PEO. This fact suggests that one can control the permeability coefficient within a certain range by crystal melting.

CONCLUSIONS

Permeation properties of the prepared composite membranes in this study were affected by the degree of crystallinity and packing fraction of the PEO. Composite membranes prepared by immersing into melts of the PEO with different molecular weights had a high permeability coefficients for CO_2. This result showed that the factor

to influence permeability is the PEO component, and CO_2 is very soluble in PEO. The temperature dependence of CO_2 permeability coefficients showed an inflection point at 40°C, corresponding to the beginning of the PEO crystal melting.

The composite membranes prepared by immersing into the PEO–benzene solution with various concentrations exhibited the slight pressure dependence of the permeability coefficient and the possibility of high permeability. These results showed that the composite membranes prepared by such a method might possibly be slightly porous membranes. The method used in this study demonstrated the possibility of controlling the pore size over a relatively wide range.

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