Polymer Bulletin 20, 521–524 (1988)

Polymer Bulletin

Selective permeation of CO_2 and O_2 by membrane of poly(maleic acid-co-styrene)-poly(ethylene glycol) interpolymer complexes

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SUMMARY

Contrary to most polymer membranes, the membrane composed of poly(maleic acid-co-styrene)-poly(ethylene glycol)(PMS-PEG) complexes gives separation factor for CO_2 to O_2 smaller than 1. While the unit molar ratio reaches 1, the separation factor for CO_2 to O_2 exhibits a minium. The temperature dependence of CO_2 permeability is larger than O_2 permeability, i.e. the permeation activation energy of CO_2 (16 kcal/mol) is larger than that of O_2 (3 kcal/mol). The separation factor for CO_2 to O_2 increases with increasing temperature. A tentative explanation is proposed for the results.

INTRODUCTION

Polymeric membranes for selective gas permeation have attracted a great deal of research in recent years.(1)Blending of two or more polymers is a simple physical approach to provide some special polymer molecular structure for gas transport properties.(2,3) It is generally found that the permeability of CO_2 is higher than that of O_2 for most polymer membrane. A recent work in our laboratory revealed that the PAA-PVA interpolymer complexes gave a contrary result.(4)

In the present investigation, the permeabilities of O_2, N_2, CO_2 ,CO and H_2 in poly(maleic acid-co-styrene)-poly(ethylene glycol)(PMS-PEG) complexes membranes were measured. It is reported here that the permeability of CO_2 is smaller than that of O_2. Such membranes might be of great importance in preservation of frutage or vegetables.

EXPERIMENTAL

The commercial samples of PEG was used without futher treatment. Poly(maleic acid-co-styrene) was prepared as follow : copolymerization of styrene and maleic anhydride initiated by benzoyl peroxide gave poly(maleic anhydride-co-styrene). (PMAnS) PMAnS was dissoved in 2N sodium hydrate and precipitated in 2N hydrochloric acid and futher reprecipitated by dioxane/H_2O.

The interpolymer complexes membrane of PMS-PEG was prepared by casting the mixture of initial polymers in dioxane solution directly on PTFE plate. Permeation rate of gas through membrane with a 5cm diameter was measured by gas chromatography. The detector was a thermal conductivity cell. The volume of gas permeated per unit time was measured from the peak area on the chromatogram, from which the permeability of gas under standard conditions was calculated according to the following equation

$$P = T_o pVl \;/\; 76 p_o TAt \qquad (1)$$

where p_o and T_o are the pressure and temperature under standard conditions, p and T are the experimental pressure and temperature, V is the volume of gas permeated through the membrane, l is the membrane thickness, A is the membrane area, and t is the time of permeation.

RESULTS AND DISCUSSION

Dependence of the permeability of gases on membrane with different PEG content is shown in Table 1. The permeability of H_2, O_2, N_2, especially CO and CO_2 decreases with the increase of the content of PEG in complexes. The separation factor for CO_2/O_2 decreases by the addition of PEG to PMS while the separation factor for O_2/N_2 does not change. Usually, small molecules have high permeability because they are small and have high diffusion coefficients. Whereas large molecules such as CO_2 have high permeability because they are more condensable and have high solubility, as a result, the permeability of CO_2 are almost larger than O_2 in polymer membrane. The result of Table 1 indicates that the PEG incorporated in PMS does not behave as plasticizer. The addition of PEG to PMS might result in a loss in free volume available for solution of the permeant species and an increase of the molecular interaction which hinders polymer segmental motions. The effect of increasing cohesive forces between polymer chains on permeability for CO_2 is even more pronounced than they are for O_2, which leads to a decrease of separation factor for CO_2/O_2. The hydrogen bonding can be formed between PMS and PEG macromolecular chains,(5) which increases the interaction of macromolecules and inhibits the motion of molecular segments. The amount of hy hydrogen bonding increases with the PEG content.

TABLE 1
Gas Permeability of PMS-PEG Complexes Membrane

Unit molar ratio a)	P_{H_2}	P_{CO}	P_{CO_2}	P_{O_2}	P_{CO_2}/P_{O_2}	P_{N_2}	P_{O_2}/P_{N_2}
0/100	-	0.33	2.1	3.4	0.42	1.3	2.7
20/80	1.1	0.069	1.5	4.2	0.37	1.6	2.7
30/70	0.77	0.048	0.52	3.5	0.15	1.2	2.8
40/60	-	0.033	0.43	3.0	0.14	1.1	2.8
50/50	0.44	0.036	0.47	2.2	0.21	0.74	2.9

a): PEG/PMS
Unit of Permeability: $10^{-10} cm^3 (STP) cm/cm^2 cmHg$
Temperature: 296K
Driving Pressure: 1.8 kg/cm^2

The relationship between permeation coefficient and temperature obeys the Arrhenius equation. The influence of temperature on the permeability of CO_2 in PMS-PEG is higher than those for O_2 and N_2 as shown in Table 2. The separation factor for CO_2 over O_2 increases with increasing temperature while the separation factor for O_2 over N_2 does not change as shown by Figure 1.

TABLE 2
Activation Energy of Gas Permeation in PMS-PEG with Unit Molar ratio of 1:1 in Driving Pressure of 1.8 kg/cm^2

Gas	E_p (kcal / mol)
CO_2	16
O_2	2.8
N_2	3.0

There are two effects of temperature on the membrane: 1). When the mobility and diffusivity of macromolecular chain increase with increasing temperature , the diffusion of gases through the membrane becomes easier. The gas with big size is more sensitive to the temperature in diffusion rate than the small one. 2). The amount of hydrogen bonding might decrease with increasing temperature. For CO_2/O_2 pair with big difference in molecular size, the CO_2/O_2 separation factor is small than 1 whether or not depends on the temperature of membrane, as shown by Figure 1.

The permeability of CO_2, O_2 and N_2 in PMS-PEG is dependent of the driving pressure, as shown by Figure 2. This result suggests that the permeation of CO_2, O_2 and N_2 in PMS-PEG is dual mode transport, i.e., the solution in Henry mode and the adsorption in Langmuir mode.

CONCLUSIONS

Gas permeability in the membrane of poly(maleic acid-co-

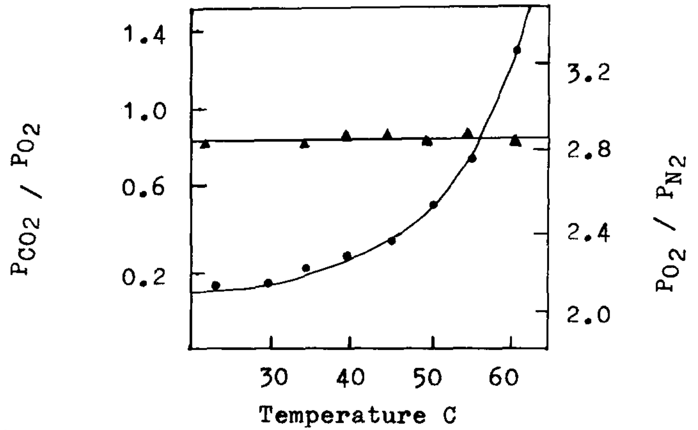

Fig. 1. Separation factors of PMS-PEG as a function of the measuring temperature.(•)CO_2/O_2; (▲)O_2/N_2

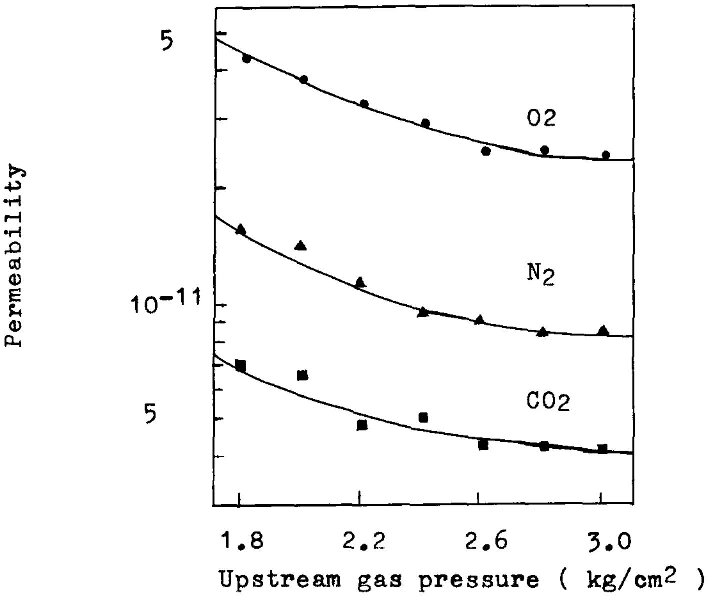

Fig. 2. Effect of upstream gas pressure on permeation coefficient for PMS-PEG with unit molar ratio 1:1 at 296K.

styrene)-poly(ethylene glycol) interpolymer complexes decreases with increasing PEG content. The separation factor for CO_2/O_2 in PMS-PEG is smaller than 1, which is quite different from most polymers. The dependence of permeability on temperature is greater for CO_2 than for O_2, so the separation factor for CO_2/O_2 increases with increasing temperature.

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Accepted October 15, 1988 S