

# Gas Permeabilities of Cellulose Nitrate/Poly(ethylene Glycol) Blend Membranes

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## Synopsis

The permeability ( $P$ ) of cellulose nitrate (CN)/poly(ethylene glycol) (PEG) blend membranes for  $N_2$ ,  $O_2$ , and  $CO_2$  has been measured as a function of film composition. The system CN/PEG-300 showed excellent miscibility, and films of the composition from 100/0 to 50/50 could be used for permeability measurements.  $P$  for each gas has been found to be almost constant or rather slightly lowered up to ca. 20 wt % PEG-300 content and then increased appreciably with increasing fraction of PEG. The increment of permeability was most remarkable for  $CO_2$ , and hence the permselectivity for  $CO_2$  was considerably enhanced. Such a behavior of  $P$  has been found to be attributable to the plasticizing effect of PEG molecule lowering the glass transition temperature of the blend polymers. The effect of the molecular weight of PEG and that of closed voids generated in glassy blend membranes fabricated from acetone cast on gas permeabilities have been also discussed.

## INTRODUCTION

In the field of membrane separation technology, homogeneous polymer alloys have recently appeared as novel materials. Cabasso et al. have developed asymmetric alloy membranes of aromatic polyphosphonates or poly(4-vinyl pyridine) blended with cellulose esters and found such membranes to be very effective for separation of azeotropic liquid and for water desalination through reverse osmosis.<sup>1-3</sup> Cellulose nitrate (CN), which is usually mixed with a plasticizer, pigment, or resin, has been widely used as a paint film. The compatibility of CN with many polymer materials has been extensively studied,<sup>4</sup> and it is generally accepted that CN has excellent miscibility with a variety of polymers. However, few investigations have so far been made on the gas permeabilities of blend polymers containing CN. Although CN homopolymer has relatively poor gas permeabilities among various polymers,<sup>5</sup> the alloying of polymer has a possibility of yielding new materials which may show excellent properties. In the present work, this possibility was examined by using a blend of CN with poly(ethylene glycol) (PEG); that is, the change of gas permeabilities with the film composition of CN/PEG blend was systematically studied. In addition the effect of closed-type voids generated in the interior on membranes of gas permeabilities was investigated. The results presented here will show a new and easy line of approach to improve gas permeabilities and permselectivities.

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## EXPERIMENTAL

### Film Preparation and Characterization

Commercial extra pure PEG-300, -1000, and -4000 (Wako Pure Chem. Ind.) and CN ( $N = 10.9$  wt %) were used as starting materials. Film specimens were prepared by casting-air drying method on a glass plate using acetone or tetrahydrofuran (THF) as a cast solvent. After being vacuum-dried at room temperature for several days, they were subjected to characterization and permeability measurements. The surface and the cross section of films were observed under a JEOL JSM-U3 scanning electron microscope. Glass transition temperatures were determined with a differential scanning calorimeter (Rigaku Denki) in the range between  $-30^{\circ}\text{C}$  and  $80^{\circ}\text{C}$  at the rate of  $5\text{ K/min}$ . The apparent densities were measured by the flotation method using methanol/water.

### Permeability Measurement

Permeability measurements were performed at  $298\text{ K}$  by the partition cell method. The measuring part of apparatus was outgassed before each run by evacuation until there was no appreciable increase in pressure on a Pirani gauge for about  $30\text{ min}$  after the system was isolated from a vacuum pump. Subsequently, a penetrant gas was introduced into the upstream side compartment and the pressure increase in the downstream side compartment was followed on a Pirani gauge connected to a recorder.  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{CO}_2$  of  $99.9\%$  minimum purities (Seitetsu Kagaku Co.) were employed as penetrant gases.

From the pressure change at steady state ( $\Delta p/\Delta t$ ), the permeability coefficient ( $P$ ) was calculated with the expression

$$P = \frac{273.2}{76T} \frac{L}{A} \frac{V}{p^*} \frac{\Delta p}{\Delta t}$$

where  $V$  and  $T$  are the volume and the temperature ( $298\text{ K}$ ), respectively, of the measuring chamber,  $p^*$  is the upstream pressure of a penetrant gas, and  $A$  and  $L$  are the area and the thickness of a film, respectively. Further, the time lag method was applied to evaluate the diffusivity ( $D_{\theta}$ ), where  $D_{\theta}$  is related to the diffusion time lag ( $\theta$ ) by the equation  $D_{\theta} = L^2/6\theta$ . Then, the solubility constant ( $S_{\theta}$ ) was evaluated with the relation  $S_{\theta} = P/D_{\theta}$ .  $P$  as well as  $D_{\theta}$  was confirmed to be practically independent of  $p^*$  up to ca.  $76\text{ cm Hg}$  ( $= 101,325\text{ Pa}$ ). The blend membranes of lower PEG content were glassy, as will be shown later. Usually, the sorption behavior of glassy polymers tends to deviate from Henry's law at high pressures, which is interpreted by the dual mode sorption.<sup>6</sup> In this study, however, the contribution of immobilized sorption species was found to be negligible in the present pressure range.

## RESULTS AND DISCUSSION

### Membrane Characterization

The system of CN/PEG-300 showed excellent compatibility, and we could obtain transparent or translucent blend membranes of the composition from 100/0 to ca. 30/70 using THF as a cast solvent. However, those of more than 60 wt % of PEG-300 were so sticky and intractable that they could not be subjected to the permeation experiments. For the membrane characterization, dense CN/PEG-300 membranes fabricated from THF cast were used unless otherwise noted.

CN/PEG blend showed single glass transition temperature ( $T_g$ ) in the range of temperature applied here. The change of  $T_g$  with the composition is illustrated in Figure 1.  $T_g$  was lowered monotonically with increasing fraction of PEG and that of the blend of 50 wt % PEG was 310 K. These results demonstrate that CN and PEG are homogeneously compatible and the latter acts as a plasticizer. The observed densities of CN/PEG blends agreed closely with those calculated from the densities of pure CN and PEG. This suggests that no volume change occurs upon mixing. Further, the effective thickness of blend membrane estimated from the weight per unit area of a film and the calculated density was confirmed to be in fair agreement with that measured on electron photographs of cross section for dense membranes.

### Change of Permeability with Film Composition

Variations of permeability and permselectivity with the film composition were studied for the system of CN/PEG-300. The results are shown in Figure 2(A) and (B), where closed and open symbols denote the data for membranes of THF and acetone cast, respectively. The former will be discussed first. Permeability coefficient for each gas is almost constant or rather slightly lowers up to ca. 20 wt % PEG and then increases with increasing fraction of PEG. The permeability ratio  $P_{\text{CO}_2}/P_{\text{N}_2}$  fairly increases with the fraction of PEG, while  $P_{\text{O}_2}/P_{\text{N}_2}$  is practically constant. This indicates a selective increase in  $P_{\text{CO}_2}$ . Diffusion coefficients and solubility constants are shown in Figures 3(A) and (B), respectively,

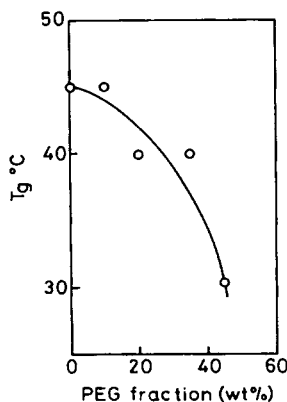


Fig. 1. Variation of the  $T_g$  with the composition of CN/PEG-300 blend membranes.

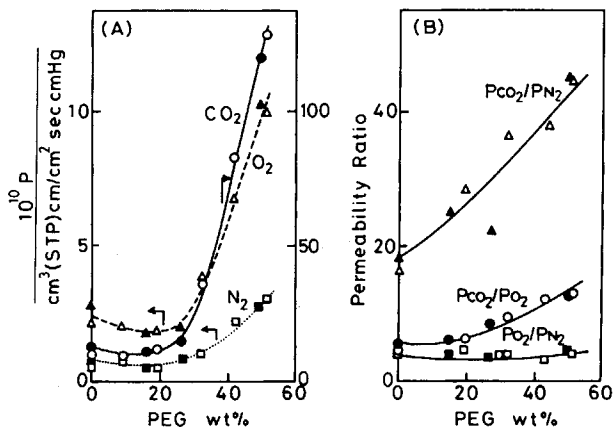


Fig. 2. Gas permeabilities (A) and permeability ratios (B) of CN/PEG-300 blend membranes cast from THF (●, ▲, ■) and acetone (○, △, □) at 298 K.

as a function of film composition. The value of  $D_{\theta}$  for each penetrant gas increases significantly in the region higher than 30 wt %. On the other hand, the value of  $S_{\theta}$  for each gas decreases initially and subsequently increases after a minimum at 20–40 wt % PEG content. The dependence of  $S_{\theta}$  for CO<sub>2</sub> is especially remarkable. Thus the marked increase in  $P_{CO_2}$  above 30 wt % PEG content is attributable to the increments in both  $D_{\theta}$  and  $S_{\theta}$ .

The behavior yielding a minimum in the relation between gas permeability and the film composition has been observed for various systems containing a plasticizer as one component.<sup>7–10</sup> This has been generally interpreted as an increase in diffusivity resulting from the spreading effect of the plasticizer on the polymer chain and a decrease in diffusivity or solubility caused by the blocking effect of the plasticizer in the diffusion path or by absorption of the plasticizer on active sites originally available for dissolution of penetrant gases. In the present system the spreading effect of PEG molecule would appear more significantly, resulting in higher mobilities of CN segments and, consequently, in increased diffusivities. This is well supported by the results of  $T_g$  measurements.

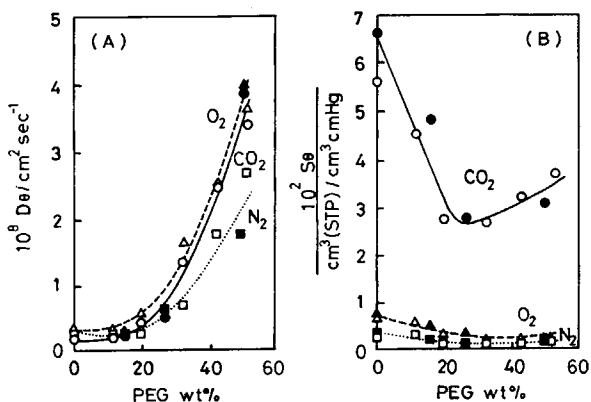


Fig. 3. Diffusivities (A) and solubilities (B) of gases in CN/PEG-300 blend membranes cast from THF (●, ▲, ■) and acetone (○, △, □) at 298 K.

However, the change of  $S_{\theta}$  with with fraction of PEG cannot be explained from above discussion. One possible explanation might be offered from the viewpoint of the change of the state of polymer matrix. The  $T_g$  for blend film of 40 wt % PEG content was close to the measurement temperature; that is, the blend films of lower PEG content were glassy at the measurement temperature, whereas those of higher PEG content were rubbery. The remarkable changes in transport and equilibrium properties observed around ca. 30 wt % PEG might be associated with the phase transition. Stern et al. have found that transport properties of cellulose acetate membrane showed discontinuous dependence on temperature at the glass transition point.<sup>11</sup> However, we have no answer at the present to the question why such variations are so dramatic especially about the parameters for CO<sub>2</sub>. The permeability ratio of  $P_{CO_2}/P_{N_2}$  and the equilibrium solubility coefficient for CO<sub>2</sub> of pure PEG-300 liquid membrane are ca. 20 and 0.02 cm<sup>3</sup> (STP)·cm<sup>-3</sup>·cm Hg<sup>-1</sup>, respectively.<sup>12</sup> Thus, the property changes of the present polymer alloy system cannot be expected from the characters of separate component polymers.

Permeability data for the blend membranes containing PEG of different molecular weight are presented in Table I. Each membrane of the same composition has been prepared from acetone cast. Clearly  $P$  is larger when PEG of lower molecular weight is blended. This is because a smaller molecule, which has higher mobility and can enter into the stiff CN matrix more easily, may exert a larger plasticizing effect on the mobility of CN segments.

### Generation of Closed Voids and Its Effect on Permeability

Films of pure CN and of lower PEG content fabricated from acetone cast were stiff and opaque white, while those containing more than 40 wt % PEG were relatively soft and translucent. For whitish membranes, appreciable unevenness of the surface and a great number of voids were observed under an electron microscope. Typical examples of electron micrographs are shown in Figure 4. These voids are discoid, and larger ones take the size of ca. 4–5 μm in diameter. Such cavities were observed only when acetone was employed as a cast solvent, and thus they might result from atmospheric moisture introduced into the cast solution upon the air-drying treatment due to the hygroscopic property of acetone. Moisture concentrated during the vaporization of acetone would act as a nonsolvent to CN and yield porous membranes through the phase-inversion or the coacervation process.<sup>13</sup> The amount of moisture is considered to be so small that closed-type voids would be generated. Disappearance of voids in the

TABLE I  
Effects of Molecular Weight of PEG on Gas Permeabilities of CN/PEG(57/43) Blend Membranes

MW of PEG	10 <sup>11</sup> Pa			$P_{CO_2}/P_{N_2}$
	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	
300	2.2	6.7	82	37.8
1000	2.1	6.2	72	33.6
4000	0.5	1.6	14	28.6

<sup>a</sup> cm<sup>3</sup> (STP)·cm/cm<sup>2</sup>·s·cm Hg.

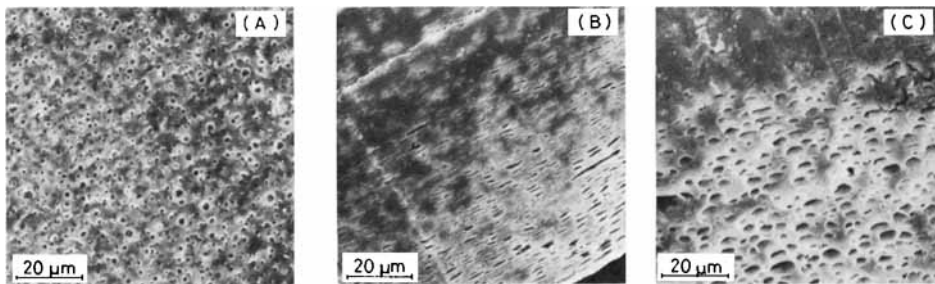


Fig. 4. Scanning electron micrographs of membranes prepared from acetone solutions: (A) Surface of CN/PEG-300(90/10); (B) cross section of pure CN; (C) oblique cross section of pure CN.

films with more than 32.6 wt % PEG content can be explained on the basis of the role of PEG. Namely, the glass transition temperature is lowered with the fraction of PEG which exerts the plasticizing effect to CN matrix. The mobility of segments should be considerably increased with increasing content of PEG so that voids can no longer remain in a film.

In Figures 2 and 3 open symbols denote the transport properties of blend membranes cast from acetone. Here, the thickness of a film was estimated from the weight per unit area and the calculated density of blend. The agreement between the data for membranes from THF and acetone casts is excellent even in the region of lower PEG content. This demonstrates no significant effect of closed-type voids on the gas permeabilities regardless of many sorption-desorption processes at the gas-polymer interface.

## CONCLUSION

Homogeneous blend membranes were fabricated from cellulose nitrate and low molecular weight poly(ethylene glycol). The permeability and the permselectivity for  $\text{CO}_2$  have been found to increase with the content of PEG-300. The remarkable increase in  $P_{\text{CO}_2}$  above 30 wt % PEG content could be attributed to both increases in diffusivity and solubility for  $\text{CO}_2$ . These behaviors are interpreted by the plasticizing effect of PEG which lowers the  $T_g$  of blend polymers to the temperature for gas permeability experiments. The present observations might be significant from the following two points of view. First, the CN/PEG blend membranes would be useful for the separation of  $\text{CO}_2$  from  $\text{N}_2$  and/or  $\text{O}_2$  in order to recover carbon resources or to control  $\text{CO}_2$  concentration in an artificial atmosphere. Second, the possibility has been evidently demonstrated that alloying of a glassy polymer and elastic one (or plasticizer) can improve not only gas permeability but permselectivity.

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