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# Effect of gelation conditions on gas separation performance for asymmetric polysulfone membranes<sup>1</sup>

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## Abstract

Asymmetric gas separation membranes were prepared by the phase inversion technique under different gelation conditions from polysulfone/*N,N*-dimethylacetamide (DMAc) solutions. The dual bath method was employed to control the skin layer properties: the cast film was immersed in 2-propanol bath and water bath in sequence. The membranes were characterized by the permeance of oxygen and nitrogen gases and the observation with scanning electron microscopy (SEM). A thin layer of silicone rubber (PDMS) was laminated on the surface of each asymmetric polysulfone membrane to eliminate the effect of defects in the skin layer. The oxygen permeance was inversely proportional to the square root of immersion time in the first (2-propanol) bath. The skin layer thickness determined by SEM observation increased with an increase in the immersion time in the first bath. For a given immersion time, the oxygen permeance decreased with an increase in the polymer concentration in the casting solution. Selectivity of oxygen over nitrogen also depended both on the immersion time in the first bath and the polymer concentration.

**Keywords:** Polysulfone membranes; Gas separations; Gelation; Permeation

## 1. Introduction

In recent years, attention has been focussed increasingly to the development of gas separation membranes [1–3]. Practical gas separation membranes have, without exception, asymmetric structures to achieve high permeation rates. There are several ways to prepare asymmetric membranes. The most common one is the phase-inversion technique [4,5]; polymer solution is cast onto a glass plate to

form a flat film. After a partial evaporation of solvent, the membrane is immersed into a coagulation media which is non-solvent of the polymer. In the coagulation bath, solvent exchange and phase inversion take place and solidification of polymer film occurs. Since the top and the bottom parts of the membrane are exposed to different conditions during the process, an asymmetric structure with a dense skin layer and porous sublayer is formed. This process has been intensively studied by many authors [4,5] for liquid separation membranes such as reverse osmosis membranes. However, it is difficult to predict the structure and the performance of a membrane without experimentation. For gas separation

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membranes, on the other hand, existence of defects in the skin layer obscures the permeance data except for membranes prepared by a method recently developed [6–8]. The correlation between membrane preparation conditions and permeation performances cannot be readily obtained.

The objective of this study is to correlate the preparation conditions with permeation performance for polysulfone gas separation membranes. The focus of the study is placed on the control of the skin layer properties: the dual bath method [9] by van 't Hof et al. was employed to control the growth of the skin layer in the coagulation process. For the evaluation of the permeation performance, the lamination technique is proposed in this study. The asymmetric membrane is laminated with a thin, homogeneous PDMS (polydimethylsiloxane) membrane to prevent the gas leak through the defects in the skin layer of the substrate asymmetric membrane and force the gas to permeate through the polymer matrix in the skin layer. Although coating would have a similar effect [10], the lamination method is far easier to apply on the flat sheet membranes and the results are more reproducible.

## 2. Experimental

### 2.1. Materials

Polysulfone (UDEL P-1700) polymer was supplied by AMOCO Ltd. Polysulfone is an amorphous hydrophobic polymer and its glass transition temperature is 185°C [12]. Commercially available *N,N*-dimethyl acetamide (DMAc) (Sigma, special grade) was used as solvent without further purification.

### 2.2. Membrane preparation

The polymer was dried in an oven (100°C) for more than 3 days to remove absorbed water vapor before use. The polymer was then dissolved in DMAc thoroughly at 50°C. The filtered and degassed solution was cast onto a glass plate to a thickness of 8 mils (200  $\mu\text{m}$ ) in a glove box, of which the relative humidity was controlled at 10%. The casting temperature was ambient. The membrane was immersed in a coagulation bath of 2-propanol (IPA) at 25°C

immediately after casting and kept there for a predetermined period. Then, the membrane was placed into water bath for more than 12 h to leach out the solvent. The membrane was vacuum-dried in a desiccator for several days prior to the permeation measurement. Scanning electron microscopy (SEM) was used to investigate the sectional view of the membranes. The thickness of the skin layer of the asymmetric membrane was obtained from the SEM picture.

### 2.3. Permeation experiment

A constant pressure system was used for the measurement of permeation rates. A schematic diagram of the equipment is shown in Fig. 1. The membrane was mounted in a stainless steel cell with an effective permeation area of 9  $\text{cm}^2$ . The upstream pressure was kept at 100 psig (6894.8 kPa gauge), while the downstream was kept open to atmosphere. A steady-state permeation rate was measured by a mass flow meter (the minimum detectable flow rate was 0.01 cc/min). All the measurements were carried out for pure oxygen and nitrogen at 25°C with and without lamination. A 3 mils (75  $\mu\text{m}$ ) polydimethylsiloxane (PDMS) membrane was laminated on the skin layer side of a polysulfone membrane. The two membranes adhered to each other under pressure.

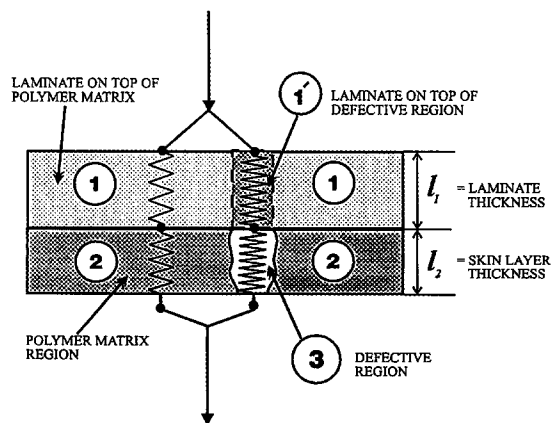


Fig. 1. Schematic diagram for the resistances in a defective skin layer laminated with silicone rubber.

## 2.4. Theoretical

When the substrate asymmetric membrane is laminated with a silicone rubber layer of a uniform thickness, the overall gas flow is decomposed into flows through two arms of resistances connected in parallel (see Fig. 1). The overall resistance for the laminated membrane,  $R_1$ , is written as

$$R_1 = \frac{(R_1 + R_2)(R'_1 + R_3)}{(R_1 + R_2 + R'_1 + R_3)} \quad (1)$$

The meaning of each component resistance is shown in Fig. 1. The method to obtain each component resistance from a pair of permeation experiments using a substrate membrane and a composite membrane in which the substrate membrane is laminated with a thin silicone rubber layer was described in detail in our earlier paper [11]. By applying the method to all asymmetric membranes prepared in this work (160 membranes), it was found that the calculated resistance by the  $(R'_1 + R_3)$  is more than 10 times greater than that by the  $(R_1 + R_2)$  arm. In other words, more than 90% of permeating gas is forced to flow through the polymer matrix region (2) and the flow through the defective region (3) is practically stopped.

Under these circumstances

$$R_1 = R_1 + R_2 \quad (2)$$

$R_1$ , the resistance of the laminated silicone rubber film, can be known from the permeability, thickness and area of the silicone rubber film.  $R_2$  can be obtained from Eq. (1), since  $R_1$ , the overall resistance of the laminated membrane is known experimentally. Then,  $P_2/l_2$  (mol/m<sup>2</sup> s Pa) can be obtained by

$$P_2/l_2 = 1/(R_2 A_2) \quad (3)$$

where  $A_2$  is also nearly equal to the sum of  $(A_1 + A'_1)$ .  $P_2/l_2$  is called hereafter the permeance of polymer matrix and reported for each asymmetric membrane prepared in this work with respect to oxygen and nitrogen gases.

## 3. Results and discussion

Permeance data of a silicone rubber membrane with a thickness of 3 mil (76.2 μm) were obtained

experimentally. They are  $5.70 \times 10^{-8}$  (mol/m<sup>2</sup> s Pa) for nitrogen and  $1.35 \times 10^{-7}$  (mol/m<sup>2</sup> s Pa) for oxygen, respectively, at 25°C. These values are in good agreement with literature values [12]. Therefore, all calculations were based on the above experimental values.

### 3.1. Effect of coagulation media

Fig. 2 shows the structure of a membrane observed with SEM. The membrane was cast from a solution comprised of 27.5 wt% polymer and 72.5 wt% DMAc, and immersed in a 2-propanol (IPA) bath for 300 s at room temperature before being immersed in a water bath for more than 12 h. The oxygen permeance of the membrane was  $6.7 \times 10^{-10}$  (mol/m<sup>2</sup> s Pa), which was almost equal to the lower limit of the permeation measurement for our system. The permeation rate of nitrogen was even lower. Note that all the permeance data referred to in this paper are based on the lamination experiments. This membrane has a distinctive skin layer of which the thickness is about 8 μm, and the porous layer has a sponge-like structure. The skin layer corresponds to the dark smooth region without any visible pores. Obviously, the skin layer of this membrane is too thick to obtain a reasonably high permeation rate. To control the skin layer growth, it is necessary to stop the growth of the skin layer. Fig. 3 shows the structure of the membrane immersed only in a water bath for 12 h without immersion into an IPA bath.

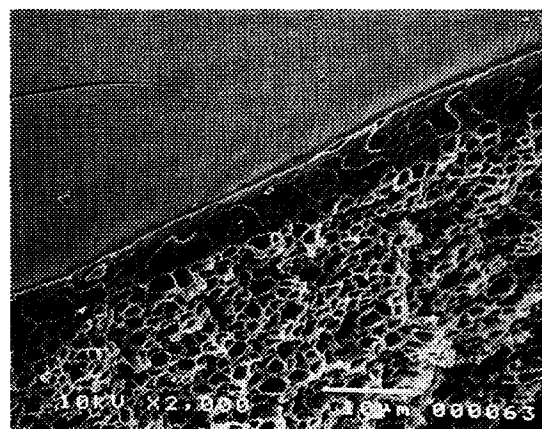


Fig. 2. SEM Image for the membrane with 300 s immersion time in IPA bath (cast from 27.5 wt% polymer solution).

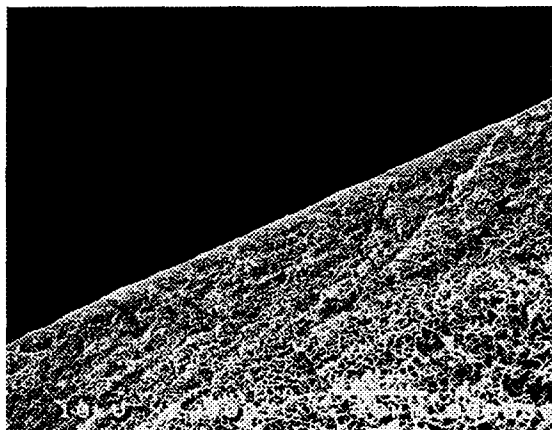


Fig. 3. SEM Image for the membrane immersed only in water bath (cast from 27.5 wt% polymer solution).

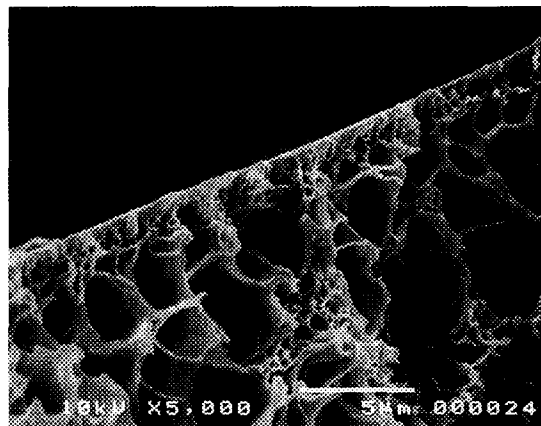


Fig. 5. SEM Image for the membrane with various immersion times in IPA bath (cast from 27.5 wt% polymer solution), immersion time = 5 s.

Although the membrane was cast from the same polymer solution, this membrane had no distinctive skin layer and the permeance of the membrane was  $7.95 \times 10^{-10}$  (mol/s m<sup>2</sup> Pa) for oxygen and  $3.56 \times 10^{-10}$  (mol/s m<sup>2</sup> Pa) for nitrogen with lamination.

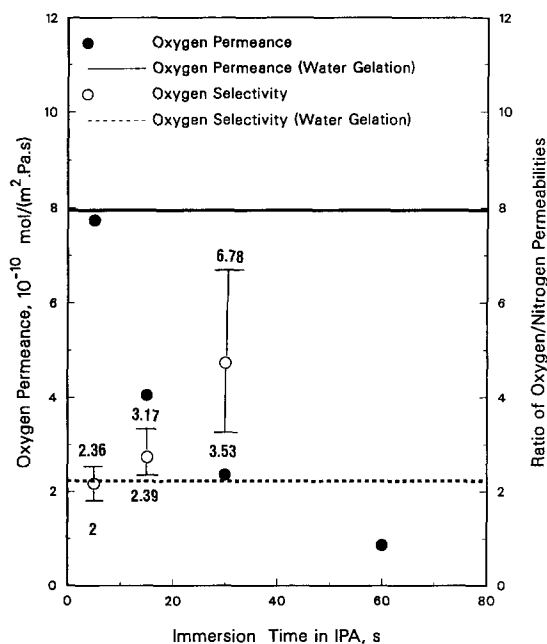


Fig. 4. Effect of immersion time in IPA bath on the performance of the membranes (cast from 27.5 wt% polymer solution).

These results indicate that the growth in the thickness of the skin layer did not take place in the water bath. Fig. 4 demonstrates the effect of immersion time in the IPA bath on the permeance of oxygen (12 h in water bath). The oxygen permeance decreased with an increase in the immersion time in the IPA bath. The growth of the skin layer by comparing the SEM pictures shown in Fig. 2 (300 s) and Fig. 5 (5 s immersion). The skin layer thickness increased from nearly equal zero (5 s immersion) to 8 μm (300 s immersion). Therefore, the skin layer thickness can be controlled by changing the immersion time in the IPA bath.

In Fig. 4 the effect of immersion time in IPA bath on the permeance ration ( $O_2/N_2$ ) is also shown. With an increase in the coagulation time, the selectivity of the membrane increased continuously. In order to show the precision and accuracy of the data points, data in Fig. 4 was chosen to show the maximum and minimum selectivity for each data point if we considered the error in reading the mass flow meters. The selectivity value for the 60 s immersion time sample is not shown due to excessive uncertainty caused by difficulty in measuring  $N_2$  permeance in this sample. It is shown that if we considered a constant error in the measurements of flow rate which is given by the manufacturer as  $\pm 0.01$  cc (STP)/min (or equivalent to a permeance = 0.120

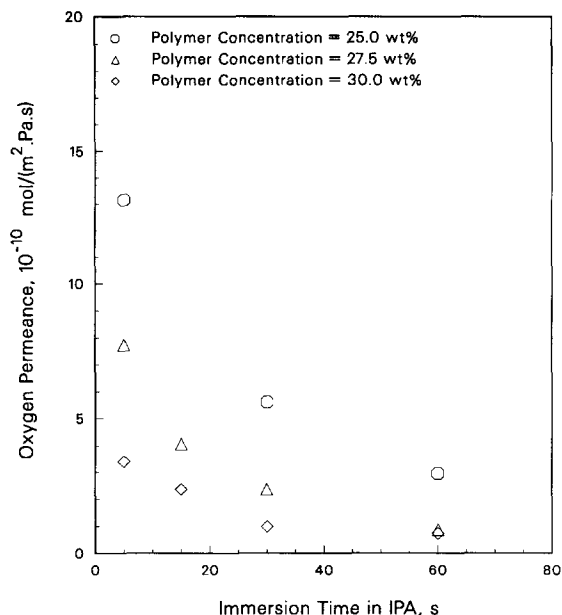


Fig. 6. Effect of immersion time in IPA bath on oxygen permeance.

mol/s m<sup>2</sup> Pa), we can calculate the maximum and minimum oxygen selectivity from the following equation:

$$\text{Maximum Selectivity} = \frac{(\text{O}_2 \text{ permeance} + 0.120)}{(\text{N}_2 \text{ permeance} - 0.120)} \quad (4)$$

$$\text{Minimum Selectivity} = \frac{(\text{O}_2 \text{ permeance} - 0.120)}{(\text{N}_2 \text{ permeance} + 0.120)} \quad (5)$$

As expected, the error increases at lower permeation data which resulted from laminating the membranes with silicone rubber layer. For such low flow rate it is recommended to use constant volume permeance measurements for more accurate measurements.

### 3.2. Effect of polymer concentration

Fig. 6 shows the effect of immersion time in IPA bath on the oxygen permeance of the membranes cast from solutions of different polymer concentrations. The permeance decreased with an increase in the immersion time for all polymer concentrations. For a given immersion time, the oxygen permeance decreased with an increase in the polymer concentra-

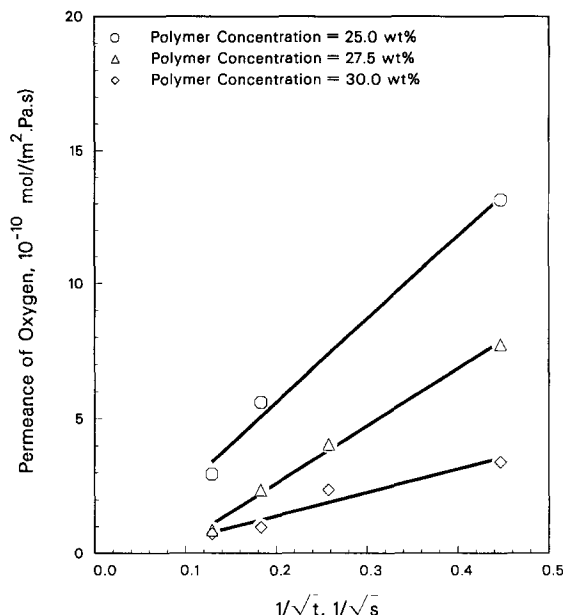


Fig. 7. Correlation of oxygen permeance with the immersion time in IPA bath.

tion. In Fig. 7 the permeance was replotted against  $1/\sqrt{t}$ . A linear relationship was found for each polymer concentration. Since the permeance is supposed to be inversely proportional to the skin layer

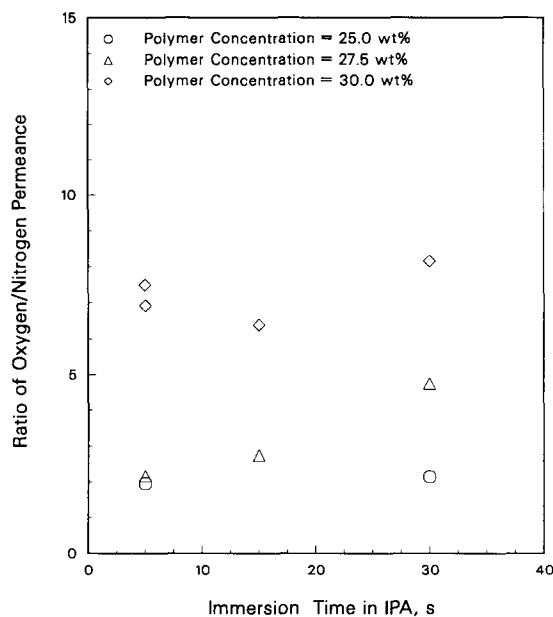


Fig. 8. Effect of the immersion time on oxygen selectivity of oxygen.

thickness,  $\delta$ , this result demonstrates a linear relationship between  $(1/\delta)$  and  $(1/\sqrt{t})$ . It suggests that the growth rate of skin layer is determined by a diffusion process [13,14]. The slope of the straight line decreased as the polymer concentration increased.

The permeance ratio ( $O_2/N_2$ ) depended on the initial polymer concentration as shown in Fig. 8. The oxygen selectivity of the membrane cast from 25.0 wt% solution was about 2 and was independent of the gelation time. The membranes cast from 30.0 wt% solution showed higher selectivity at about 7 and also was independent of the gelation time. On the other hand, the selectivity of the membrane cast from 27.5 wt% solution increased with increasing gelation time.

#### 4. Conclusions

1. The growth of the skin layer can be controlled by changing the immersion time in the IPA (first) bath in the dual bath method. Longer immersion time results in the increase in the skin layer thickness and the decrease of oxygen permeance.
2. Oxygen permeance can be correlated by a  $\sqrt{t}$  law. This suggests that some diffusion process is a rate-determining step in the gelation procedure.
3. The selectivity depended on the polymer concentration of the casting solution as well as the immersion time.

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