# Effect of Solvent Evaporation Conditions on Gas Separation Performance for Asymmetric Polysulfone Membranes

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ABSTRACT: Asymmetric polysulfone membranes were prepared by the phase inversion technique under different solvent evaporation conditions prior to the gelation step. The membranes were cast from the two component system of polymer and N,N-dimethylacetamide in which the polymer concentration was changed from 25.0 to 30.0%. The solvent evaporation temperature was changed from 70 to 120°C, and the evaporation time was 0–15 min. Ethanol, water, or 2-propanol was used as the gelation media. The membranes were characterized by the measurement of oxygen/nitrogen permeation with the lamination technique and by observation with scanning electron microscopy. With an increase in the solvent evaporation time, the oxygen permeance decreased and its selectivity over nitrogen increased; although the permeance was in the range of 1–2 GPU, the oxygen selectivity over nitrogen exceeded 8. A correlation between the permeation performance and the operational parameters involved in the solvent evaporation process was obtained. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1367–1374, 1999

**Key words:** solvent; evaporation conditions; gas separation; asymmetric polysulfone membrane

## INTRODUCTION

In our previous article we attempted to elucidate the correlation between the gas permeation performance of asymmetric polysulfone (PSF) membranes and the operational parameters involved in the gelation step of the phase inversion process<sup>1</sup> using the dual-bath method.<sup>2</sup> It was found that the growth of skin layer thickness could be controlled by changing the gelation time in the 2-propanol bath; with an increase in the gelation

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time the skin layer thickness increased and the oxygen permeance decreased.

The  $(O_2/N_2)$  permeance ratio depended on the initial polymer concentration; when the initial polymer concentration in the casting solution was as high as 30.0%, the  $(O_2/N_2)$  permeance ratio was constant at 7, irrespective of the gelation time. For the membranes cast from a 27.5% polymer solution, the selectivity increased with an increase in the gelation time from 2 to 7 but for a given selectivity the permeance was smaller than the one from a higher polymer concentration. Therefore, the higher initial polymer concentration and shorter gelation time are necessary to obtain high selectivity and a high permeation

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rate. However, there is a limit to the solubility of the polymer in solvents. Moreover, when the polymer concentration is high, casting of the membrane becomes harder because of higher viscosity. Partial solvent evaporation should be a way to obtain a higher concentration region that should be converted to a skin layer; solvent evaporation leads to the increase in the polymer concentration in the vicinity of the top layer of the cast membrane.

Once a high concentration region of polymer is formed, the gelation time can be short because a short gelation time would not sacrifice the selectivity. It is expected that the growth of the skin layer could be controlled by changing the evaporation conditions, for example, a shorter evaporation time for a thinner skin layer. The present study was focused on the solvent evaporation process in the formation of asymmetric PSF gas separation membranes; we attempted to elucidate the correlation between the parameter related to the solvent evaporation process and the gas permeation performances.

## **EXPERIMENTAL**

#### **Membrane Preparation**

PSF was supplied from AMOCO under the trade name of UDEL P-1700. Commercially available N,N-dimethylacetamide (DMAc, laboratory grade) was used as solvent without further purification. Kang et al.<sup>3</sup> measured the viscosity of PSF in Nmethyl pyrrolidinone (NMP) with different shear rates and extrapolated the results at zero shear rate. They listed their results for different casting solution compositions consisting of PSF : NMP : formic acid. The zero shear viscosity of 20% PSF : 80% NMP was found to be 1.287 Pa s. Zero shear Newtonian viscosities for various PSF : NMP casting solutions were measured and reported by Tam et al.<sup>4</sup> Some of their measurements are listed in Table I.

The polymer was dried in an oven  $(100^{\circ}\text{C})$  for more than 3 days to remove the absorbed water vapor before use. The polymer was dissolved in DMAc by applying heat (50°C). A filtered and degassed solution was cast onto a glass plate [thickness of 8 mil (=200  $\mu$ m)] in a glove box in which the relative humidity was controlled at about 10%. The casting temperature was room temperature. After the casting the membrane

Polysulfone (wt %)	Viscosity (Pa s)
15.0	0.41
20.0	1.72
22.0	2.74
23.5	9.84
30.0	23.64

Table IZero Shear Newtonian Viscositiesfor Various PSF : NMP Casting Solutions

Adapted from Tam et al.<sup>4</sup>

was dried either in a gravity convection (no forced air flow) or in a forced convection oven for a predetermined period. After the solvent evaporation process, the membrane was immersed in a 2-propanol (IPA) bath for a given period at room temperature. Then the membrane was immersed in a water bath to quench the gelation (skin layer) growth. After overnight immersion in the water bath the membrane was vacuum dried at room temperature for several days before the permeation measurements.

## **Permeation Measurement**

The permeation rate was measured by the same method reported in a previous article.<sup>1</sup> A constant-pressure system was used for the measurement of permeation rates. The effective membrane area was 9  $cm^2$ . The pressure of the upstream side was 100 psig, and the downstream side was open to the atmosphere. The permeation rate was measured by a mass flow meter (minimum range was 0.01 or 0.001 mL/min). All the measurements were carried out for pure oxygen and nitrogen at 25°C. To eliminate the undesirable effect of the defects in the skin layer, the lamination technique was used for all the gas permeation measurements. The function of the lamination technique was as follows: the PSF membrane was laminated with a homogeneous 3-mil thick polydimethylsiloxane (PDMS) membrane that was practically defect free. The total permeation rate can be expressed as follows:

$$J_{t} = [xQ_{d} + (1 - x)\{Q_{p}Q_{s} / (Q_{p} + Q_{s})\}] (p_{1} - p_{2}) \quad (1)$$

where *x* is the area fraction of the defect in the PSF membrane;  $J_t$  [mol/s  $\cdot$  m<sup>2</sup>] is the total perme-



**Figure 1** Effect of evaporation time on oxygen permeance.

ation flux per unit area of the membrane;  $Q_d$ ,  $Q_p$ , and  $Q_s$  [mol/s  $\cdot$  m<sup>2</sup>  $\cdot$  Pa] are the permeance through the defect, PDMS, and nondefect region, respectively; and  $p_1$  and  $p_2$  (Pa) are the pressure at the upstream side and downstream side, respectively. The area fraction of defect x is usually much smaller than 1, and  $Q_d$  is not much larger than  $Q_s$ . Therefore, the first term in the bracket in the right-hand side of eq. (1) can be negligible compared with the second term. Then we obtain eq. (2) as the final form that contains the no defect related term.

$$J_t = \{Q_p Q_s / (Q_p + Q_s)\} \ (p_1 - p_2) \tag{2}$$

Because the permeance of the PDMS membrane  $Q_p$  can be measured separately, we can calculate the defect-free permeance of the PSF membrane  $Q_s$ .

#### **Structure Investigation**

Scanning electron microscopy (SEM) was used for the investigation of the cross-sectional structure of the membranes. Skin layer thickness was measured from the SEM pictures.

## **RESULTS AND DISCUSSION**

## **Effect of Evaporation Time**

Figure 1 shows the effect of evaporation time on

the oxygen permeance. The membranes were cast from 25.0, 27.5, and 30.0% polymer solutions. Solvent evaporation was carried out in an oven at 95°C for 0-15 min with gravity convection. Gelation time was fixed as 5 s. For a given polymer concentration in the casting solution, the permeance of oxygen decreased with an increase in the evaporation time. The decreasing rate depended on the polymer concentration; for the membrane cast from 27.5 and 30.0% solutions, the oxygen permeance decreased moderately with an increase in the evaporation time while it decreased more quickly for the membrane cast from a 25.0% solution. It is obvious from Figure 1 that the decreasing rate could not be correlated by the  $1/\sqrt{t}$  law, which could be applied to the gelation process.<sup>5</sup> For a given evaporation time, the oxygen permeance of the membrane cast from the 27.5% solution was the largest except for the very short evaporation time, where the membrane cast from the 25.0% solution showed the highest permeance. The membranes cast from the 30.0% polymer solution always gave the smallest oxygen permeance for a given evaporation time.

Figure 2 shows the effect of the evaporation time on the  $(O_2/N_2)$  permeance ratio. When the membranes were cast from a 30.0% polymer solution, the  $(O_2/N_2)$  permeance ratio was almost independent of the evaporation time; the selectivity was about 7. The same trend was observed between selectivity and gelation time when mem-



Figure 2 Effect of evaporation time on  $(O_2\!/N_2)$  permeance ratio.



Figure 3 Evaporation time versus skin layer thickness.

branes were cast from the 30% polymer solution. These results suggest that the  $(O_2/N_2)$  permeance ratio for the membrane cast from the solution of more than 30.0% would be 7, independent of the polymer concentration. The  $(O_2/N_2)$  permeance ratio for the membrane cast from the 27.5% solution increased with an increase in the evaporation time and was over 7 except for the zero evaporation time. Note that the ratio of the oxygen permeance to the nitrogen permeance in the literature is between 6 and 7 for a homogeneous PSF membrane.<sup>6</sup> For the membranes cast from a 25.0% solution, the selectivity was about 2 and was independent of the evaporation time up to 5 min. It suddenly increased to 7 with an increase in the evaporation time thereafter. These results show that the membrane cast from the 27.5%solution showed the highest performance in both selectivity and permeance.

The  $(O_2/N_2)$  permeance ratio of the membranes with solvent evaporation was always higher than those of the membranes without solvent evaporation for a given permeance. Moreover, the time scale of the solvent evaporation was much larger than that of gelation time; it was much easier to control the evaporation process.

Figure 3 shows the growth of the skin layer thickness observed with SEM. As mentioned in the previous article,<sup>1</sup> the dark part without visible pores was considered to be the skin layer and the skin layer thickness was defined as the thick-

ness of the dark region. Note that the membrane with 45-min evaporation was transparent and homogeneous. The cross section of the above membrane looked dark from the top to the bottom, which was similar to the skin layer. When the initial polymer concentration was 25.0%, the skin layer thickness increased continuously with an increase in the evaporation time. The growth of the skin layer thickness of the membranes cast from 27.5 and 30.0% solutions had a flat region in the range of 2.5–7.5 min of evaporation time and showed a rapid increase thereafter.

These results suggest that for the membranes cast from higher polymer concentrations, a thin layer of high polymer concentration should be formed at an earlier stage of the solvent evaporation, retarding the solvent evaporation in the intermediate range of the evaporation time. Figure 4 shows the relationship between the skin layer thickness and the reciprocal of the oxygen permeance (equivalent to the overall permeation resistance). A linear relationship was observed for each polymer solution, and the slope depended on the polymer concentration. The slope stands for the permeation resistance per unit skin layer thickness; the membranes cast from a 30.0% solution showed higher resistance than the membranes from solutions of lower polymer concentrations. The slope for the membrane cast from 30.0% was  $0.528 \times 10^{10}$  m<sup>2</sup> Pa s/(molµm), which is close to the value for the membranes without



**Figure 4** Skin layer thickness versus the reciprocal of oxygen permeance.



**Figure 5** Effect of evaporation time on oxygen permeance.

solvent evaporation.<sup>1</sup> On the other hand, the slopes for the membranes cast from 25.0 and 27.5% solutions were smaller or almost equal to the resistance value calculated from the literature data for the intrinsic permeance of homogeneous PSF membranes.<sup>7</sup> A higher skin layer resistance results from a higher polymer density in the skin layer. Similarly, higher selectivity should result from higher polymer density. Consequently, it is expected that a skin layer of higher permeation resistance has a higher selectivity. This rule applies when membranes cast from 30% solutions are compared with those cast from 25% solutions. However, it should be noted that membranes cast from the 30% solution do not necessarily have the highest selectivity, so the above-mentioned rule does not apply when the membranes cast from a 30% solution are compared with those cast from a 27.5% solution.

### **Effect of Evaporation Temperature**

In Figure 5 the evaporation time and the oxygen permeance are correlated for different evaporation temperatures. All the membranes were cast from the 27.5% polymer solution and gelled in an IPA bath for 5 s. The oxygen permeance data were almost equal for evaporation temperatures of 70 and 95°C up to the evaporation time of 10 min. When the solvent evaporation was done at 120°C, the oxygen permeance decreased steeply with an increase in the evaporation time. For a given evaporation time, the oxygen permeance corresponding to 120°C was smaller than the solvent evaporation at lower temperatures.

In Figure 6 the  $(O_2/N_2)$  permeance ratio is plotted against the evaporation time. The  $(O_2/N_2)$  permeance ratio of the membranes increased with an increase in the solvent evaporation time for all the evaporation temperatures. The  $(O_2/N_2)$  permeance ratio for the membrane with solvent evaporation at 95°C was the largest for a given evaporation time. Therefore, the solvent evaporation at 95°C was the optimum temperature for the oxygen.

Figure 7 shows the growth of the skin layer thickness observed by SEM. The membrane at the 120°C evaporation temperature showed the steepest growth of the skin layer thickness while the membrane at the 70°C evaporation temperature showed very slow growth of the skin layer. These results reflect the fact that the evaporation rate becomes higher when the evaporation temperature is increased. For a given evaporation time the higher evaporation rate results in the thicker region of high polymer concentration that will be converted to the skin layer later in the gelation process.

In Figure 8 the reciprocal of the oxygen permeance is plotted against the skin layer thickness. A single correlation curve can represent all the data, irrespective of evaporation temperature,



Figure 6 Effect of evaporation time on  $(O_2/N_2)$  permeance ratio.



Figure 7 Evaporation time versus skin layer thickness.

although considerable scattering is observed. The scatter in the data can be attributed to several experimental factors such as the following:

- 1. At 120°C the evaporation rate is relatively high, so it could create large pin holes and affect the permeance in the membrane, even after laminating with silicone rubber.
- 2. The skin layer thickness was measured



**Figure 8** Skin layer thickness versus the reciprocal of oxygen permeance.



Figure 9 Skin layer thickness versus  $(O_2/N_2)$  permeance ratio.

from the SEM pictures that can introduce some error to the data. Because the pictures were taken of a very small region, it might not represent the global average skin layer thickness of all membrane areas.

3. The scatter of the data observed at the same measured skin layer thickness can support this reasoning; however, it still shows a rough correlation between the reciprocal of oxygen permeance and the skin layer thickness.

This correlation implies that the permeation resistance per unit thickness and the density of the skin layer are independent of the evaporation temperature. The above conclusion can be supported by Figure 9 that demonstrates the relationship between the skin layer thickness and the  $(O_2/N_2)$  permeance ratio. For a given skin layer thickness, the  $(O_2/N_2)$  permeance ratio was almost equal for the evaporation temperatures of 70 and 95°C. As for the membranes at 120°C, a much lower  $(O_2/N_2)$  permeance ratio was observed, probably because of the large number of the defects introduced by rapid evaporation, the effect of which could not be eliminated by the lamination method.

Evaporation rate can also be changed by the convection pattern in the oven, which may also affect the membrane performance. As shown in



Figure 10 Effect of evaporation method on oxygen permeance and  $(O_2/N_2)$  permeance ratio.

Figure 10, the oxygen permeance of the membranes prepared by forced convection was much smaller than those prepared by the gravity convection method. However, the oxygen selectivity shown in Figure 10 is independent of the convection pattern.

### **Effect of Gelation Parameters**

In the previous section the effect of the operational parameters involved in the solvent evaporation step were discussed while the parameters related to the gelation process were fixed. The effect of the latter parameters is discussed in this section.

Figure 11 shows the effect of gelation time on the oxygen permeance. It also shows the gelation effect on the  $(O_2/N_2)$  permeance ratio of the membrane. The squares indicate the oxygen permeance for the membranes with 5-min solvent evaporation at 95°C. The circles indicate the results for the membranes without solvent evaporation. Both membranes were gelled in the IPA bath for a specified time and then immersed in a water bath for more than 12 h. The polymer concentration in the casting solutions was 27.5%. The permeation rate of the membrane decreased with an increase in the gelation time. The permeation rate for a given gelation time was higher for membranes without evaporation than those with



Figure 11 Effect of gelation time on oxygen permeance and  $(O_2/N_2)$  permeance ratio.

evaporation. On the other hand, the  $(O_2/N_2)$  permeance ratio did not change very much with the gelation time for the membranes with solvent evaporation as shown in Figure 11. This is in contrast to the membrane prepared without solvent evaporation for which the  $(O_2/N_2)$  permeance ratio increased with an increase in the gelation time. Figure 12 shows the relationship between



**Figure 12** Correlation of (1/permeance) versus skin layer thickness.



**Figure 13** Effect of gelation media on  $O_2$  permeance and  $(O_2/N_2)$  permeance ratio.

the skin layer thickness observed with SEM and the reciprocal of the oxygen permeance (equivalent to the overall permeation resistance). A single correlation curve represents all data; this implies that the permeation resistance per unit skin layer thickness and the polymer density are in the skin layer.

Figure 13 shows the effect of evaporation time on the permeation performance for the membranes that were gelled in different nonsolvents. For all gelation media the permeation rate decreased and the  $(O_2/N_2)$  permeance ratio increased with an increase in the evaporation time. Above an evaporation time of 2 min, the permeation rate decreased in the order of water > 2propanol > ethanol. The oxygen selectivity increased in the order of 2-propanol > ethanol > water.

## CONCLUSIONS

- 1. The optimum initial polymer concentration was 27.5%, which showed the highest oxygen permeance and selectivity for a given evaporation time.
- 2. The evaporation temperature affected the oxygen permeance; the higher evaporation temperature resulted in the lower permeance. However, the selectivity was slightly affected by the evaporation temperature.
- 3. The evaporation process increased the  $(O_2/N_2)$  permeance ratio for a given permeation rate.

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