

Actual Air Separation across Multilayer Composite Membranes

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ABSTRACT: Multilayer composite membranes are fabricated from six types of thin films as selective layers, an ethyl cellulose (EC) thin film as a flexible spacer, and poly(ether sulfone) (PES) with 15–45 nm pore size or 100–120 μm thickness as a porous support layer. The effects of the thin-film type and its layer number, operating temperature, and transmembrane pressure difference, as well as the operational time on the actual air-separation properties through the composite membranes, are investigated by a constant pressure-variable volume method. The results show that a pure polystyrene thin-film composite membrane exhibits poor actual air-separation performance due to its brittleness, although it has a higher ideal oxygen over nitrogen separation factor. The oxygen-enrichment air (OEA) flux through all of the composite membranes tested increases significantly with increasing operating temperature and pressure difference. The oxygen concentration in the OEA increases slightly with an increase in operating temperature, and the oxygen concentration through the polystyrene/cholesteryl oleyl carbonate blend, top layer composite membrane exhibits the maximal value. As the transmembrane pressure difference increases, the oxygen concentration in the OEA also exhibits the maximal value. The maximum oxygen concentration can reach 39.1%, which is achieved by the multilayer composite membrane consisting of a polystyrene/cholesteryl oleyl carbonate (95/5) monolayer, an EC single flexible spacer, and a PES support at 35°C and a transmembrane pressure difference of 550 kPa. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2396–2403, 2000

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INTRODUCTION

Membrane separation techniques have many potential applications and a huge market that are due to their economics, energy savings, low investment, and easy operation.^{1–7} As we know, the key factor of the membrane separation technique is the membrane material itself, which hinders membrane performance. Unfortunately, no mate-

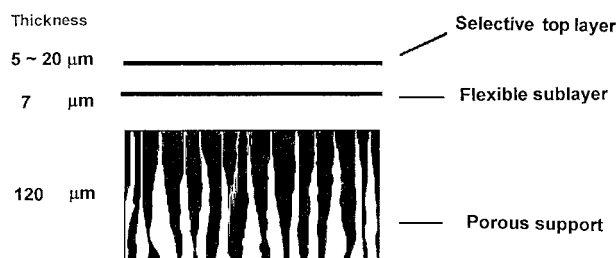


Figure 1 A structural model of a multilayer thin-film composite membrane.

rial exhibiting superior separation properties is available at present. Therefore, researchers and specialists on membrane gas separation have made every effort in the following three areas:

1. to improve the separation properties of conventional materials by means of physical or chemical methods such as blending, coating, dipping, plasma sinking, and grafting,⁷⁻¹³
2. to prepare thin films through a variety of membrane preparation techniques including water casting, mercury casting, spin casting, interfacial polymerizing, and phase transition, then fabricating them into multilayer thin-film composite membranes,^{7,8} and
3. to synthesize new materials possessing high separation performance,¹⁴⁻¹⁹ for example, a porphyrin cobalt complex, molten salt, and organic polymers containing many nitrogen atoms in their molecular structures.⁵⁻⁷

Obviously, the first two are shorter paths for attaining high performance membranes because of their easier operation and simplicity, while the last needs much effort to be realized.

Having considered the complexity of synthesizing new polymers and the poor stability and lower separative ability of monolayer thin-film composite membranes,^{7,8} a series of multilayer thin film composite membranes is shown in Figure 1. The advantages of these composite membranes lie in their flexibility. We can select materials exhibiting excellent separation properties as the top layer no matter how weak it is, because the mechanical properties can be provided by the porous support layer. Thus, these composite membranes can be quite durable. The performance of these membranes would be easily optimized by means

of changing the material, film thickness, and layer number of the top layer.

EXPERIMENTAL

Materials

Polycarbonate (PC) pellets were purchased from the Second Organic Chemical Factory (Tianjin China).²⁰ Ethyl cellulose (EC) produced by Shantou Xinning Chemical Works (Guangdong Province, China) has a viscosity of 0.04–0.08 Pas that is measured in ethanol/toluene. The degree of substitution of the EC was about 2.4. Polysulfone (PSF) particles with an intrinsic viscosity of 0.62 dL/g were from the Shanghai Shuguang Chemicals Works of China.²¹ Styrene-maleic anhydride (SMA) copolymer chips produced by Gaoqiao Petrochemical Institute (Shanghai, China) were kindly supplied by Associate Professor Hongting Pu (Tongji University). The MA unit content in the SMA copolymer was about 10%. Polystyrene (PS) chips were made in Japan. Cholesteryl oleyl carbonate (COC) was purchased commercially and is a low molecular liquid crystalline material possessing the cholesteric phase transition temperature of 25–39°C.

The PES ultrafiltration membrane (10–45 nm pore size and 100–200 μm thickness) used as the porous support in this study was evaluated in our previous article.⁸

Membrane Preparation

The thin films of PC and EC and the blend thin films of PSF or PC with COC and PS or SMA with EC were made by pouring the casting solutions in chloroform with concentrations of 0.50–3.0 wt % onto glass plates and evaporating the casting solvent at temperature for about 20 h. These thin films had a thickness of 2–20 μm . The composite membranes were fabricated from the thin films' selective top layers, the EC flexible spacer, and the porous PES support.

Air-Separation Measurements

Actual air-separation measurements were performed using a constant pressure-variable volume method reported previously.²² The feed gas was compressed air (oxygen content of 20.9 vol %) directly from an air compressor. The permeate flux of oxygen-enriched air (OEA) through the composite membranes was calculated by measur-

Table I Oxygen Enrichment through Several Multilayer Thin-Film Composite Membranes with EC Film (7- μm Thickness) as Flexible Spacer and PES Ultrafiltration Membrane as Porous Support

Selective Top Layer			Oxygen Enrichment through Composite Membranes	
Composition (wt %)	Solution Conc. (wt %)	Thickness (μm)	$Q_{\text{OEA}} \times 10^5$ [mL(STP)/s cm^2]	Y_{O_2} (%)
PC ^a	1.0	5×2^b	10.5	31.3
	2.0	9	12.8	33.0
	3.0	20	11.4	30.0
(95PC + 5COC)/ (95PC + 5COC)/ PC terlayer	0.5	2/2/2	4.72 ^c	31.3 ^c
PSF/COC	96/4	1.2	8	32.3
	95/5	0.55	3	33.4
	90/10	0.89	8	30.0 ^c
EC/PS	83/17	1.2	15	23.8
	86/14	1.4	17	31.6
	86/14	1.4	17×2^b	36.1
EC/SMA	83/17	1.2	10	26.0
	86/14	1.4	19	35.7

The conditions were 25°C and 400-kPa pressure difference.

^aThe porous support is a polysulfone amide ultrafiltration membrane.

^bA bilayer of the same film.

^cData were measured at 20°C.

ing the change in the volume of the OEA at a constant pressure gradient across the composite membranes. The measurement of the oxygen concentration (Y_{O_2}) in the permeated OEA was performed on a QF1901 gas analyzer. The effective membrane area was 50 cm^2 . The actual air-separation property of the composite membranes was evaluated with the devices operating at a steady-state condition of temperature and pressure.

RESULTS AND DISCUSSION

Relationships between Air Separation and Thin Film

The actual air-separation properties through a series of multilayer thin-film composite membranes with an EC thin film as a flexible spacer and a PES ultrafiltration membrane as a porous support are presented in Table I. It can be seen from Table I that composite membranes with different top layer materials show different air-sep-

aration properties, in spite of the use of the same flexible spacer and the same porous support. One of the best membranes is the multilayer composite membrane with a monolayer PC thin film as a selective top layer. The OEA flux, oxygen concentration, and actual separation factor through the composite membrane can reach 12.8×10^{-5} mL (STP)/s cm^2 , 33.0%, and 1.9, respectively.

Comparing the air-separation performance of composite membranes using a PC monolayer as a top layer with that using a PC bilayer or trilayer having a similar total thickness, it can be found that the OEA flux decreases with an increase in layer number, especially when the top layer number increases to 3, the OEA flux dramatically drops to 4.72×10^{-5} mL (STP)/s cm^2 , and the oxygen concentration is essentially the same. This is mainly related to the increase of the flow resistance between layers (i.e., the gas-permeated path would be prolonged), and the time of permeating gas would be delayed because of redesorption and resolution of the gas in the second or

third selective layer. A similar phenomenon can be observed in a multilayer composite membrane with EC/PS as a top layer (Table I). It follows that the multilayer composite membrane should have a reasonable number of layers of no more than two; thus, the total number of layers in the composite membrane should be no more than four, otherwise the OEA flux through the composite membrane would decrease abruptly.

It has been reported that PS has a good intrinsic oxygen over nitrogen permselectivity with a P_{O_2}/P_{N_2} of 6.28 and P_{O_2} of 2.63 Barrer,⁸ which implies that the Y_{O_2} across the PS membrane might be higher than 50% theoretically. To investigate the actual air-separation properties of this material, a composite membrane with PS as a top layer and EC as a flexible spacer was fabricated. Unfortunately, PS tends to be too brittle to be cast into a thin film without pinholes under the testing transmembrane pressure difference. In order to reduce the brittleness of PS, flexible EC was introduced into the PS. The small percentage of EC, however, did not work up to 86 wt %, although the EC/PS blend film looked homogeneous to the naked eye. For example, the OEA flux was 76.8×10^{-5} mL (STP)/s cm² and Y_{O_2} was 23.8% through the composite membrane with an EC/PS (83/17) thin film as a top layer, implying that there are some defects in the EC/PS (83/17) top layer (Table I). Only after the EC/PS blend weight ratio reached 86/14 did the composite membrane show a little higher oxygen over nitrogen permselectivity. The OEA flux and Y_{O_2} through the composite membrane can reach 4.85×10^{-5} mL (STP)/s cm² and 31.6%, respectively. If the top layer is doubled, the magnitude of Y_{O_2} will increase to 36.1% while the OEA flux will decrease to some extent (see Table I). It appears that the blending modification of PS with EC is not significantly effective.

The other method that could enhance the impact resistance of PS is copolymerization of styrene with MA to form SMA copolymer. It is a pity that the composite membrane with SMA (containing 10 mol % MA) as the top layers still shows no oxygen over nitrogen permselectivity because of some defects in the SMA film under testing conditions, in spite of the transparent and homogeneous virgin films of SMA. If SMA was blended with EC, the brittleness of SMA could be further lowered. Therefore, the composite membrane with the EC/SMA film as a top layer has somewhat better actual air-separation properties than that with the EC/PS film with the same blend

ratio as a top layer. This is related to the higher flexibility of SMA, which could form a pinhole-free thin film more easily than PS.

The PES support composite membrane with a 1–3 μ m thick thin EC film (no flexible spacer) has an OEA flux of 7.16×10^{-4} mL (STP)/s cm² and Y_{O_2} of 35.9% at the 25°C and 0.41-kPa pressure difference according to our previous investigation.²³ A small amount of PS or SMA introduced into the EC has no effect on Y_{O_2} but makes the OEA flux decrease dramatically (see Table I). It seems that the PS or SMA containing about 10 mol % MA is an ineffective material for the preparation of high performance thin-film composite membranes.

However, based on the superior intrinsic oxygen over nitrogen permselectivity of PS,⁸ we estimated that, if the brittleness of the PS membrane could be overcome, its excellent actual air-separation properties would be useable. The copolymerization of styrene with a small amount of butadiene and the introduction of some plasticizers to the PS would help to realize this purpose.

Relationship between Air Separation and Operating Temperature

The actual air-separation properties through several types of composite membranes (listed in Table I) were obtained at 18–60°C and a 550-kPa transmembrane pressure drop. For all the composite membranes measured, the OEA flux increases linearly with increasing operating temperature, as shown in Figure 2(a). It is evident that the higher diffusion rate of the OEA through the membranes and the enlarged free volume between macromolecular chains are responsible for the increase of the OEA flux. We also found that the higher the top layer number of the PC selective top layer composite membranes, the lower the OEA flux is. This agrees with that discussed above.

Figure 2(b) shows that the PC top layer and PSF/COC top layer composite membranes exhibit different Y_{O_2} variational regularity. The oxygen concentration through the PC monolayer, bilayer, and trilayer top layer composite membranes tends to increase with increasing temperature, which is different from that typically observed for most composite membranes such as EC, cellulose triacetate (CTA), and cellulose diacetate (CDA) top layer composite membranes and homogeneous dense thick membranes.^{8,23–27} The abnormal Y_{O_2} versus temperature relationships may be

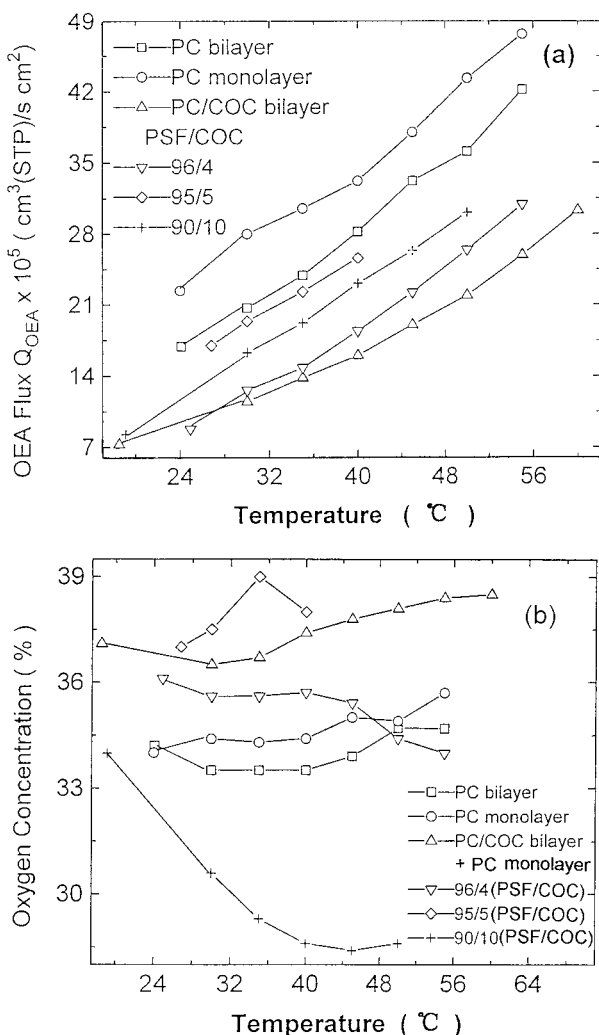


Figure 2 The effect of the operating temperature on the (a) OEA flux and (b) oxygen concentration at a 550-kPa pressure difference in a single stage through the PES porous support composite membranes with a (○) PC monolayer, (□) PC bilayer, (△) PC/COC bilayer and PC monolayer, and PSF/COC monolayers at (△) 96/4, (◇) 95/5, and (+) 90/10 as selective top layers and an EC film as a flexible sublayer. The feed air contains 20.9% oxygen.

explained by compaction of the membranes because of the fact that no operating time was taken before testing. The higher the layer number, the stronger the compaction effect; thus, the more obvious the increasing trend is with increasing temperature. On the other hand, the free volume in the selective layer will enlarge as the temperature increases, which results in a decline of Y_{O_2} . Nonetheless, the former dominates so that the Y_{O_2} value increases with increasing temperature. It is expected that the OEA flux and Y_{O_2} through the

membranes increases with temperature simultaneously because the combined variation of the parameters favors obtaining a higher OEA flux and higher Y_{O_2} at the same time in the oxygen over nitrogen separation operation.

On the contrary, the OEA flux through the PSF/COC top layer composite membranes decreased with increasing temperature. The Y_{O_2} versus temperature relationship is akin to that typically observed for other gas-separation membranes.^{27–30} This is because the enlarged free volume in the top layer, which results from increasing temperature, impairs the selectivity of the membrane.

It is shown in Figure 2(b) that the air-separation properties of the PSF/COC top layer composite membrane vary with the COC content and the PSF/COC (95/5) top layer composite membrane shows the maximum Y_{O_2} of 39.1%. Moreover, the small change in the COC content can result in a larger change in Y_{O_2} through the membrane. It appears that the phenomenon is related to the liquid crystalline behavior of COC. The COC, a low molecular liquid crystal material, exhibits a liquid crystal temperature range from 25 to 39°C.^{28,29} It is a semisolid and sticky at room temperature. If the COC concentration introduced into the polymer material was too high, some pinholes appeared in the thin film during membrane evaluation (at a certain transmembrane pressure difference) that were due to the easy fluidity of the COC. Therefore, the COC content should generally be controlled to below 10 wt %. For the PSF/COC top layer composite membrane, the best COC content was 5 wt % (see Fig. 2).

It should be appreciated that the addition of a small amount of COC to the PC will make the PC thin film form some defects so that the PC/COC (95/5) monolayer or bilayer composite membranes show no air-separation ability at all.⁸ If the third top layer PC thin film was added, the composite membrane showed better oxygen over nitrogen permselectivity. The Y_{O_2} approached 38.4% at the operating temperature of 60°C.

Relationship between Air Separation and Pressure Difference across Membrane

The effect of the variation of operating pressure from 350 to 650 kPa on the actual air-separation properties through the composite membranes is shown in Figure 3. For all composite membranes measured, an increase in operational pressure

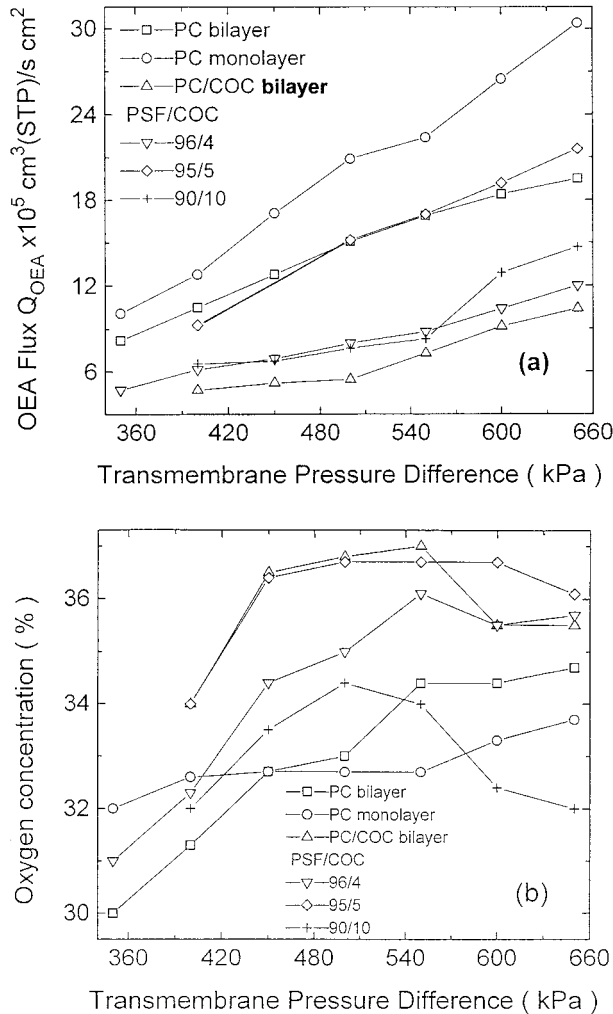


Figure 3 The effect of a transmembrane pressure difference on the (a) OEA flux and (b) oxygen concentration at 25°C in a single stage through the PES porous support composite membranes with a (○) PC monolayer, (□) PC bilayer, (△) PC/COC bilayer and PC monolayer, and PSF/COC monolayers at (△) 96/4, (◇) 95/5, and (+) 90/10 as selective top layers and an EC film as a flexible sublayer. The feed air contains 20.9% oxygen.

difference was found to increase the OEA flux, which is similar to that typically observed in other composite membranes and homogeneous dense membranes.^{8,30–33} An increase in OEA flux may result from an acceleration of the rate of the OEA through the membranes with increasing pressure drop. As shown in Figure 3(b), the effect of the operating pressure drop on Y_{O_2} is more complicated. For composite membranes containing no COC, that is, the PC monolayer and PC bilayer composite membranes, the Y_{O_2} essentially

increases with increasing pressure drop. This observation can be explained by the impaction effect. An increasing pressure drop compresses the amorphous regions in the membranes, the intervals between the different types of thin films, and the space in the porous support. All of the above lead to an enhancement in Y_{O_2} . On the other hand, the composite membranes containing COC exhibit an abnormal relationship between Y_{O_2} and the pressure drop. The Y_{O_2} first increases and then decreases with an increasing pressure difference from 400 to 650 kPa. Therefore, the maximum Y_{O_2} was observed. Moreover, the higher the COC content, the more obviously the Y_{O_2} decreases. It can be inferred that the COC might be squeezed out of the membrane under increasing pressure difference, although the COC is compatible with PC or PSF to the naked eye. This could be the main reason for the decrease in the Y_{O_2} .

In any case, all of these composite membranes still exhibit better oxygen over nitrogen permselectivity with both the OEA flux and Y_{O_2} higher than $5 \times 10^{-5} \text{ mL (STP)/s cm}^2$ and 30%, respectively (Fig. 3).

It should be noted that the PSF/COC (95/5) top layer composite membrane possesses the best comprehensive air-separation property of the highest OEA flux of $2.2 \times 10^{-4} \text{ mL (STP)/s cm}^2$ and the highest Y_{O_2} of 36.0% under the testing operation parameters.

Relationship between Air Separation and Operating Temperature

The variation of the OEA flux and Y_{O_2} through the PSF/COC (96/4) top layer composite membrane with operating time is given in Figure 4. It is obvious that there are no significant changes in the OEA flux and Y_{O_2} for operating times as long as 33 h. The OEA flux and Y_{O_2} stabilized at about $2 \times 10^{-4} \text{ mL (STP)/s cm}^2$ and 36%, respectively. The results suggest that a long-term stable air separation could be carried out efficiently with this composite membrane.

CONCLUSIONS

Multilayer composite membranes that contain several traditional polymer thin films, which possess higher ideal oxygen over nitrogen separation factors, as selective top layers, in combination with a single EC thin film as a flexible spacer and

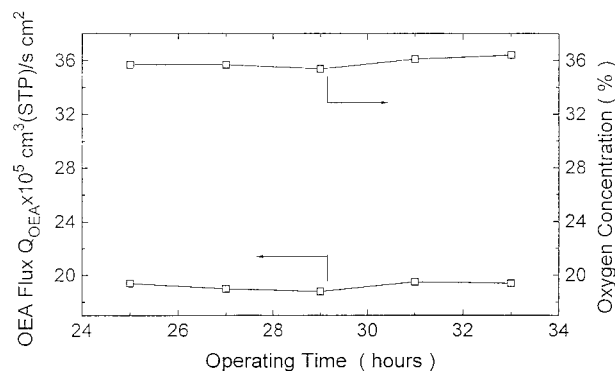


Figure 4 The effect of operating time on the OEA flux and oxygen concentration at 40°C and a 550-kPa transmembrane pressure difference in a single stage through the PES porous support composite membrane with PSF/COC (96/4) as a selective top layer and an EC film as a flexible sublayer. The feed air contains 20.9% oxygen.

a PES ultrafiltration membrane as a thick support layer, were fabricated and evaluated for their actual air-separation properties. The air-separation performance through these composite membranes were different with the variation of the top layer material and top layer number. The actual air-separation performance through the composite membranes with PS and SMA (containing no more than 10% MA) as the selective top layer was disappointing because of their brittleness, which made it difficult to form a pinhole-free thin film at an operating pressure drop, although the ideal oxygen over nitrogen separation factor of PS is higher at approximately 6. On the contrary, the PC top layer composite membranes and PSF/COC top layer composite membranes exhibited better oxygen-enrichment performance with the OEA flux higher than $7 \times 10^{-5} \text{ mL (STP)/s cm}^2$ and the oxygen concentration higher than 34%, except for the PSF/COC (90/10) top layer composite membrane at a temperature range of 18–60°C and a transmembrane pressure difference of 550 kPa. The result also illustrates that the OEA flux through these multilayer composite membranes increases with increasing temperature and transmembrane pressure difference. On the other hand, the oxygen concentration through the PC top layer multilayer composite membranes increases slightly with increasing temperature and increasing transmembrane pressure difference, while that through the PSF/COC top layer multilayer composite membranes exhibits a maximal value with increasing temperature and increas-

ing transmembrane pressure difference. The maximum oxygen concentration can reach 39.1% through the multilayer composite membrane consisting of a PSF/COC (95/5) monolayer, an EC single flexible spacer, and a PES support at a temperature of 35°C and a transmembrane pressure difference of 550 kPa.

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