Bilayer Thin-Film Composite Membranes for Air Separation

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SYNOPSIS

Bilayer composite membranes suitable for separating air, consisting of poly(4-methylpentene-1) (PMP) thin film as a selective top layer, an ethylcellulose–heptylcellulose (ECHC) blend thin film as a selective sublayer, and polysulfone as a porous support, were investigated using a constant pressure–variable volume method. By varying operating temperature, pressure, time, as well as stage cut, the membranes were characterized for their oxygen-enriched air (OEA) flux and oxygen concentration in the OEA permeated in a single step. The results show that both the OEA flux and oxygen concentration through the membranes increase with increasing operating pressure. With the increase of operating temperature, the OEA flux increases largely but the oxygen concentration decreases slightly. The oxygen concentration also decreases slightly with the stage cut. On the contrary, the OEA flux decreases and oxygen concentration increases slightly with operating time. It is found that a PMP thin film plays an important role in enhancing the air-separation capability of the membrane. The PMP/ECHC bilayer thin-film composite membrane could enrich the OEA containing 43.6% oxygen at the OEA flux of 5.06×10^{-4} cm^3 (STP)/s cm^2 with a good performance stability. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Membrane-based air separation has attracted much interest as an economic process during the last two decades. Various classes of polymeric materials have been developed as the membranes for air-separation applications.[1-4] To raise air-separation capability through the membranes, two families of membranes have evolved—asymmetric and thin-film composite. The first family, the asymmetric membrane, is prepared through an anisotropic coagulation of the same polymer solution yielding a densified selective surface growing out of the porous substrate.[4] The second family consists of a porous substrate coated or laminated by a thin film of another polymer. The principal advantages of the thin-film composite membrane over the asymmetric membrane are two-fold: (1) The need to develop a rather complex method suitable for preparing a defect-free asymmetric structure is eliminated, and (2) a large variety of polymers can be feasibly employed because the quantity of the polymer required to laminate such a defect-free layer (with the thickness less than 1 μm) is much lower than that used in the preparation of the porous support.

Our previous studies on the preparation and characterization of ethylcellulose–heptylcellulose (ECHC) monolayer thin-film composite membranes on a porous polysulfone (PSF) revealed that they exhibited better air-separation properties.[5,6] To enhance their air-separation capabilities further, a poly(4-methylpentene-1) (PMP) thin film, as a selective top layer, was laminated on the aforementioned ECHC thin-film composite membrane. This article describes the air separation of the monolayer and bilayer thin-film composite membranes. The monolayer membrane comprises a PSF porous substrate laminated by a thin layer of the ECHC blend with two EC/HC ratios, as shown in Figure 1(a); in the bilayer membrane, the ECHC layer is topped with the PMP thin film, as shown in Figure 1(b). In the first, the ECHC serves as a selective layer; in the second, it acts as both a selective layer and an intermediate layer that might channel the permeate

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Journal of Applied Polymer Science, Vol. 55, 1145–1150 (1995)
 CCC 0021-8995/95/071145-06

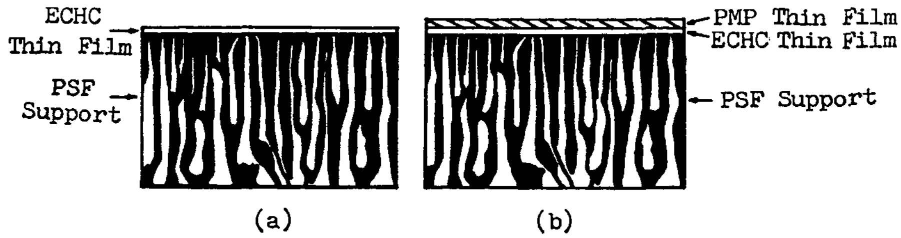

Figure 1 Illustration depicting cross sections of (a) single layer of ECHC blend and (b) bilayer PMP/ECHC composite membranes on the porous PSF.

to the surface pores in the PSF support.[1] The main goal of the present work was focused on the dependence of the air-separation capability through the composite membranes on operating parameters including temperature, pressure, time, and stage cut.

EXPERIMENTAL

Materials

The polysulfone (PSF) ultrafiltration membrane with 10–40 nm pores, determined using an electron microscopy technique, was kindly provided by Dalian Institute of Chemical Physics of China. The total thickness of the PSF layer, supported by a backing fabric, was ca. 120 μm. The air-permeation rate through the PSF membrane was ca. 0.05 cm^3 (STP)/cm^2 s cmHg at 30°C. Ethylcellulose (EC) with a viscosity in ethanol/toluene of ca. 0.06 Pa-s was obtained from Guangdong Province of China. Heptylcellulose (HC) was an experimental sample that was described in an early paper.[7] The intrinsic viscosity of the HC in chloroform was 26 mL/g. This HC was a gummy liquid crystalline material showing fluidity even at room temperature. Poly(4-methylpentene-1) (PMP), designated as TPX MX-004, was supplied by Mitsui Petrochemical Co. The respective oxygen permeability and oxygen/nitrogen selectivity parameters through 50–90 μm-thick PMP membrane were 1.24×10^{-9} cm^3 (STP) cm/cm^2 s cmHg and 4.08 at 25°C.[8] It can be predicted that the theoretically maximum O_2 purity for pure PMP membrane was ca. 52%.[9] All solvents used were reagent grade.

Membrane Preparation

The ECHC or PMP dilute solutions were cast on a dry, clean glass plate at room temperature.[10] After the solvents were completely evaporated, the solvent-free thin films were obtained and were laminated on the porous PSF support to fabricate composite membranes. The respective thicknesses of the ECHC and PMP thin films were about 0.5 and 1.0 μm.

Membrane Evaluation

The air-separation performance of the membranes was evaluated by a constant pressure–variable volume testing equipment. It consists of two detachable stainless-steel parts. A circular porous material was fixed in the upper part to support the membranes. The two parts were tightly fixed in proper alignment with a rubber O-ring. The air-separation experiment was performed as follows: A circular membrane of an effective permeated area of 50 cm^2 was placed on the porous material of the same area and, then, the membrane was fixed in its position in the testing cell. Feed air directly from an air compressor was introduced into the testing cell. The applied air pressure was controlled by using an exact pressure gauge that recorded pressure from 0 to 1000 kPa. In all air-separation experiments, the selective thin-film layer of the composite membranes was facing the feed air. Each membrane was characterized for oxygen-enriched air (OEA) flux and oxygen concentration in the OEA in a single step. Approximately 30 min were required to attain equilibrium.

RESULTS AND DISCUSSION

Comparison of ECHC Monolayer with PMP/ECHC Bilayer Thin-Film Composite Membranes

To compare membrane performance before and after laminating with a PMP thin film, the ECHC monolayer and the PMP/ECHC bilayer thin-film composite membranes on a porous PSF support were prepared and examined for their air-separation capabilities by varying the EC/HC weight ratio, as presented in Table I. This comparison suggests that at the same temperature and the same casting solution concentration of 0.15 ECHC wt % the PMP/ECHC bilayer thin-film composite membranes ex-

Table I Comparison of ECHC Monolayer with PMP/ECHC Bilayer Thin-film Composite Membranes; Conditions: 22°C; 500 kPa Pressure Difference; 10 h Operating Time; 0.15 Stage Cut

Effective Permeated Area of Thin Film[a] (cm^2)	OEA Flux [cm^3 (STP)/s cm^2]	Oxygen Concentration (%)	Actual O_2/N_2 Separation Factor[b]
PMP/ECHC (EC : HC = 96 : 4 wt)			
0/50	9.73×10^{-4}	31.9	1.77
25/50	8.36×10^{-4}	33.1	1.87
50/50	4.94×10^{-4}	42.9	2.84
PMP/ECHC (EC : HC = 98 : 2 wt)			
0/50	7.61×10^{-4}	37.4	2.26
15/50	6.95×10^{-4}	40.1	2.53
50/50	6.29×10^{-4}	42.3	2.77

[a] PMP layer was prepared from the casting solution of 0.26 wt % in cyclohexane. The ECHC layer was prepared from the casting solution of 0.15 wt % in tetrahydrofuran.

[b] For the calculation of the actual separation factor, refer to Refs. 1 and 10.

hibit an oxygen concentration higher than 42.3%, but a somewhat lower OEA flux than do the corresponding ECHC monolayer composite membranes. Even if the ECHC thin film is partially laminated with the PMP thin film, the higher oxygen concentration (33.1 and 40.1%) is still available. It follows that membrane performance after laminating with a PMP thin film is, indeed, improved. However, the composite membrane laminated with only a PMP layer (ca. 1 μm) cast from the same casting solution directly on the surface of the anisotropic PSF support exhibits a very poor selectivity at a very high OEA flux. This could be explained by the fact that the two polymers are glassy (T_{gPMP} = 42°C, T_{gPSF} = 189°C) and a thin PMP film does not interface with the PSF support without formation of defects under the transmembrane pressure difference of 500 kPa.[1] Nevertheless, PMP/ECHC bilayer thin-film composites might provide an effective method to improve the air-separation capabilities of the membranes in which the intermediate ECHC layer is necessary and might serve as a resilient support for the glassy selective thin PMP layer.

Effect of Temperature on Air Separation Through the Bilayer Membrane

A PMP/ECHC bilayer thin-film composite membrane was studied for its air-separation properties by varying the operating temperature as presented in Figure 2. It is noted that the OEA flux permeated through the bilayer membrane increases significantly as a function of operating temperature at 500 kPa transmembrane pressure and after a 20 or 220 h operation period. However, the oxygen concentration in the OEA permeated across the membrane decreases with increasing temperature, which is in agreement with ordinary membranes.

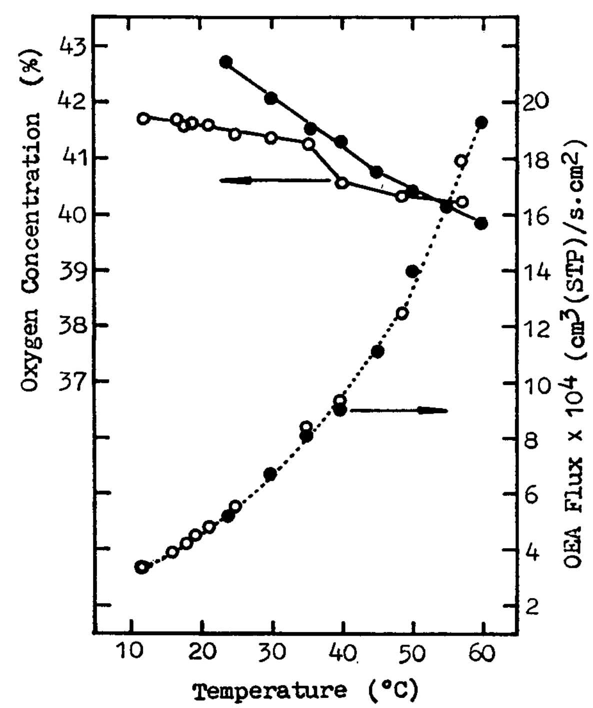

Figure 2 OEA flux (dotted lines) and oxygen concentration (solid lines) vs. operating temperature at 500 kPa pressure difference and the stage cut less than 0.15 after two operating periods of (○) 20 h and (●) 220 h for the PMP/ECHC bilayer thin-film composite membrane.

From these results, it is evident that the higher temperature would bring about the stronger molecular motion in the membrane and a membrane structure with more free volumes will be produced. Consequently, the membrane exhibits higher OEA flux with lower oxygen concentration at the higher temperature. Note that the temperature dependence of the air-separation properties through the bilayer thin-film composite membrane is somewhat similar to that through the monolayer composite membranes.[6]

It must be appreciated that the variation of the air-separation properties with temperature is reversible. When the temperature decreases from 60°C back to the room temperature, the air-separation properties remain the initial values through the initial membrane before increasing temperature. This means that the membrane structure may not change irreversibly with increasing temperature from room temperature to 60°C.

Effect of Pressure on Air-Separation Through Bilayer Membrane

A correlation between the operating pressure and the air-separation properties through the PMP/ECHC bilayer thin-film composite membrane is illustrated in Figure 3. Note that both the OEA flux and oxygen concentration in the OEA permeated increase at the same time with increasing operating pressure difference. The increase in air-separation capabilities with pressure is expected for most gas-separation membranes. This effect occurs because increasing pressure will result in a denser membrane structure and directly increases the flux of the oxygen through the membrane. Hence, more oxygen in the permeate leads to higher separation abilities. The highest oxygen concentration of 43.2% at the OEA flux of 4.5×10^{-4} cm^3 (STP)/s cm^2 can be obtained when the transmembrane pressure difference reaches 500 kPa at 25°C. It is found that extrapolation of the data shown in Figure 3 leads to an intercept that indicates ca. a 1.7×10^{-3} cm^3 (STP)/s cm^2 available OEA flux at the transmembrane pressure difference of 1000 kPa. Note, however, that this extrapolated value should be taken cautiously since the number of data points is limited. It should be pointed out that the pressure dependence of the air-separation properties of this bilayer thin-film composite membrane is very analogous to that of the ECHC monolayer thin-film composite membrane.[6]

In addition, at the end of a several-day period of operation, the air-separation operation of the membrane was stopped for a 1 week period and restarted when it was found that the air-separation properties had not changed. This indicates that no delamination, shifting, or relaxation of or damage to the membrane had occurred.

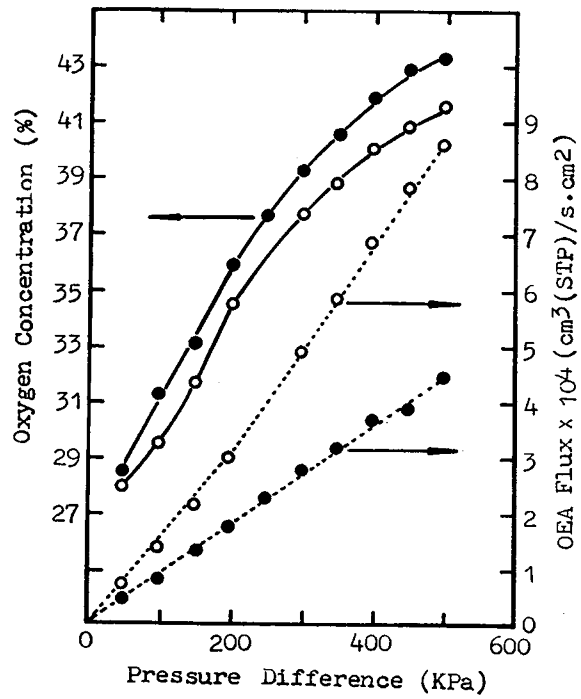

Figure 3 OEA flux (dotted lines) and oxygen concentration (solid lines) vs. transmembrane pressure difference for the PMP/ECHC bilayer thin-film composite membrane at the stage cut less than 0.15 under two conditions: (○) 35°C and operating time of 10 h; (●) 25°C and operating time of 210 h.

Effect of Operating Time on Air Separation Through Bilayer Membrane

The variation of the air-separation properties through the PMP/ECHC bilayer thin-film composite membrane with operating time is presented in Figure 4. It can be seen that the oxygen concentration increases and the OEA flux declines slightly after the membrane is operated continuously for 320 h, suggesting membrane compaction. But the effect of compaction will be somewhat obviated by heating. For instance, the OEA flux and oxygen concentration at 24°C through the membrane that had been slightly compacted after the continuous operation of 220 h are 4.58×10^{-4} cm^3 (STP)/s cm^2 and 42.9%, respectively. Having been heated to 40°C for ca. 1 h and then cooled to the same temperature (24°C), the membrane exhibits a higher flux of 5.32×10^{-4} cm^3 (STP)/s cm^2 and somewhat lower oxygen con-

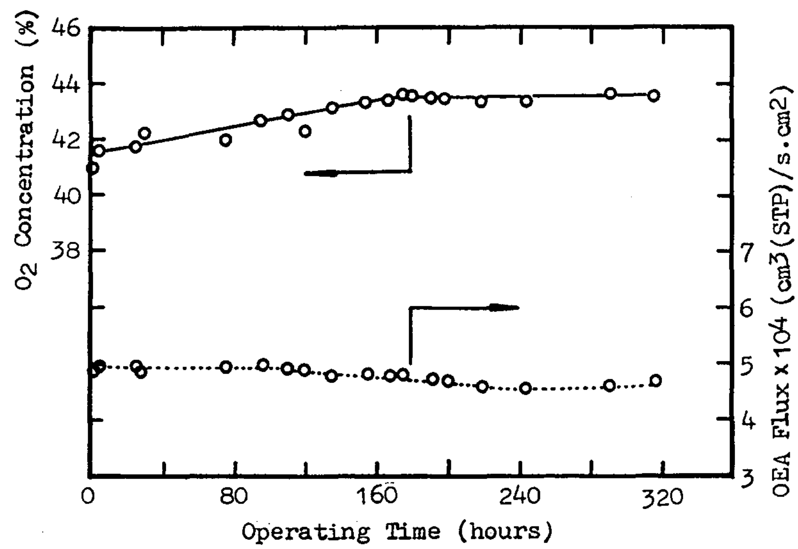

Figure 4 OEA flux (dotted line) and oxygen concentration (solid line) vs. operating time for the PMP/ECHC bilayer thin-film composite membrane at 20°C, 500 kPa pressure difference, and stage cut less than 0.15.

centration of 42.5%, which are the same as the air-separation properties of the initial membrane.

It can be also seen from Figures 2 and 3 that the temperature and pressure dependencies of the air-separation properties of the membrane might vary with the operating time. With prolongating the operating time from 20 to 220 h, the effect of operating temperature on the oxygen concentration becomes remarkable (see Fig. 2). Figure 4 illustrates that the highest oxygen concentration of 43.6% can be obtained when the operating time is longer than 180 h.

Effect of Stage Cut on Oxygen Concentration Permeated Across Bilayer Membrane

In addition to the operating temperature, pressure, and time, the air-separation properties through the membrane also depend on the stage cut, which is the ratio of permeate flow to retentate flow. At a given pressure difference of 500 kPa, the variation of the oxygen concentration in the permeate OEA through the PMP/ECHC thin-film composite membrane with the stage cut is shown in Figure 5. As observed, the oxygen concentration decreases slightly with increasing the stage cut from zero to 0.25. This is because there is not enough time to supplement the oxygen that has permeated through the membrane, resulting in the nitrogen concentration higher than 20.9% on the membrane surface. Consequently, the stage cut should be exactly adjusted during the membrane-based air-separation processes in order to achieve the maximum air-separation efficiency.

CONCLUSIONS

A novel PMP/ECHC bilayer thin-film composite membrane has been fabricated and characterized by its ability of air separation. The air-separation properties through the membrane are significantly influenced by the operating temperature and pressure difference, but the efficiency of enriching oxygen from air is more or less constant after 160 h of continuous operation or within the range of the stage cut less than 0.1. As expected in the Introduction, the air-separation capability through the PMP/

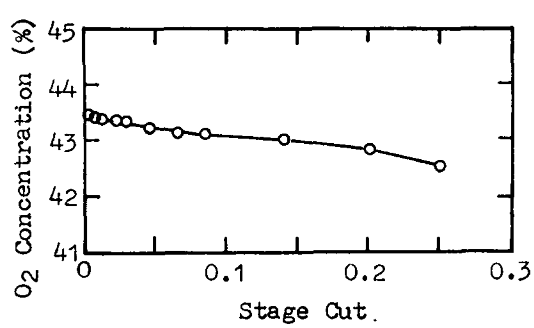

Figure 5 Effect of operating stage cut on the oxygen concentration in the OEA permeated through the PMP/ECHC bilayer thin-film composite membrane at 22°C; 500 kPa pressure difference and 200 h operating time.

ECHC bilayer thin-film composite membrane has been proved to be higher than that through the ECHC or PMP monolayer thin-film composite membrane. The bilayer thin-film composite membrane could yield an oxygen-enriched air containing 43.6% oxygen at the OEA flux of 5.06×10^{-4} cm^3 (STP)/s cm^2 at a transmembrane pressure difference of 500 kPa. The aforementioned bilayer composite membrane may be used for the medical treatment of patients.

The authors acknowledge the help of Professors P.-C. Yang and G. Lin in evaluating the air-separation performance through the membranes. This research was supported by the National Natural Science Foundation of China and by the 21st Century Young Scientists Foundation of Tianjin City in China.

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Received June 19, 1994
Accepted August 20, 1994