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Air Separation through Modified Ethyl Cellulose Thin Film Supported on Porous Polyethersulfone

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ABSTRACT

Composite membranes for air separation were prepared from a liquid crystal DYC-modified ethyl cellulose (EC) thin film ranging in thickness from 1 to 7 μm and a porous polyethersulfone support with a thickness of 120 μm. The effects of DYC/EC (9/91) solution concentration, water, and operating parameters such as temperature, pressure, and time on the air-separation properties of the composite membranes were examined by a constant pressure–variable volume method. The permeate flux and oxygen concentration of the oxygen-enriched air (OEA) through the membranes increase significantly with increasing operating pressure difference. With decreasing casting solution concentration, or with increasing humidity around the membranes or operating temperature, the OEA flux increases greatly while the oxygen concentration sometimes decreases slightly. An increase in the operating time leads to an OEA flux decline, but the oxygen concentration rose when the operating time was varied for 70 hours. However, a further increase of the operating time from 70 to 500 hours does not lead to further changes of the OEA flux and oxygen concentrations. A thin-film composite membrane exhibits a slightly lower oxygen concentration accompanied by a very significant enhancement in the OEA flux and membrane stability compared to a homogeneous dense membrane of the same materials.

Key Words. Liquid crystal; Ethyl cellulose; Composite membrane; Operating condition; Air separation; Oxygen enrichment

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INTRODUCTION

Membrane separation processes are playing an increasing role in the application of gas separation. In order to enhance air flux through membranes and to minimize membrane cost, some composite membranes have been used for air separation with poly(phenylene oxide) (1), poly(4-methyl-1-pentene) (2, 3), polydimethylsiloxane (4), and poly(1-(trimethylsilyl)-1-propyne) (5) as dense selective thin layers. The composite membranes are in widespread use for air separation: the production of oxygen-enriched air (OEA) for medical purposes, technology, and other goals; and of nitrogen-enriched air for the long-term storage of fruits, vegetables, and foods. In a recent article we reported the preparation of homogeneous dense blend membranes composed of low molecular weight liquid crystals and ethyl cellulose (EC). Air-separation properties of membranes ranging in thickness from 15 to 35 μm were discussed in relation to membrane composition, operating temperature, and pressure difference across the membranes (6). However, there is little information in the literature regarding high flux composite membranes containing a liquid crystal/EC blend dense selective thin layer. For this reason, composite membranes in which a DYC/EC selective layer could be made as thin as 1 μm were used for further experiments. Here we present air-separation studies of a liquid crystal DYC-modified EC thin film on a porous polyethersulfone support in an effort to understand better the operating conditions and the enhanced OEA flux of DYC/EC thin-film composite membranes over thick homogeneous dense membranes from the same materials.

EXPERIMENTAL

Materials

Low molecular mixture liquid crystal DYC, whose liquid crystal temperature range is between 29 and 32°C, was purchased from the Second Chemical Reagent Works of Tianjin City in China. EC whose viscosity in ethanol/toluene solution is 0.06 Pa·s was obtained from Shantou Xinning Chemical Works of Guangdong Province in China. The porous polyethersulfone support membrane was from the Development Center of Water Treatment of State Oceanic Administration at Hangzhou in China. Its thickness and pore size are 120 μm and 15–45 nm, respectively.

Preparation of Composite Membranes

A DYC/EC selective thin layer was prepared with tetrahydrofuran as the casting solvent by a solution casting technique. The thickness of DYC/

EC layers ranging from 1 to 7 μm was controlled by varying the DYC/EC (9/91) concentration in the casting solution. The resulting composite membranes are composed of a dense thin layer made of the DYC/EC (9/91) blend on a porous support layer made of the polyethersulfone. The whole structure is mechanically supported by an unwoven web.

Air Separation Measurements

Air-separation properties through the composite membranes were measured at different temperatures, different pressure differences, and lower recovery of air with a constant pressure–variable volume method according to ASTM D143V. The entire testing cell was immersed in an air bath at a certain temperature. The effective area of the membranes is ~50 cm^2. The desired pressure difference was applied to the upstream side of the membranes, and enough time was allowed for a steady air permeation rate to be established. A detailed method for the measurements is given in References 6–8.

RESULTS AND DISCUSSION

Effects of Casting Solution and Membrane Thickness

The effects of the DYC/EC (9/91) concentration in the casting solution on the membrane properties were examined. The results obtained are shown in Fig. 1. With increasing casting concentration from 0.15 to 1.0 wt%, the thickness of the DYC/EC thin film increased from 1 to 7 μm. Furthermore, the oxygen concentration in the permeated OEA increased but the OEA flux decreased linearly, indicating that air transport through the membranes is diffusion-controlled (9). However, a DYC/EC concentration lower than 0.15 wt% was unsuitable for casting the thin film without pinholes. Thus, a DYC/EC concentration of no lower than 0.15 wt% was required to form pinhole-free composite membranes. While the film thickness does not, in principle, affect the oxygen concentration in the OEA permeated, different oxygen concentrations can be obtained from films with identical DYC/EC ratios but with different thicknesses, which may be due to the morphological difference and the effect of asymmetry in the preparation of films of various thicknesses.

Effect of Operating Temperature

The effect of operating temperature on air-separation properties through the composite membranes is shown in Fig. 2. The membranes were formed by casting the DYC/EC solutions at concentrations of 0.15 and 0.3 wt%, and the air separation experiment was carried out at 25–63°C and a 0.41

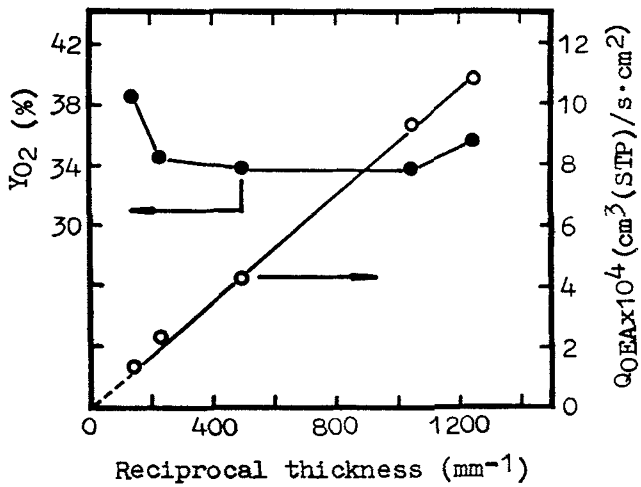

FIG. 1 Effect of DYC/EC (9/91) thin-film thickness on composite membrane performances. Feed gas: Compressed air with an oxygen content of 20.9%; operating temperature: 30°C; transmembrane pressure difference: 0.41 MPa; operating time: 24 hours.

MPa pressure difference. It was found that the oxygen concentration decreased slightly and the OEA flux increased linearly with an increase in the operating temperature, especially at the lower DYC/EC concentration of 0.15 wt%. This temperature dependence of gas-separation properties is observed with most polymer membranes. When a membrane is measured at high temperature, the membrane will have expanded, and the free volume in the membrane which takes part in sorbing and transporting gases will be larger. This will make the membrane more permeable and less selective.

The stronger dependence of Q_{OEA} on temperature shown in Fig. 2 for composite membranes compared to a 15-μm-thick defect-free membrane from the same materials (6) might imply that the composite membranes are defect-free or else their oxygen concentrations would be approaching 21% due to pore flow through the defects in the thin layer (10).

In addition, the OEA flux shown in Table 1 through the composite membrane is about 7 to 10 times the size of the OEA flux through a 15-μm-thick homogeneous dense membrane with the same DYC/EC (9/91) ratio at the same temperature (6). The oxygen concentration through the composite membrane is only slightly lower than that through the dense membrane (6). These results illustrate that the composite-membrane process can greatly enhance OEA flux through the membrane.

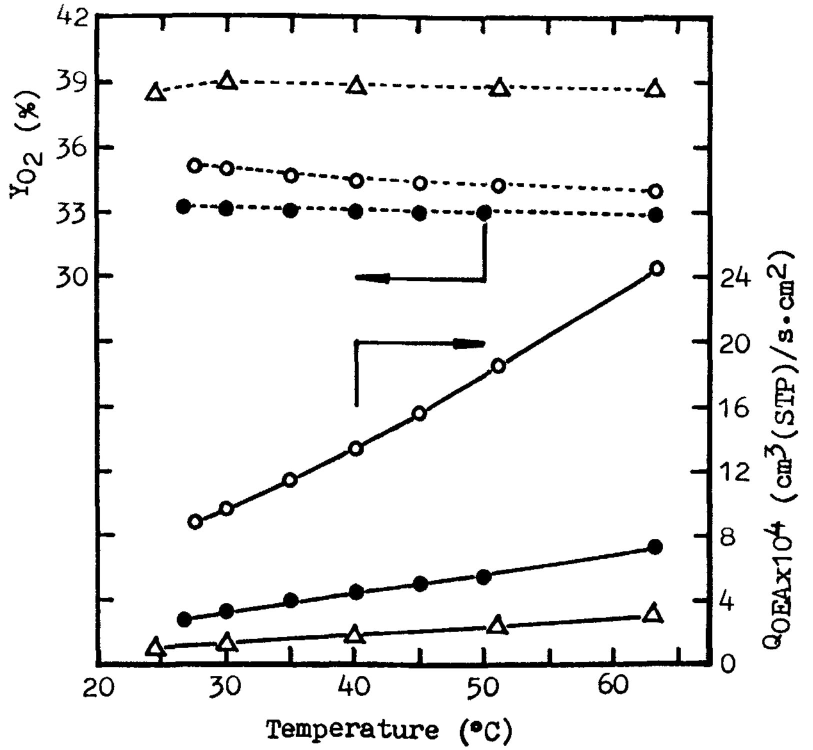

FIG. 2 Effect of operating temperature on the air-separation properties through composite membranes and homogeneous dense membrane. Composite membranes with DYC/EC (9/91) thin film were cast from solutions of (○) 0.15 wt% and (●) 0.3 wt% concentrations; (△) 15 μm-thick self-supporting DYC/EC (9/91) dense membrane. Pressure difference: 0.41 MPa.

TABLE 1

Comparison of the Air-Separation Properties of 1 μm Thick DYC/EC (9/91) Thin-Film Composite Membrane with 15 μm Thick DYC/EC (9/91) Homogeneous Dense Membrane

Operating temperature (°C)	Q_{OEA} (cm^3(STP)/s·cm^2)		Y_{O_2} (%)	
	Composite membrane[a]	Dense membrane[b]	Composite membrane[a]	Dense membrane[b]
30	1.08×10^{-3}	1.10×10^{-4}	36.0	39.2
40	1.23×10^{-3}	1.66×10^{-4}	34.5	39.0
51	1.85×10^{-3}	2.37×10^{-4}	34.2	38.9

[a] Under a transmembrane pressure difference of 0.41 MPa.
[b] Under a transmembrane pressure difference of 0.43 MPa.

Effect of Applied Pressure Difference

The effect of the applied pressure difference on the air-separation properties of composite membranes composed of a DYC/EC (9/91) thin layer (~1 μm) and a porous polyethersulfone support layer (120 μm) is shown in Fig. 3. The thin layers were formed by casting DYC/EC solution at 0.15 and 0.2 wt% concentration on a glass plate. The air separation experiment was carried out under applied pressure differences ranging from 0.05 to 0.49 MPa and at 30°C. As shown in Fig. 3, the OEA flux is proportional to the applied pressure, but the oxygen concentration was found to be a linear function of the pressure when the pressure is not higher than 0.2 MPa. By increasing the pressure difference from 0.25 to 0.49 MPa, the increasing rate of the oxygen concentration obviously declines. A similar

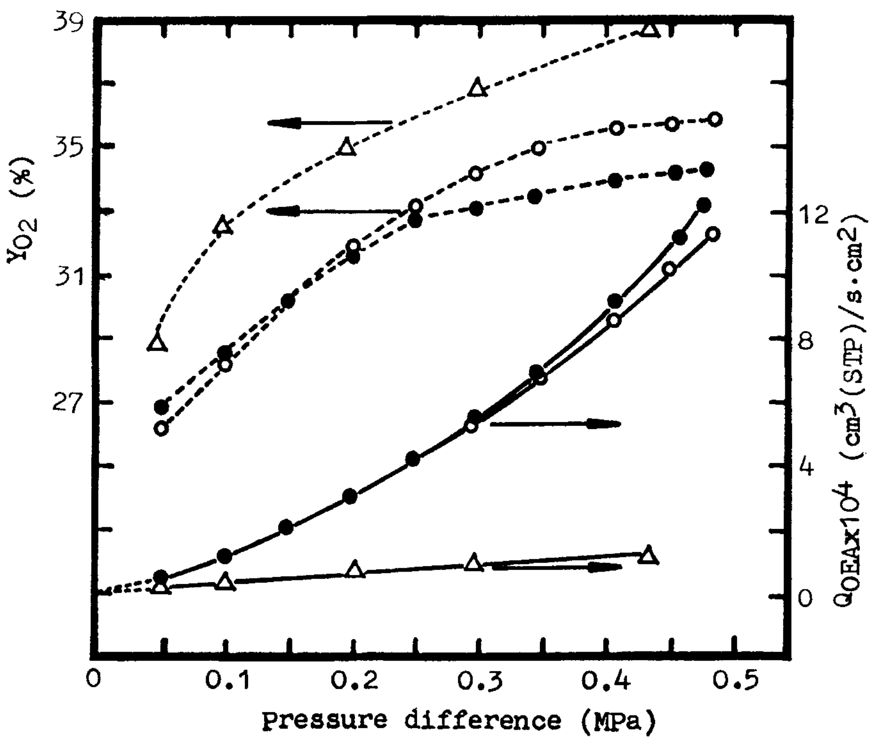

FIG. 3 Effect of applied pressure difference on the air-separation properties through composite membranes and homogeneous dense membrane. The composite membranes with DYC/EC (9/91) thin film were cast from solutions of (○) 0.15 wt% and (●) 0.2 wt% concentrations; (△) 15 μm-thick self-supporting DYC/EC (9/91) dense membrane. Temperature: 30°C.

pressure dependence of the gas-separation properties was also observed in a poly(phenylene oxide) composite membrane (1). Such an effect of pressure difference can be interpreted as follows: When a membrane is pressurized at a high pressure difference, a hydrostatic compressive effect causes a reduction in free volume, resulting in more selectivity, while the high OEA flux is maintained due to the high drive force of the transporting gases. From Fig. 3 it can be conservatively extrapolated that the OEA flux through the composite membrane will reach ~2.6×10^{-3} cm^3(STP)/s·cm^2 at a pressure difference of 1.0 MPa.

Additionally, the stronger increase of the oxygen concentration with applied pressure shown in Fig. 3 also indicates that the composite membranes might be defect-free, otherwise the oxygen concentration would not increase as a result of enhanced flow through pores in the thin-film layer.

Effect of Operating Time

The effect of operating time on air-separation properties through the membranes was examined at 30°C and under a pressure difference of 0.41 MPa. The results obtained are shown in Fig. 4. When the operating time is varied for 0–70 hours, an increase in the operating time leads to an OEA flux decline and an oxygen concentration rise through the membranes since the membranes were compacted under the applied pressure for this period. However, when the operating time is longer than 70 hours, the OEA flux and oxygen concentration scarcely changed. These changes in air-separation properties with operating time are not permanent. A recovery is measurable following removal of the applied pressure. It is believed that DYC/EC thin-film composite membranes are able to maintain their defect-free character over a working life of at least 500 hours in the presence of long-term pressurization.

Effect of Water

The effect of water on air-separation properties were roughly examined at 30°C and a pressure difference of 0.41 MPa. The results obtained are listed in Table 2. It is apparent that the water in the membranes examined results in a significant increase of the OEA flux and a decrease of the oxygen concentration through the membranes, as is often the case for gases in hydrophilic polymer membranes. This is because swelling of the membranes by water is responsible for an increase of the free volume in the membranes.

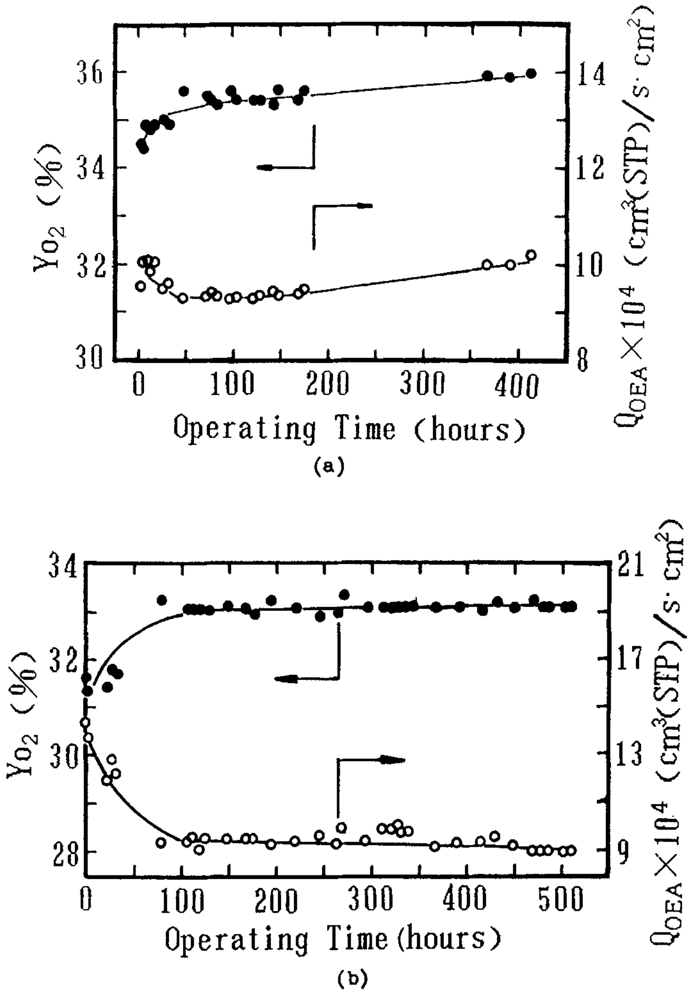

FIG. 4 Effect of operating time on the air-separation properties through the DYC/EC (9/91) thin-film composite membranes. Casting: (a) 0.15 wt%, (b) 0.2 wt%. Temperature: 30°C; transmembrane pressure difference: 0.41 MPa.

CONCLUSIONS

Air-separation properties through composite membranes prepared from a DYC/EC (9/91) thin film with a porous polyethersulfone as a substrate have been measured as a function of membrane-forming solution concentration and operating conditions. It was found that a more suitable concen-

TABLE 2
Effect of Water in the Membranes on the Air-Separation Properties through DYC/EC (9/91) Thin-Film Composite Membranes at 30°C and 360 hours of Operation and under 0.41 MPa of Pressure Difference

Thin film thickness (μm)	Without water		With water	
	Q_{OEA} (cm^3(STP)/s·cm^2)	Y_{O_2} (%)	Q_{OEA} (cm^3(STP)/s·cm^2)	Y_{O_2} (%)
1	8.31×10^{-4}	33.4	1.69×10^{-3}	32.2
0.8	1.06×10^{-3}	35.9	3.80×10^{-3}	29.3

tration is 0.15 wt%. The OEA flux is proportional to the operating temperature and pressure difference across the membranes. Oxygen concentration decreases slightly with increasing operating temperature but obviously increases with the pressure difference. Additionally, the water in the membranes can increase the OEA flux and reduce the oxygen concentration through DYC/EC composite membranes. However, the air-separation properties are almost independent of operating time at operating time longer than 70 hours. The composite membranes give an acceptable oxygen-enriching ability, viz., an OEA flux of 1.14×10^{-3} cm^3(STP)/s·cm^2 with an oxygen concentration of 35.9% under an applied pressure difference of 0.49 MPa and 30°C. This study has demonstrated that composite membranes exhibit much higher OEA fluxes than thick self-supporting membranes with the same composition.

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