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Air Separation Properties and Stabilities of Blend Membranes of Liquid Crystals with Ethyl Cellulose

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ABSTRACT

Air separation properties and stabilities of four blend membranes, 1–30-μm thick, prepared from ethyl cellulose (EC) with a small amount of nematic and cholesteric liquid crystals, such as *p*-heptyl-*p*′-cyanobiphenyl (7CB), *p*-pentylphenol-*p*′-methoxybenzoate (5PMB), benzoate-containing liquid crystal mixture (DYC), and cholesteryl oleyl carbonate (COC), were investigated by the variable volume method. To provide more significant information guiding membrane-based air separation, air was directly used as the test gas. The membranes showed both higher oxygen permeability, P_{O_2}, and oxygen over nitrogen separation factor, P_{O_2}/P_{N_2}, in the temperature range of the liquid crystalline phase. Oxygen-enriched air (OEA) flux, Q_{OEA}, and oxygen concentration, Y_{O_2}, increased simultaneously with increasing transmembrane pressure difference. Stability studies revealed that the efficiencies of concentrating oxygen using 1–7-μm thick DYC/EC (9/91) membranes laminated to porous polyethersulfone membranes were almost constant for a 120–510-hour operating time. The membrane possessed a Q_{OEA} of 9.0×10^{-4} cm^3(STP)/s·cm^2 and Y_{O_2} of 40% at 30°C and 0.41 MPa for a single-stage process. The results suggest that the membranes could be used effectively in enriching oxygen from air.

Key Words. Blend membrane; Liquid crystal; Ethyl cellulose; Oxygen enrichment; Stability

INTRODUCTION

Recently, much attention has been paid to membranes for gas separation because membrane-based gas separation is of current practical interest to industry. It has been found that membranes containing liquid crystals (LC), which have higher thermal expansion coefficients and exhibit the ordered supermolecular arrangement, possess good gas permeation and separation properties in the temperature range of the LC phase (1, 2). Previous LC-containing membranes, however, consisted primarily of *N*-(*p*-ethoxy-benzylidene)-*p*'-butylaniline (EBBA) LC, poly(vinyl chloride) (PVC), and polycarbonate (PC). These membranes, besides their expense, tend to be not only difficult to cast into defect-free thin membranes, but also fail to meet the practical operating requirements when they have a high LC content (more than 40 wt%) (1–3). Until now there has been little detailed information in the literature about air separation through LC/EC membranes, and especially the stability of these membranes.

This paper reports our efforts to study the air separation properties of ethyl cellulose (EC) membranes blended with a small amount (4–9 wt%) of low molecular weight LC. These have not been used for gas separation to date. The relationship between oxygen permselectivity and working conditions or membrane thickness of LC/EC membranes laminated to porous polysulfone membranes has been studied in detail.

EXPERIMENTAL

Materials

All materials are available commercially. All of the low molecular weight LCs are thermotropic. Among them, the nematic LC phase transition temperatures, $T_{KN} - T_{NI}$, of *p*-heptyl-*p*'-cyanobiphenyl (7CB) and *p*-pentyl-phenol-*p*'-methoxybenzoate (5PMB) are 28.5–42 and 30–43°C, respectively. The cholesteric phase transition temperature, $T_{KCh} - T_{ChI}$, of a benzoate-containing LC mixture (DYC) and cholesteryl oleyl carbonate (COC) are 29–32 and 25–39°C, respectively. The viscosity of EC in ethanol/toluene solution (5 wt%) is ca. 0.06 Pa·s. The polyethersulfone (PES) is supported by a backing fabric. The total thickness of the PES layer is ca. 120 μm.

Preparation of Membranes

Solutions of LC and EC in tetrahydrofuran (2 wt%) were cast on glass plates and then dried at room temperature for several days to yield transparent and homogeneous membranes with thicknesses of 1–30 μm containing 4 and 9 wt% of the LC.

Observation with Polarized Microscope

Observation of the membranes under polarized light was conducted using an XPT-6 type polarized microscope to investigate the dispersed state of liquid crystalline molecules in the EC polymer matrix.

X-Ray Diffraction of Membranes

The x-ray diffraction diagrams of LC/EC and EC membranes were determined with a Rigaku D/max-r A x-ray generator with nickel-filtered CuK_α radiation to detect the compatibility of LC and EC in the membranes and any morphological changes in the membranes regarding order of crystallinity and amorphous-phase content due to the introduction of LC.

Measurement of Gas Permeability

Compressed air from an air compressor employing a regulator, which was used to vary the absolute pressure of the feed from 0.15 to 0.51 MPa, was fed into the upstream side of the membrane while the downstream pressure was held at constant atmospheric pressure during the measurement. Prior to the measurements, the membrane was compacted at 30°C and 0.41 MPa for about 3 hours until the flux, Q_{OEA}, of oxygen-enriched air (OEA) and oxygen concentration, $Y_{\mathrm{O_2}}$, became stable. The gas permeability for the membrane was measured using the variable volume method in which Q_{OEA} and $Y_{\mathrm{O_2}}$ were determined by measuring the change in the OEA volume at a constant pressure difference across the membranes and at constant temperature after the separation process had proceeded for a period of time. The volume change in the OEA could be measured with the help of a 491-type industrial gas analyzer. The effective area of the membrane permeated was ca. 50 cm^2. The oxygen and nitrogen permeability coefficients, $P_{\mathrm{O_2}}$ and $P_{\mathrm{N_2}}$, were given by the following equations:

$$P_{\mathrm{O_2}} = (Q_{\mathrm{OEA}} \times Y_{\mathrm{O_2}} \times l)/\Delta P_{\mathrm{O_2}} \qquad (1)$$

$$P_{\mathrm{N_2}} = (Q_{\mathrm{OEA}} \times (1 - Y_{\mathrm{O_2}}) \times l)/\Delta P_{\mathrm{N_2}} \qquad (2)$$

where Q_{OEA} is the flux of OEA [cm^3(STP)/s·cm^2], $Y_{\mathrm{O_2}}$ is the oxygen concentration in the OEA (%), l is the membrane thickness (cm), and $\Delta P_{\mathrm{O_2}}$ or $\Delta P_{\mathrm{N_2}}$ is the partial pressure difference of oxygen or nitrogen across the membrane (cmHg). According to the above equations, the oxygen/

nitrogen separation factor can be written as

$$P_{O_2}/P_{N_2} = (Y_{O_2} \times \Delta P_{N_2})/(1 - Y_{O_2}) \times \Delta P_{O_2} \qquad (3)$$

RESULTS AND DISCUSSION

Compatibility of LC and EC in the Membranes

Figure 1 shows the x-ray diffraction diagrams measured for COC/EC and EC membranes. The diffraction diagrams exhibit two peaks, one at the *d*-spacing of 1.11 nm for the EC membrane, or 1.26 nm for the COC/EC membrane, and another at 0.46 nm for both membranes. Obviously, the addition of a small amount of LC to EC not only caused a shift toward higher *d*-spacing, but also caused the peaks to become lower and wider, which suggests interaction between the LC and the EC, i.e., the LC was miscible with the EC. In addition, the field of vision of the LC/EC membrane containing no more than 9 wt% LC was almost dark under the polarized microscope, which suggested that no continuous LC phase formed. These results are consistent with visual observation of the transparent membranes. It can be concluded that LC and EC were confirmed to be compatible up to 9 wt% LC-content, in agreement with other LC/polymer blends (1, 4).

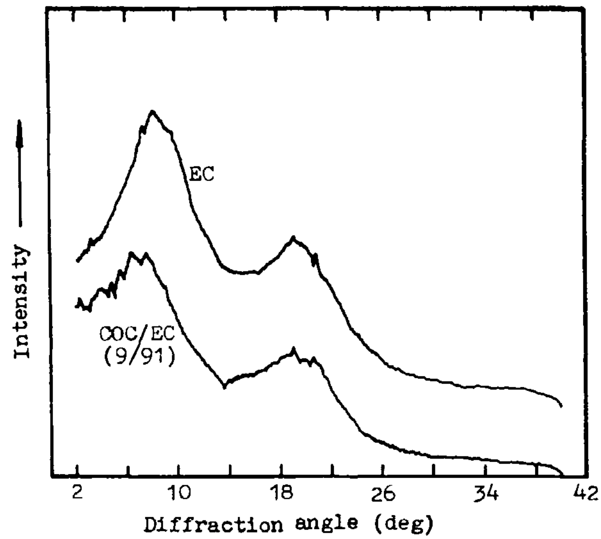


FIG. 1 X-ray diffractograms (CuK$_\alpha$) of the virgin membranes for COC/EC (9/91) and EC.

Also, a decrease in crystallinity and an increase in amorphous-phase content can be inferred from the lower and wider peaks of COC/EC membranes. These indicate a possible plasticizing effect of COC on EC (1, 5). It is this plasticizing effect that enables the LC/EC membrane to show higher gas permeability.

Air Separation Properties

The oxygen permeability coefficients, P_{O_2}, and the oxygen/nitrogen separation factors, P_{O_2}/P_{N_2}, of the membranes are shown in Fig. 2. With the exception of the 4 wt% COC/EC membrane, P_{O_2} of the other three kinds of LC/EC membranes increased, obviously due to the presence of LC, such as 7CB, 5PMB, and DYC, in the 25–72°C temperature range whereas P_{O_2}/P_{N_2} increased significantly only in the temperature range of the LC phase. The higher P_{O_2} may be attributed to the lower crystallinity order and the higher amorphous-phase content of membranes containing LC (Fig. 1). As we mentioned above, the LC component can play a role as plasticizer (1, 4). However, if one considers that LC acts only as a general plasticizer, then the P_{O_2}/P_{N_2} of the LC/EC membrane would not increase; in fact, the contrary is true. As seen in Fig. 2, in the temperature range of the LC phase, both P_{O_2}/P_{N_2} and P_{O_2} of the LC/EC membrane indeed increased at the same time, which usually cannot be effected by adding a general plasticizer. This behavior appears to be related to the novel character of the LC state. It is known that when LC materials come into LC phases with increasing temperature, they will exhibit more free volume, ordered molecular arrangement, and a higher thermal-expansion coefficient. If, however, the temperature does not fall into the temperature range of the LC phase, these characteristics of the LC would vanish. This abrupt change in the properties of LC materials would seem to account for the improvement of the oxygen-enrichment properties of LC/EC membranes.

Figure 2 shows that all P_{O_2} increased with increasing LC content from 4 to 9 wt% whereas P_{O_2}/P_{N_2} changed irregularly. The former phenomenon agreed with the above discussion; the latter was seemingly opposed to it. Similar behaviors were also observed for the EBBA/PVC membrane (1). As we know, the LC phase fluids show much lower viscosity than ordinary fluids since they have an ordered molecular structure. Furthermore, of the three broad categories in LC phases, namely, nematic, smectic, and cholesteric phases, the nematic phase has the lowest viscosity while the cholesteric phase has the highest. The exceedingly low viscosity is easily responsible for the formation of some pinholes in the membrane, espe-

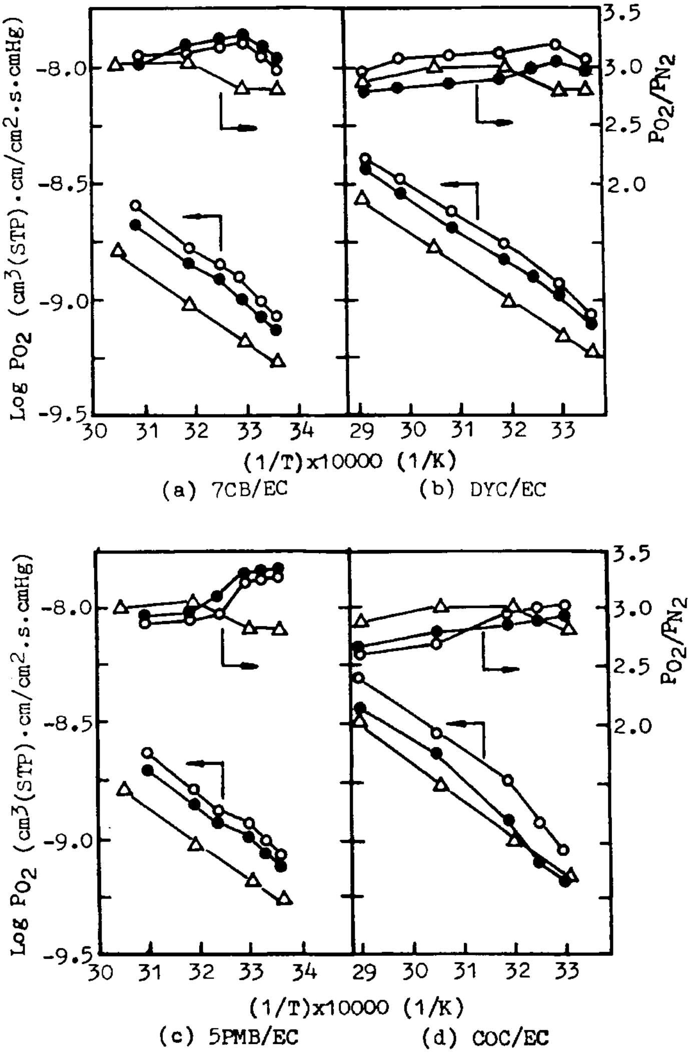


FIG. 2 Arrhenius plots of the oxygen permeability P_{O_2} for the LC/EC membranes (a) 7CB/EC, (b) DYC/EC, (c) 5PMB/EC, and (d) COC/EC with different LC/EC ratios 0/100 (△), 4/96 (●), and 9/91 (○) (ΔP = 0.41 MPa).

cially at a high transmembrane pressure difference. Generally speaking, at a given pressure difference, the lower the viscosity, the more pinholes are present. This phenomenon tends to be apparent as the LC content increases. Consequently, the P_{O_2}/P_{N_2} of membranes containing nematic LC, such as 7CB and 5PMB, decreases with increasing LC content from 4 to 9 wt%, whereas the P_{O_2}/P_{N_2} of membranes containing cholesteric LC, such as DYC and COC, increases or partially increases (Fig. 2). It must be appreciated that the selectivity of the membrane will be improved by the LC as long as the LC content is not high enough to result in pinhole formation. This means that the LC content should be as high as possible provided that no pinholes form.

It must be pointed out that the temperature dependences of P_{O_2} of the LC membranes do not fit an Arrhenius equation (1), especially in the temperature range of the LC phase. This may be due to fluctuation of the ordered structure of the LC phase, which causes the LC membranes to show different sensitivities to temperature.

A trend of both Y_{O_2} and Q_{OEA} of 7CB/EC membranes to increase simultaneously is generally observed with the transmembrane pressure difference, ΔP, in which the plots of Q_{OEA} are linear (Fig. 3). This is a trend observed with most polymer membranes without LC (6), but not observed in some other LC membranes (3). In addition, Y_{O_2} decreases slightly with increasing 7CB content from 4 to 9 wt%, which is consistent with the decrease of P_{O_2}/P_{N_2} shown in Fig. 2(a). However, it must be noted that Q_{OEA} decreases as a result of the increase of the thickness of the 9 wt% 7CB/EC membrane.

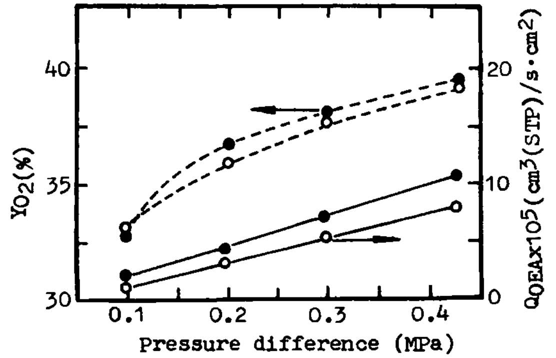


FIG. 3 Oxygen concentration, Y_{O_2}, and flux, Q_{OEA}, versus pressure difference for the 7CB/EC (4/96) (●) and (9/91) (○) membranes at 35°C.

Considering the P_{O_2}/P_{N_2} value of these LC/EC membranes in Fig. 2, one may think that the air separation properties are not very impressive. However, it should be appreciated that the real oxygen concentration for a single-stage process can reach about 40% (also see Fig. 3), which suggests that these LC/EC membranes actually exhibit high air-separation properties. These results are different from the conventional results obtained from pure gas studies. The test gas used in this paper is air directly from an air compressor rather than pure oxygen and pure nitrogen gases. Generally, the P_{O_2}/P_{N_2} obtained from pure gases are higher than that obtained from air because of the interaction between oxygen and nitrogen in the air when their molecules travel from the upstream to the downstream sides of the membranes (7).

Table 1 lists the oxygen enrichment of the LC membranes of this study and other data that we could find. Usually, P_{O_2}, P_{O_2}/P_{N_2}, Q_{OEA}, and Y_{O_2} of our membranes are all higher than the other values. In addition, the LC contents in our membranes are much lower than the others, which is apt not only to reduce the membrane cost but also to decrease the membrane thickness and improve the membrane stability. It is interesting that the LC materials may be miscible with polysulfone (PSF). This affords an opportunity for improving the oxygen enrichment of PSF. A study on the oxygen-enriching ability through a LC/PSF blend thin-film composite membrane will be reported in the near future.

Stability

Based on the superior gas selectivity and better stability of transport properties of PES compared to bisphenol-A PSF (13). 1 μm-, 2 μm-, and 7 μm-thick DYC/EC (9/91) membranes were laminated to porous PES ultrafiltration membranes. By reducing the membrane thickness from 7 to 1 μm, the Y_{O_2} decreases slightly, but the Q_{OEA} increases significantly (Fig. 4). After operating continuously for 120–510 hours at a ΔP of 0.41 MPa, Q_{OEA} and Y_{O_2} of the oxygen-enriched air remain about 1.3–9.0 × 10^{-4} cm^3(STP)/s·cm^2 and 33–38%, respectively (Fig. 4). Hence, the stability of these laminated membranes is higher than other LC membranes in which the LC components are easily forced out due to their higher LC content, especially at a higher operating pressure difference (3). This improved stability has also been shown in other EC membranes containing no more than 20 wt% polymeric liquid crystal (14). Summarizing, these results demonstrate that LC/EC membranes show remarkable stability for a long period.

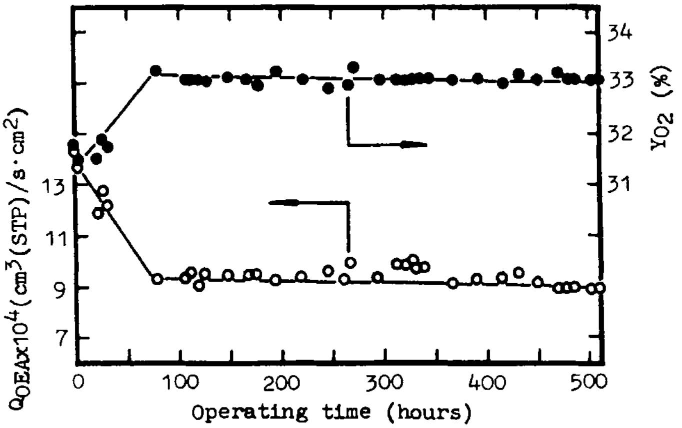
TABLE 1
Comparison of Oxygen Enrichment of LC/EC Membranes with Those of Other LC Membranes

Membrane	Thickness (μm)	Temp. (°C)	$P_{O_2} \times 10^{10}$ (cm^3(STP)·cm/cm^2·s·cmHg)	P_{O_2}/P_{N_2}	Refs.
5PMB/EC	15	27	9.33	3.33	This study
(4/96)	15	35	12.9	3.10	
DYC/EC	15	30	12.2	3.22	This study
(9/91)	15	51	25.3	3.16	
EBBA/PVC (60/40)		34	5.75	2.95	1
BEPC/PC[a] (60/40)		55	13.7	2.81	8
BBHP/PVC[b] (60/40)		35	11.3	2.73	9
			$Q_{OEA} \times 10^4$ (cm^3(STP)/s·cm^2)	Y_{O_2} (%)	
5PMB/EC:					
(4/96)	15	35	1.35	39.1	This study
(9/91)	15	30	1.13	40.0	
DYC/EC:					
(9/91)	1	30	9.00	33.0	This study
(9/91)	15	62	3.29	38.9	
EC	25	30	0.94	32.6	10, 11
				35.0	12
7CB/Alimite	50	35	8.5	25.8	2
5CH/PVC[c] (60/40)	50	46	1.0	37.0	3

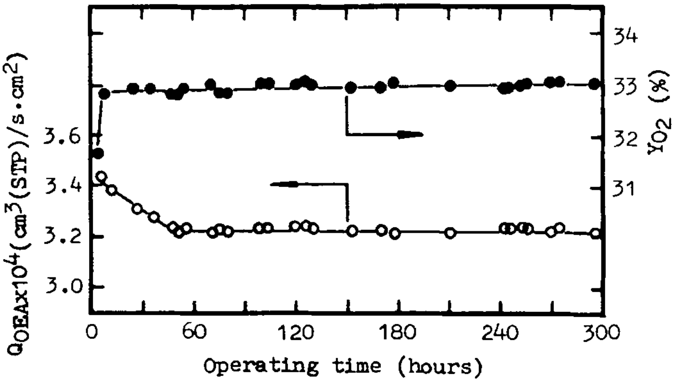
[a] BEPC: Butyl ethoxyphenoxy carbonylphenyl carbonate.

[b] BBHP: *p*-Butylbenzoic acid-*p*′-hexoxyphenyl ester.

[c] 5CH: *p*-Pentyl-*p*′-(*p*″-cyanophenyl)-cyclohexane.

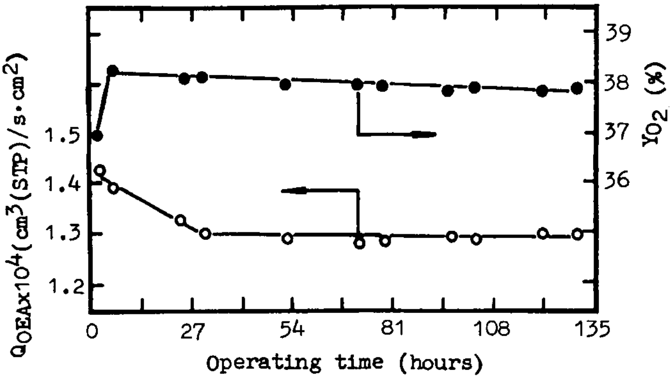


(a) Membrane thickness: 1 μm



(b) Membrane thickness: 2 μm

FIG. 4 Oxygen concentration, Y_{O_2}, and flux, Q_{OEA}, of the oxygen-enriched air through laminated membranes consisting of (a) 1 μm-, (b) 2 μm-, and (c) 7 μm-thick DYC/EC (9/91) membranes and porous polyethersulfone membranes as a function of operating time at 0.41 MPa net and 30°C.



(c) Membrane thickness: 7 μm

FIG. 4 Continued

CONCLUSIONS

Liquid crystals/ethyl cellulose have been successfully cast into dense membranes as thin as 1 μm using a solution casting technique. It has been demonstrated that the air-separation properties of LC/EC membranes are significantly improved compared to those of pure EC membranes. This is evidenced by the increases in P_{O_2} and P_{O_2}/P_{N_2} of the LC/EC membranes in the temperature range of the LC phase. The real oxygen concentration and flux of oxygen-enriched air can reach 40% and 9.0×10^{-4} cm^3(STP)/s·cm^2, respectively. In addition, the LC/EC membranes show higher stability for oxygen enrichment due to their lower LC content. Thus, these membranes might be useful for breathing systems in medical fields.

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