Actual Air Separation through Poly(aniline-*co*-toluidine)/Ethylcellulose Blend Thin-Film Composite Membranes

XIN-GUI LI, MEI-RONG HUANG, GUO-FANG GU, WEN QIU, JUAN-YING LU

Department of Polymer Materials Science and Engineering, College of Materials Science and Engineering,
Tongji University, 1239 Siping Road, Shanghai 200092, P. R. China

Received 5 January 1999; accepted 14 June 1999

ABSTRACT: Several multilayer thin-film composite membranes were fabricated of ethylcellulose (EC) and poly(aniline-*co*-ortho-toluidine) or poly(ortho-toluidine) blend as selective thin films and three ultrafiltration membranes with a 10- to 45-nm pore size and 100- to 200-μm thickness as porous supports. The relationships between the actual air-separation performance through the composite membranes and layer number, composition, casting solution concentration of the thin selective film are discussed. The oxygen-enriched air (OEA) flux through the composite membranes increases steadily with increasing operational temperature and pressure. The oxygen concentration enriched by the composite membranes appears to decrease with operating temperature, but increases with operating pressure. The actual air-separation property through the composite membranes seems to remain nearly constant for at least 320 days. The respective highest OEA flux, oxygen flux, and oxygen concentration, respectively, were found to be 4.78×10^{-5} cm^3 (STP)/s · cm^2, 2.2×10^{-5} cm^3 (STP)/s · cm^2, and 46% across EC/poly(*o*-toluidine) (80/20) blend monolayer thin-film composite membranes in a single step at 20°C and 650 kPa operating pressure. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 458–463, 2000

Key words: thin-film composite membrane; ethyl cellulose; poly(*o*-toluidine); poly(aniline-*co*-toluidine); ethyl cellulose/poly(*o*-toluidine) blend thin film; actual air separation; performance stability

INTRODUCTION

Polyaniline appears to be one of the polymers that exhibit the highest oxygen over nitrogen separation factor (P_{O_2}/P_{N_2}).[1–3] The P_{O_2}/P_{N_2} of the polyaniline membrane ranges from 9 to 30, but the intrinsic oxygen permeability through polyaniline membrane is too low (ca. 1×10^{-11} cm^3 (STP) · cm/cm^2 · s · cmHg) to be practical. The thin-film-forming ability of polyaniline is not good enough because it is soluble only in *N*-methylpyrrolidone (NMP), *m*-cresol, dimethyl propylurea, 1,4-cyclohexyl diamine, and concentrated sulfuric acid with high boiling point but low volatility. To take advantage of high P_{O_2}/P_{N_2} of polyaniline, it is necessary that the polyaniline membrane is modified chemically and physically. However, only a few reports on the chemical and physical modifications to polyaniline were found for preparation of high-performance gas separation membranes.[4]

In this article, the way of modifying polyaniline is through copolymerizing aniline with *o*-toluidine to

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Correspondence to: X.-G. Li.

Contract grant sponsor: Phosphor Plan of Science Technology of Young Scientists of Shanghai China; contract grant number: 98QE14027.

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 29804008.

Contract grant sponsor: State Key Laboratory for Modifications of Chemical Fibers and Polymer Materials at Donghua University in Shanghai, China.

Journal of Applied Polymer Science, Vol. 75, 458–463 (2000)
CCC 0021-8995/00/030458-06

introduce methyl side group on phenylene ring in polyaniline, to enhance polymer interchain free volume and solubility at a low boiling point and high volatility, and furthermore blending poly(aniline-*co*-*o*-toluidine) or poly(*o*-toluidine) with ethyl cellulose, exhibiting both intrinsic higher P_{O_2} and good film-forming ability. Several types of blend thin-film composite membranes were fabricated and evaluated by a constant pressure-variable volume method.

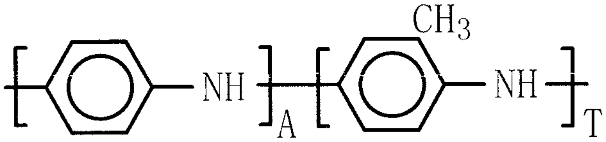
EXPERIMENTAL

Ethyl cellulose (EC) produced by Shantou Xinning Chemical Works of Guangdong Province in China has the viscosity 0.04–0.08 Pa · s measured in ethanol/toluene. The degree of substitution of the EC is ca. 2.4.

Poly(*o*-toluidine) and poly(aniline-*co*-ortho-toluidine) were synthesized by chemical oxidation polymerization in our laboratory. Detailed procedure for the synthesis of poly(*o*-toluidine) is as follows.[5]

To 200 mL of a 1*M* HCl solution is added 60 g $LiCl \cdot H_2O$ and 21.6 mL *o*-toluidine (used as received) in a 500-mL two-neck glass flask. The mixture is chilled to −21°C. Ammonium persulphate, 22.8 g, is dissolved in 100 mL water and cooled to 0°C to prepare an oxidant solution. The oxidant solution is added dropwise to the flask for 60–100 min at −15°C to −8°C. The polymerization is allowed to proceed for 82 h with continuous stirring at −15°C to −8°C. A dark blue precipitate with a coppery reflective tint is observed after the first 60 min of the polymerization. The resulting polymer is filtered on a Buchner funnel and washed with a large amount of water. The moist cake of emmeraldine hydrochloride is treated with 150–200 mL 0.15*M* NH_4OH for 24 h twice to obtain the base form. The polymer is dried under ambient air and manually ground to a fine powder. Poly(*o*-toluidine) of 6.5 g was obtained with the yield of ca. 31%.

A very similar copolymerization was carried out to obtain poly(aniline-*co*-*o*-toluidine), except that 16.8 mL aniline, 2.2 mL *o*-toluidine, and 11.4 g ammonium persulphate were used as received, and the copolymerization was allowed to proceed for 48 h. Typical yield for poly(aniline-*co*-*o*-toluidine) is 9–10%. Poly(aniline-*co*-*o*-toluidine) exhibits the following nominal structure:



The intrinsic viscosities for poly(*o*-toluidine) and poly(aniline-*co*-*o*-toluidine) in NMP at 25°C with Ubbelodhe viscosimeter are 0.52 and 0.59 dL/g, respectively.

Table I The Actual Air-Separation Properties through EC/Poly(aniline-*co*-*o*-toluidine) and Poly(*o*-toluidine) Thin-film Composite Membranes

Toplayer			Sublayer			Air Separation Properties (×10^5)cm^3 (STP)/s · cm^2		
Composition (wt %)	Solution Concn. (wt %)	Thickness (μm)	Composition (wt %)	Thickness (μm)	Porous Support	Q_{OEA}	Q_{O_2}	Y_{O_2} (%)
EC/copolyaniline (99/1)[a]	2	11	No			6.33[b]	1.81	28.6[b]
		11	EC	7	PES	2.34[b]	0.77	33.0[b]
		30 × 2[c]	No			2.40[b]	0.79	32.7[b]
EC/poly(*o*-toluidine)								
95/5	3.2	16	No		PSA	4.0	1.36	34.0
80/20	2.1	20	EC	15	PSF	2.08	0.79	37.8
80/20	1.6	15	EC	15	PSF	2.4	0.94	39.0

Conditions: 25°C, 400 kPa pressure difference.

[a] The copolyaniline from aniline (90%) and *o*-toluidine (10%).

[b] Data measured at 20°C.

[c] Separative bilayer.

PSF, PES, and PSA ultrafiltration membranes with a 10–45 nm pore size and 100–200 μm thickness as porous support in this study have been evaluated in an our previous paper.[6]

The blend thin films of poly(*o*-toluidine) and poly(aniline-*co*-*o*-toluidine) with ethyl cellulose were made by pouring the casting solutions in chloroform with concentration of 1.6–3.2 wt % onto glass plates and evaporating the casting solvent at 25°C for ca. 20 h. The concentrations of EC, poly(*o*-toluidine), and poly(aniline-*co*-*o*-toluidine) of the blend membranes in the casting solutions are 1.3–3.0, 0.16–0.42, and 0.02 wt %, respectively. The same procedure was used to prepare EC thin film as a sublayer in the composite membranes. These thin films had the thickness of 7–20 μm. The composite membranes were fabricated from the thin films and the porous PSF, PES, and PSA supports.

Actual air-separation measurements were performed using a constant pressure–variable volume method, which has been reported previously.[6–12] Feed gas was compressed air with an 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 measuring 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 OEA permeated was performed on a QF1901 type 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

Influence of Membrane Composition on Air Separation

Actual air-separation properties through two series of composite membranes are listed in Table I. It is seen that two types of monolayer thin-film composite membranes in two membranes series

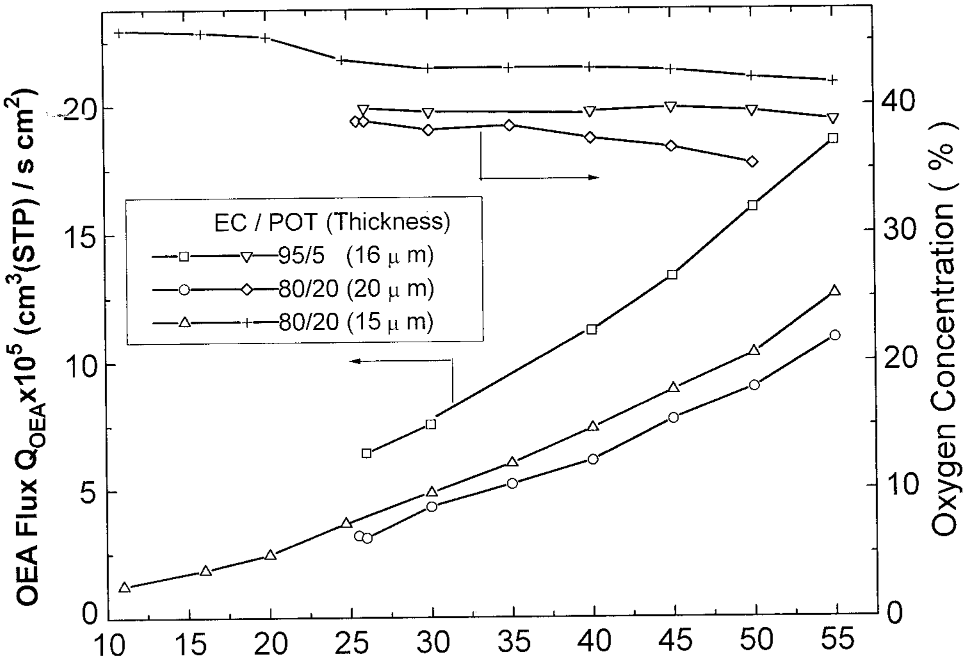


Figure 1 Variation of actual air-separation properties as a function of operating temperature (transmembrane pressure difference, 550 kPa) for PSA porous support composite membrane with a 16-μm-thick thin-film toplayer of EC/POT (95/5, —□—, —▽—) but without sublayer; for PSF porous support composite membrane with 15-μm-thick EC sublayer and EC/POT (80/20) thin-film toplayer of 20-μm thickness (—○—, —◇—) and 15-μm thickness (—△—, —+—). Feed air contains 20.9% oxygen.

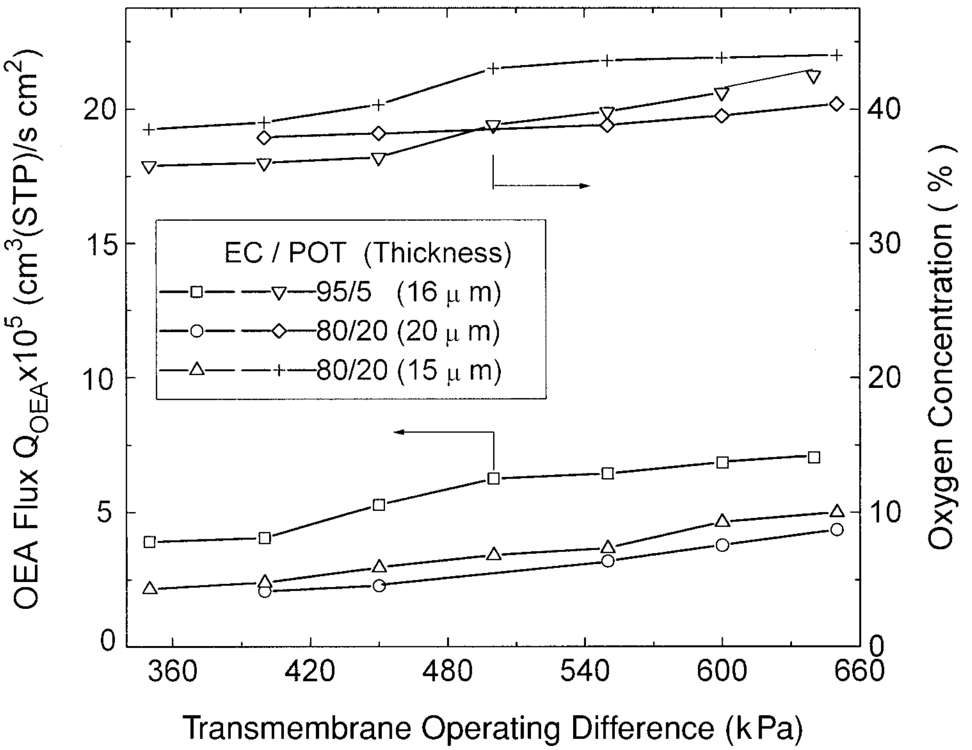


Figure 2 The variation of actual air-separation properties as a function of transmembrane pressure difference at 25°C for PSA porous support composite membrane with 16-μm-thick thin-film of EC/POT (95/5, —□—, —▽—) but without sublayer; for PSF porous support composite membrane with 15-μm-thick EC sublayer and EC/POT (80/20) thin-film toplayer of 20-μm thickness (—○—, —◇—) and 15-μm thickness (—△—, —+—). Feed air contains 20.9% oxygen.

both exhibit the highest OEA flux but the lowest oxygen concentration. It is seen from Table I that the addition of 5 wt % poly(*o*-toluidine) into EC is more effective to enhance the air-separation capability than the addition of 1 wt % poly(aniline-*co*-*o*-toluidine). The oxygen concentration will increase significantly when a flexible EC sublayer is added between toplayer and porous support. Note that the EC sublayer does not provide much resistance to the oxygen permeation, because the oxygen permeability through the EC membrane is ca. 90 and 23 times the size of the oxygen permeability through polyaniline and polyethylaniline, respectively.[6,13] Particularly, EC/poly(*o*-toluidine) (POT) (80/20) blend toplayer plus EC sublayer bilayer thin-film composite membrane shows the highest oxygen concentration 39%, medium OEA flux 2.4 × 10^{-5} cm^3 (STP)/s · cm^2, and oxygen flux 9.4 × 10^{-6} cm^3 (STP)/s · cm^2, possibly due to the thinner toplayer and sublayer (15 μm) and the highest POT content in the membrane. Thus, the following discussion focuses on the EC/POT blend thin-film composite membrane.

Influence of Operating Temperature on Air Separation

Actual air-separation properties across three EC/POT blend toplayer plus EC sublayer bilayer thin-film composite membranes at 11–55°C and 550 kPa transmembrane pressure difference are shown in Figure 1. The OEA flux increases steadily, but the oxygen concentration decreases slightly with increasing temperature. The OEA flux at 55°C is 10 times as high as in the flux at 11°C, but the oxygen concentration at 55°C is 92% the size of the oxygen concentration at 11°C. Very similar dependency of the air-separation performance on temperature was observed for the many composite membranes.[6] These results are because higher temperature is inclined to originate less discriminating gaps or more free volume in the membranes. In addition, the air will become less condensable with increasing temperature. The slope of the OEA flux versus temperature curves increases with an increase in operating temperature, which is similar to that typically

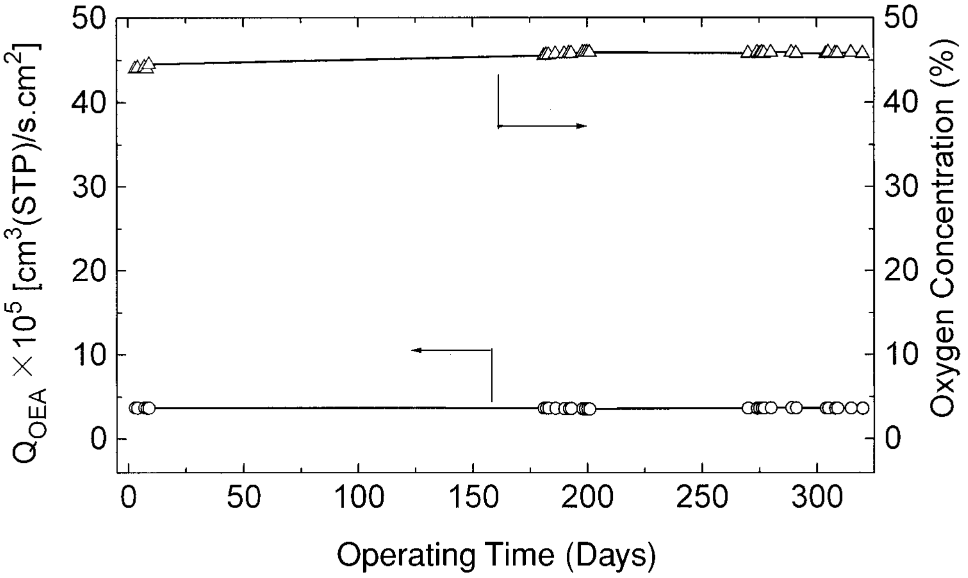


Figure 3 The variation of actual air-separation properties as a function of operating time at 25°C and transmembrane pressure difference, 550 kPa, for 15-μm-thick ethyl cellulose (EC)/poly(*o*-toluidine) (POT) (80/20) thin-film toplayer, 15-μm-thick EC sublayer, and PSF porous support trilayer composite membrane. Feed air containing 20.9% oxygen.

observed for other ultrathin-film composite membranes.[6] Within full temperature range, EC/POT (80/20, 15 μm thick) blend toplayer plus EC (15 μm thick) sublayer bilayer thin-film composite membrane of three membranes has the highest oxygen concentration of 42–45.8% and the second highest OEA flux of 3.7–12.6 × 10^{-5} cm^3 (STP)/s · cm^2. This bilayer thin-film composite membrane is supposed to exhibit the best comprehensive capability of actual air separation in the temperature range. The high oxygen flux and high oxygen concentration through the composite membrane are attributed to the high oxygen permeability across the EC film and the high oxygen/nitrogen separation factor across the poly(*o*-toluidine) film, respectively.

Influence of Transmembrane Pressure Difference on Air Separation

Figure 2 shows the influence of transmembrane pressure difference on actual air-separation properties through three thin-film composite membranes. Apparently, the OEA flux and oxygen concentration through the composite membranes increase simultaneously with an increase in transmembrane pressure difference from 350 to 650 kPa at 25°C. The OEA flux and oxygen concentration at the pressure difference 650 kPa are 1.8–2.2 times and 1.1–1.2 times as high as those at the pressure difference 350 kPa, respectively. Similar results have been observed for other ultrathin-film composite membranes.[6–8] A concurrent increase in OEA flux and oxygen concentration could be attributed to a combination of an acceleration in the OEA passing rate across the membranes with the compression between the two thin films and porous support as the transmembrane pressure difference increases. It is appreciated that the EC/POT (80/20, 15 μm thick) blend toplayer plus EC (15 μm thick) sublayer bilayer thin-film composite membrane of three membranes exhibits the highest oxygen concentration within the pressure difference range from 350 to 650 kPa. For a given pressure of 650 kPa, the trilayer composite membrane shows the highest oxygen concentration of 44%, the second highest OEA flux of 4.78 × 10^{-5} cm^3 (STP)/s · cm^2, and oxygen flux 2.1 × 10^{-5} cm^3 (STP)/s · cm^2 at 25°C. It was calculated that a 112-μm-thick polyaniline membrane (its P_{O_2} = 1.14 × 10^{-11} cm^3 (STP) · cm/cm^2 · s · cmHg and P_{O_2}/P_{N_2} = 9.5) permits production of a useful permeant of oxygen concentration 64.4%, OEA flux 1.21 × 10^{-6} cm^3 (STP)/s · cm^2, and oxygen flux 7.79 × 10^{-7} cm^3 (STP)/s · cm^2 at a feed air flux 9.44 × 10^5 cm^3/s at a stage cut 27.0 simultaneously in a single pass.[14] It is apparent that the oxygen permeance through the EC/POT blend thin-film composite membrane is ca. 27 times larger than that through the polyaniline membrane,[14] whereas the oxygen concentration through the polyaniline is only 1.46 times larger than that through EC/POT composite membrane.

Table II Stability of 20-μm-thick EC/Poly(*o*-toluidine) POT (80/20) Blend Film Toplayer, 15 μm-thick EC Film Sublayer, and PSF Porous Support Trilayer Composite Membrane

	Operating Time (h)						
	2	24	90	94	98	102	106
$Q_{\mathrm{OEA}} \times 10^5$ cm^3 (STP)/s · cm^2	3.25	3.20	3.11	3.19	3.11	3.11	3.12
$Q_{\mathrm{O_2}} \times 10^5$ cm^3 (STP)/s · cm^2	1.25	1.24	1.21	1.23	1.21	1.21	1.22
Oxygen concentration (%)	38.6	38.8	38.8	38.7	38.8	38.9	39.0

Conditions: 25°C and 550 kPa transmembrane pressure difference.

Influence of Operating Time on Air Separation

Operating stability is a significant problem in actual air separation of new composite membranes. Figure 3 and Table II show the influence of operating time on actual air-separation property through two types of EC/POT toplayer plus EC intermediate layer composite membranes. It is found that the actual air-separation performance, i.e., OEA flux and oxygen concentration, fluctuate slightly for the operating times longer than 320 days. The result implies that a long-term actual air separation can be performed efficiently and stably in the trilayer thin-film composite membranes, and the thin-film composite membranes are industrially useful.

Obviously, the oxygen concentration of 46% shown in Figure 3 is higher than the highest oxygen concentration (38%) enriched by either EC thin-film composite membranes or EC homogeneous membranes,[7] indicating that an introduction of 20 wt % POT can effectively enhance the oxygen-enriching ability of EC membranes.

CONCLUSIONS

New types of trilayer thin-film composite membranes whose separative toplayers contain poly(*o*-toluidine) or poly(aniline-*co*-*o*-toluidine) were prepared and characterized for their actual air-separation performance. The OEA flux and oxygen concentration through the composite membranes in a single stage are remarkably influenced by the separative thin-film toplayer composition and thickness, operational temperature, and transmembrane pressure difference, but the OEA flux and oxygen concentration are hardly ever influenced by the operating time. EC/POT (80/20, 15 μm thick) blend toplayer plus EC (15 μm thick) sublayer thin-film composite membrane combine high actual air-separation property with high stability. The highest OEA flux and oxygen concentration were found to be 4.78×10^{-5} cm^3 (STP)/s · cm^2 and 46%, respectively, for the above composite membrane in a single step at 25°C and the pressure difference range of 650 kPa. However, this oxygen concentration of 46% is much lower than ca. 60% predicted theoretically on the basis of $P_{\mathrm{O_2}}/P_{\mathrm{N_2}}$ values of pure polyaniline reported earlier.[1–3] Therefore, there seems a great potentiality in enhancing the oxygen concentration enriched by the composite membranes.

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