Composite Membranes of Poly(1-trimethylsilyl-1-propyne) and Poly(dimethyl Siloxane) and Their Pervaporation Properties for Ethanol–Water Mixture

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SYNOPSIS

A poly(1-trimethylsilyl-1-propyne) (PTMSP) membrane was systematically modified to prevent flux decline over time by incorporating poly(dimethyl siloxane) (PDMS) in three different ways: (1) semi-interpenetrating polymer network (I series), (2) PDMS sorption (S series), and (3) PDMS sorption and crosslinking (X series). The PTMSP and PDMS phases were partially mixed in the I series, which was confirmed by the measurement of density and glass transition temperature. The flux and separation factor in pervaporation of an ethanol–water mixture decrease with time for the I series, analogous to the behavior of pure PTMSP. However, the flux and separation factor remained steady with time in the case of the S and X series. The sorption method appears to be a good means for maintaining a time-unvarying flux and separation factor at a minimum expense. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Poly(1-trimethylsilyl-1-propyne) (PTMSP) has been studied as a potential polymeric membrane material for gas and liquid separation[1-4] because it exhibits high flux of gases and liquids. The oxygen permeability of PTMSP (7200 Barrer) is an order of magnitude higher than poly(dimethyl siloxane) (PDMS) (610 Barrer),[5,6] which is commonly considered the most permeable polymeric material developed.

Fundamental sorption and diffusion behavior in PTMSP membranes has been investigated.[7-9] The high permeability of PTMSP is believed to be associated with the large free volume due to the bulk and flexibility of the trimethyl silyl group.[7-11] Although its permeability is very high, permselectivity is low. Another drawback of PTMSP as a membrane material is the decline of the transport properties with time.[7] This decline is caused by free volume

reduction that is attributable to relaxation or physical aging of PTMSP chains.[1,5,7-11]

Several attempts have been made (1) to improve the separation characteristics, in particular the permselectivity, and (2) to retard or prevent the physical aging of PTMSP membranes, thus maintaining their good transport properties steady with time. Toward these objectives, the structure of PTMSP has been chemically modified with various aliphatic or PDMS groups on the PTMSP side chains[1,4,12,13] as well as UV irradiation.[14] Another common method is to incorporate various polymers or additives into PTMSP membranes. For instance, poly(hexafluorobutyl methacrylate),[15] PDMS, or various additives[5,13,16] were incorporated into PTMSP.

In this study, PTMSP was modified with PDMS in three different ways in order to retard the physical aging process while maintaining the ethanol–water permeation properties unchanged. Semi-interpenetrating polymer network (semi-IPN), PDMS-sorbed, and PDMS-sorbed and crosslinked membranes were prepared and their permeation properties were measured and analyzed.

EXPERIMENTAL

Materials

1-Trimethylsilyl-1-propyne (Tokyo Kasei, Japan) was distilled twice with CaH_2. $TaCl_5$ (Johnson Matthey, U.S.A.) was employed as a polymerization catalyst. Polymerization was carried out by the method developed by Masuda et al.[2] and modified by Nakagawa et al.[5] Hydroxyl-terminated PDMS, of two different viscosities (35 and 1000 cS), tris(dimethylamino)-methyl silane (TDMS), and vinyl triacetoxy silane (VTAS) were supplied by Petrach, U.S.A. The other chemicals were used as received unless specified otherwise.

Materials Characterization

A density gradient column of water–ethanol was used to measure the density of the composite membranes. A differential scanning calorimeter (DSC) (DuPont, Model 2100) was utilized to measure the glass transition temperature.

Membrane Preparation

Pure PTMSP Membrane

Two hundred milliliters of 2.0 wt % PTMSP solution in dehydrated toluene was cast on a glass plate with a knife gap of 900 μm, followed by drying at 40°C for 24 h in a vacuum oven. The dry membrane was annealed at 100°C for 4 days *in vacuo*. The thickness of all membranes used in this study was fixed at 32 μm.

Semi-IPN Membrane (I Series)

Fifty milliliters of 2.0 wt % PDMS solution in dehydrated toluene was mixed with varying amounts of 2.0 wt % PTMSP and the crosslinking agent TDMS solution in dehydrated toluene. These solution mixtures were cast on glass plates with a knife gap of 900 μm and dried at 40°C for 24 h *in vacuo*. The amount of PDMS incorporated in the composite membrane was controlled to be 3.0, 5.0, 10.0, and 15.0 wt %. TDMS was added at a 10 : 1 ratio to the total hydroxyl groups in the PDMS used. This ratio was chosen because of TDMS's volatility.

PDMS-sorbed Membrane (S Series)

Dry PTMSP membranes were immersed in varying amounts of 2 wt % PDMS solution in methyl ethyl ketone for 2 days. The surface of the membranes were wiped with filter paper to remove excess PDMS

from the membranes' surface. The weight ratio of PTMSP to PDMS in the solution was controlled to be 0.03, 0.05, 0.10, and 0.15. The amount of PDMS in dry PDMS-sorbed membranes was found to be 1.1, 5.9, 11.7, and 12.0 wt %, respectively.

PDMS-sorbed and -crosslinked Membrane (X Series)

PDMS-sorbed membranes were immersed in 2.0 wt % of solutions of crosslinking agent VTAS in methyl ethyl ketone for 3 days, crosslinked, and dried at 40°C for 24 h *in vacuo*. The amount of VTAS used was also 10 : 1 with respect to the hydroxyl groups of PDMS.

Pervaporation Experiment

A conventional vacuum pervaporation experimental procedure was followed here. The effective surface area (A) of the membrane is 6.16 cm^2. The downstream pressure was maintained at 5–7 torr during the entire experimental period and the temperature at 30°C. The feed composition was fixed at 5 wt % ethanol in water. The flux J was determined by measuring the amount of permeant Q passed through the membrane during the time interval t at steady state.

$$J = Q/At \tag{1}$$

The separation factor α of ethanol over water is defined in the usual manner:

$$\alpha = \frac{y_e/y_w}{x_e/x_w} \tag{2}$$

where x_i and y_i are weight fractions of feed and permeate, respectively. The subscripts e and w stand for ethanol and water. The feed and permeate concentration were measured by a gas chromatograph (Varian Model VISTA 8000) with a Porapak Q column. A large feed reservoir of 5 L was used in order to minimize the change in the feed concentration during the experimental time (typically 7 days).

RESULTS AND DISCUSSION

Phase Miscibility of Composite Membranes

The measured density d_m and the theoretically estimated density d_t of the composite membranes and their difference Δd ($= d_m - d_t$) are listed in Table I. The d_t value was estimated, by assuming the simple additive rule of individual components, from

Table I   Composition and Density of Composite Membranes

Code	Viscosity of PDMS (cSs)	PDMS Content (wt %)	d_m (g/cm^3)	d_t (g/cm^3)	Δd [a] (g/cm^3)
I-1000-3	1000	3.0	0.955	0.941	0.014
I-1000-5	1000	5.0	0.958	0.942	0.016
I-1000-10	1000	10.0	0.974	0.944	0.030
I-1000-15	1000	15.0	0.991	0.946	0.045
I-35-3	35	3.0	0.950	0.941	0.009
I-35-5	35	5.0	0.952	0.942	0.010
I-35-10	35	10.0	0.950	0.944	0.006
I-35-15	35	15.0	0.960	0.946	0.014
S-35-1	35	1.1	0.934	0.941	−0.007
S-35-5	35	5.9	0.930	0.942	−0.012
S-35-11	35	11.7	0.933	0.945	−0.012
S-35-12	35	12.0	0.934	0.945	−0.010
X-1000-2	1000	2.4	0.945	0.941	0.004
X-1000-6	1000	6.4	0.958	0.943	0.015
X-1000-7	1000	7.7	0.981	0.943	0.038
X-1000-8	1000	8.9	0.978	0.944	0.034
PDMS			0.980		
PTMSP			0.940		
PTMSP (annealed)			0.943		

[a] $\Delta d = d_m - d_t$.

$$d_t = \frac{v_1 d_1 + v_2 d_2}{v_1 + v_2} \qquad (3)$$

where v and d are volume and density of pure component used for the composite membrane. The subscripts 1 and 2 denote PTMSP and PDMS, respectively. The measured density increases with the increase in the amount of PDMS contained in the composite membranes, because PDMS is simply more dense than PTMSP. The I- and X-series membranes have higher density than the uncrosslinked S series because the uncrosslinked PDMS chains have higher mobility and higher free volume. Here, Δd is positive and increases with the amount of PDMS except for the S series. This implies that the PDMS phase would be partially mixed with the PTMSP phase in the I and X series. The partial mixing was also manifested by the increase in the glass transition temperature as shown in Table II. The glass transition temperature measured by DSC was increased from −117 (pure PDMS) to the range of −92, to −98°C for the I series.

Pervaporation of PDMS and Pure PTMSP Membrane

The PDMS membrane has steady flux (35 g/m^2 h) and separation factor (6.4) during a 7-day run as

shown in Figure 1. In contrast, both the flux and separation factor through the PTMSP membrane simultaneously decrease with time, which is consistent with previous studies.[4] It has been known that PTMSP has a large excess free volume, which diminishes with time by the physical aging process. A free volume decrease affects the ethanol flux more pronouncedly than water because ethanol has a large kinetic diameter and is also more permeable than water. Therefore both the flux and separation factor decrease simultaneously, resulting from the decrease in the free volume. The physical aging process is accelerated by annealing, which causes a rapid decrease in the free volume. The PTMSP membrane annealed at 100°C for 4 days, clearly demonstrated much lower flux and separation factor than unan-

Table II   Glass Transition Temperatures of Composite Membranes

Code	T_g (°C)
I-1000-3	−91.7
I-1000-10	−91.7
I-1000-15	−98.7
PDMS	−117.3
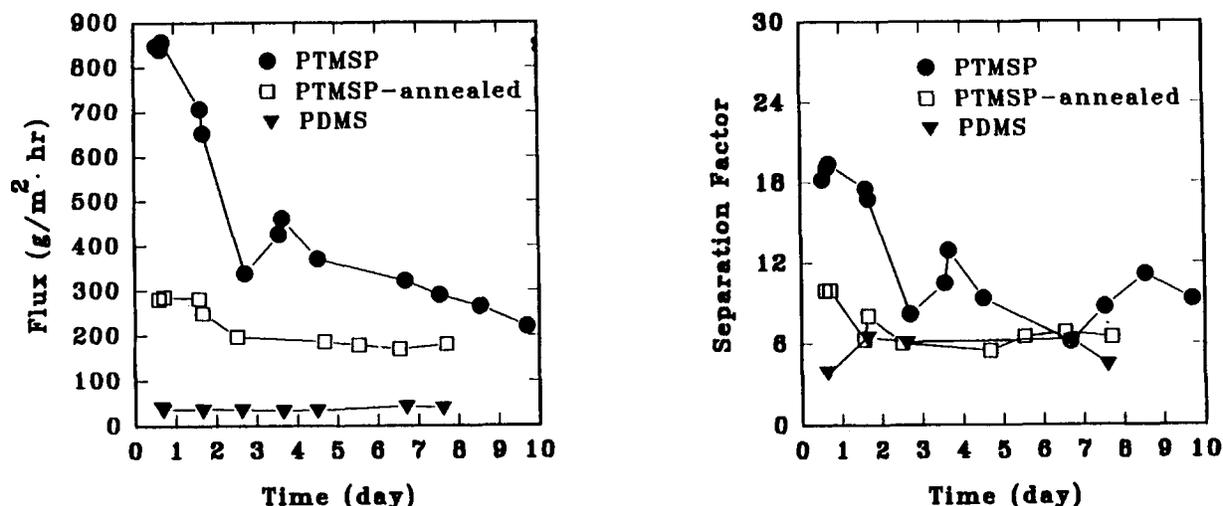
Figure 1   Total flux and separation factor vs. time in the pervaporation of ethanol–water mixture through pure membranes at 30°C (Feed: 5 wt % aqueous ethanol).

nealed PTMSP. This was also confirmed by the density increase from the unannealed PTMSP of 0.940 g/cm^3 to that of the annealed one of 0.943.

Pervaporation of Composite Membranes

I Series

Figures 2 and 3 present the pervaporation results of the I-series membranes for two different molecular weights of PDMS (1000 and 35 cS) incorporated. In the I-series membranes, it was attempted to

maintain the PTMSP chain mobility by introducing and crosslinking PDMS using a semi-IPN technique. Figure 2 shows that the total flux typically decreases from 600 to 200 (g/m^2 h) in a time span of 7 days. The separation factor also decreases markedly. This behavior is very similar to that of unmodified PTMSP membranes. As the amount of PDMS in the composite membrane increases, both the flux and separation factor decrease. This is due to the fact that PDMS has a lower flux as well as a lower separation factor than PTMSP. The effect of molecular weight of PDMS was examined while
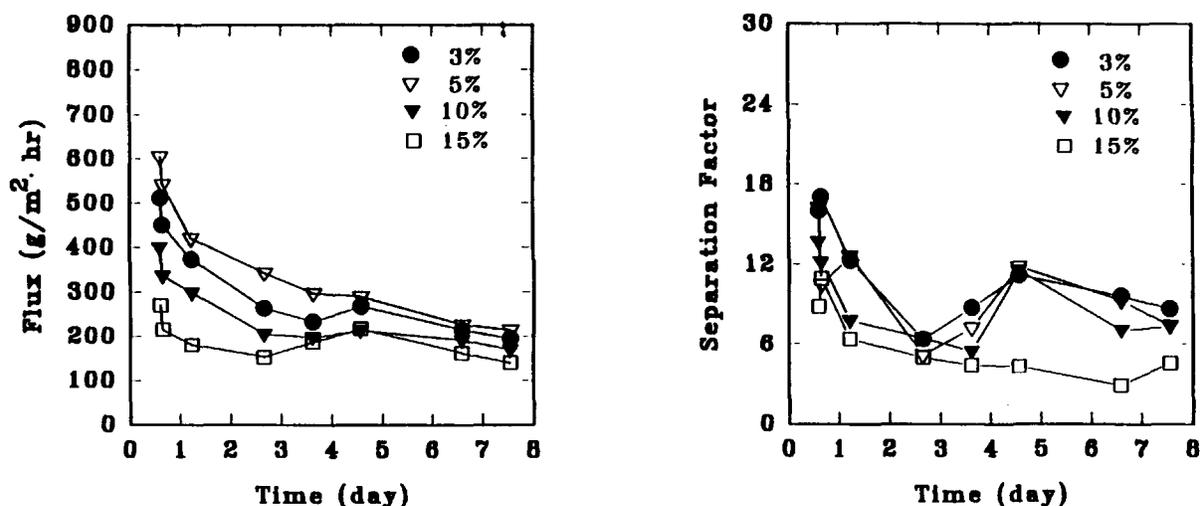
Figure 2   Total flux and separation factor vs. time in the pervaporation of ethanol–water mixture through I-series membranes with PDMS of 1000 cS at 30°C (Feed: 5 wt % aqueous ethanol).
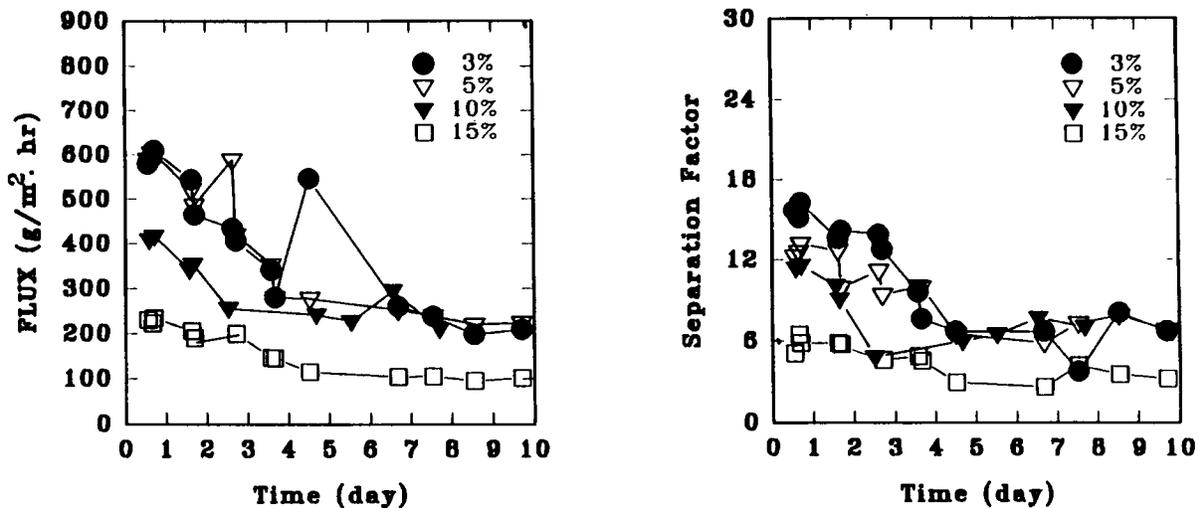
Figure 3 Total flux and separation factor vs. time in the pervaporation of ethanol–water mixture through I-series membranes with PDMS of 35 cS at 30°C (Feed: 5 wt % aqueous ethanol).

maintaining the PDMS content the same. Comparing Figure 2 (1000 cS) and 3 (35 cS), the transport behavior is similar. In other words, it is hard to observe any effect of PDMS molecular weight on transport properties in this experimental range.

S Series

The pervaporation results of the PDMS-sorbed PTMSP composite membranes (S series) are shown in Figure 4. In contrast to the I series, the flux and separation factor remain nearly constant during a

7-day run. This appears to be due to the fact that PDMS could be sorbed or filled into the PTMSP phase's free volume. The "PDMS filler" presumably restricts the physical aging process and blocks the favorable penetration path of PTMSP. Therefore the transport properties are steady with time, but lower than fresh PTMSP and higher than PDMS. Surprisingly, the addition of 1 wt % of PDMS made the membrane very stable with time. As the amount of PDMS increases, pervaporation performance deteriorates as expected.
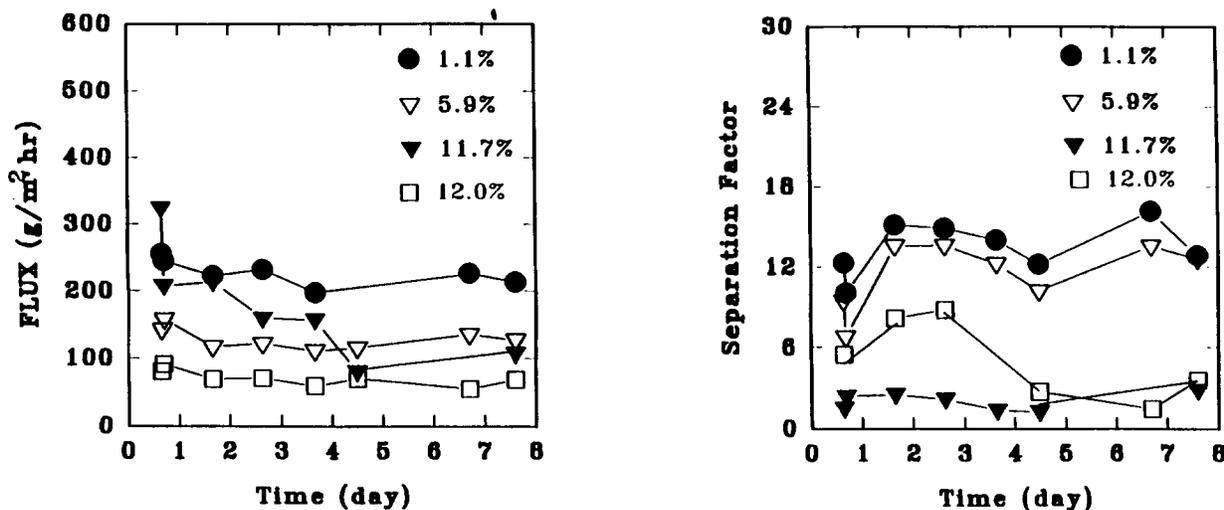
Figure 4 Total flux and separation factor vs. time in the pervaporation of ethanol–water mixture through S-series membranes at 30°C (Feed: 5 wt % aqueous ethanol).
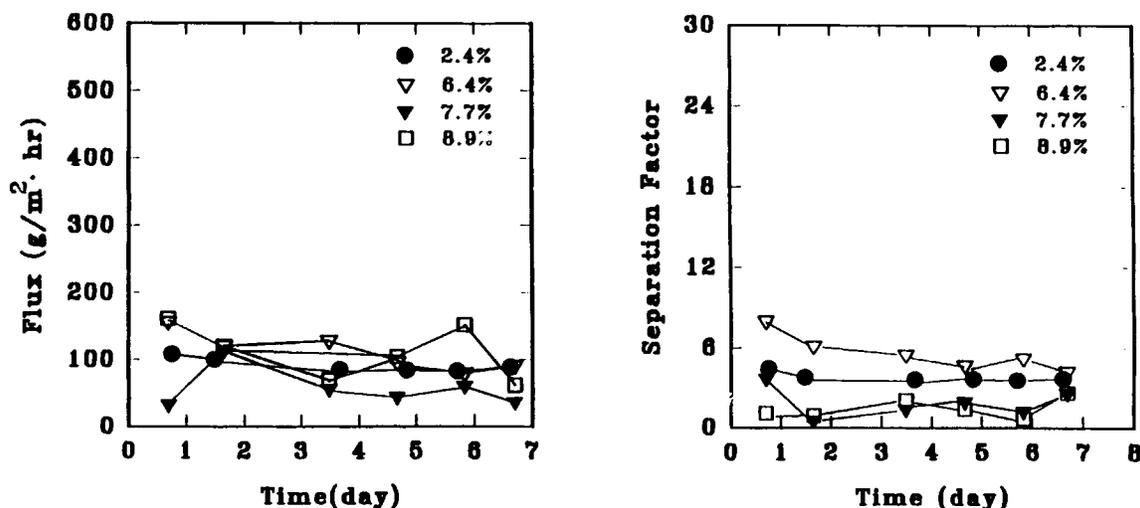
Figure 5   Total flux and separation factor vs. time in the pervaporation of ethanol–water mixture through X-series membranes at 30°C (Feed: 5 wt % aqueous ethanol).

According to the density data in Table I, the S series have more free volume than the I or X series and consequently are expected to have higher flux. However, the S series do not show higher fluxes than the I or X series. This implies that PDMS molecules, in the S-series membranes, fill into the PTMSP phase's free volume and swell the membrane. Although the free volume of the PTMSP phase has been mostly occupied by PDMS, the overall free volume possibly could still be enhanced because the uncrosslinked PDMS phase adds its own free volume as well as swells the PTMSP phase's.

X Series

Figures 4 and 5 compare the transport properties of the S- and X-series membranes. The X-series membranes are prepared by crosslinking PDMS-sorbed membranes with VTAS. The high density of the X-series vs. S-series membranes indicates that the free volume of the X series would be less than the S series. As expected, both the flux and separation factor of the X series are lower than the S series and the former's pervaporation properties do not change over time.

crosslinking (X series). The I and X series have higher density and consequently lower free volume than the S series. The measurement of density and glass transition temperature demonstrates that PTMSP and PDMS are partially mixed in the I-series membranes. The flux and separation factor decrease from 600 to 200 g/m^2 h, and from 13.7 to 7.3, respectively, in the I series. However, the transport behavior of the S and X series remains more steady with time. In particular, the addition of 1 wt % of PDMS made the PTMSP membrane's properties steady with time. The transport properties of the composite membranes are lower than PTMSP but are higher than PDMS. The sorption method appears to be a good means to prevent flux decay, but the resulting flux is low compared to that of the initial, fresh PTMSP membrane. Therefore, new membrane preparation methods should be further studied to make the transport properties of fresh PTMSP steady with time.

CONCLUSIONS

Three different attempts were made to retard and/ or prevent the physical aging of PTMSP by incorporating PDMS: (1) semi-IPN (I series), (2) PDMS sorption (S series), and (3) PDMS sorption and

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