

Effect of Preparation Parameters on Performance of Dense Homogeneous Polycarbonate Gas Separation Membranes

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ABSTRACT: The aim of this study is to determine the effect of preparation parameters on the membrane permeation mechanism and separation performances of dense homogeneous poly(bisphenol A carbonate) (PC) membranes. Blade-casting and drop-casting techniques are used for casting films from solutions with varying concentrations. Chloroform and methylene chloride are used to determine the effect of the properties of the casting solvent. Permeation measurements are done with Ar, N₂, O₂, CH₄, CO₂, and H₂ gases. The selectivity values of dense homogeneous membranes with a PC composition of 7% (w/v chloroform) are 1.7 for Ar/N₂, 1.1 for CH₄/N₂, 18 for CO₂/N₂, 26 for

H₂/N₂, and 9.7 for O₂/N₂. These values with a PC composition of 15% (w/v methylene chloride) are 2.7, 1.3, 25, 44, and 13 for the same gases, respectively. In addition to the importance of the solvent type and composition, the casting type and thermal history also affects the performance of the membrane. Increasing the annealing period enhances the selectivity while decreasing the permeability for both casting solvents, yet this thermal history effect strongly depends on the solvent type because of solvent-polymer interactions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 776–785, 2003

Key words: gas separation; membranes; polycarbonate

INTRODUCTION

The development of membranes for the separation and purification of gases based on the selective permeation of one or more components of a mixture has attracted considerable interest during the last decade, and modifications in the physical and chemical structures of polymer films have been made to achieve better separation characteristics.^{1,2} This interest is fueled by the potential economic advantages of membrane separation technologies.³ Identifying new membrane materials and morphologies for industrial separations has become an important research objective.^{4–7}

The membrane structure may determine the separation mechanism and hence the application; thus, membrane morphology is one of the most important parameters that affects performance.⁸ A dense homogeneous polymeric membrane has the simplest morphology, which is composed of a nonporous, dense, single polymer layer that is homogeneous in all directions. Therefore, it is the simplest and most suitable structure to investigate different polymers and the effect of chemical modification; yet, even for this simple morphology, the fabrication protocol may influence the membrane properties.^{9–11} The properties of the solvents used in preparing polymer solutions, the

solution concentration, the surface (glass, steel, teflon, etc.) on which the membrane is cast, the casting techniques (drop casting, blade casting), the casting temperature, and the annealing temperature and period are the factors that may affect the membrane morphology and separation performance. The literature on membranes includes only a few studies related to the effects of these preparation parameters on the separation performance of dense homogeneous membranes. In many studies the values of most of these parameters, especially the polymer concentrations, were not even reported.^{12–14}

Joly et al.¹⁴ investigated the effects of the type of residual solvent remaining after fabrication on the permeation properties of 6FDA-*m*PDA polyimide films. These films were prepared by dissolving polyimide at a concentration of 150 g/L in *N*-methyl pyrrolidone (NMP), *N,N'*-dimethylacetamide (DMAc), tetrahydrofuran (THF), dichloromethane, and dioxane and testing for N₂ and CO₂ permeabilities. Joly et al.¹⁴ concluded that the diffusion coefficient decreases with the decrease in residual solvent, whereas the permeability and solubility coefficients increase. The permeability coefficients for films treated for 90 min are smaller than for films treated for 2880 min, regardless of the solvent used. This could be attributed to the polymer plasticization by the solvent, which facilitates the movements of polymer segments. Another observation is that the interactions of the solvent molecules with the permeant are dependent on the nature of the gas. The solvents with a high molar volume leave

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TABLE I
Permeability Data for Dense Homogenous Flat Sheet PC Membranes

Permeability (barrer)						Preparation Parameters	Reference
N ₂	O ₂	CO ₂	CH ₄	H ₂	Ar		
0.28	1.48	7.01	0.29	—	—	Lexan PC film operated at 1 atm and 35°C	23
0.21	1.17	—	—	—	0.549	Lexan PC knife cast with methylene chloride (10–15% w/v PC) operated at 1 atm and 25°C	20
0.29	1.4	—	—	—	0.8	Uplion S-2000 PC	26
0.29	1.9	—	—	—	—	Cast with methylene chloride	21
—	—	8.0	0.30	—	—	Lexan 131-111 PC operated at 1 atm and 35°C	27
0.24	1.5	—	—	—	—	Uplion S-2000 PC knife cast with chloroform (8% w/v PC)	28
0.25	1.0	—	—	—	—	Uplion S-2000 PC knife cast with methylene chloride lexan PC film	29
0.255	—	6.65	—	—	—	Annealed at 125°C for 2 h	30
0.26	—	6.75	—	—	—	Annealed at 125°C for 7 days, operated at 4 atm and 35°C	
0.289	1.484	6.0	0.257	—	—	Operated at 1 atm and 35°C	31
0.33	1.6	6.8	0.358	—	—	Operated at 1 atm and 35°C	32
0.93	2.4	—	—	—	—	Uplion S-2000 PC knife cast with methylene chloride evaporated at 25°C for 1 h	33
0.30	—	8.5	0.32	—	0.6	Lexan PC Operated at 1 atm and 35°C	34
0.28	2.0	8.0	0.34	—	—	Lexan PC operated at 5 atm and 35°C	35
0.38	1.6	6.8	0.36	—	—	Lexan 8800-112 PC operated at 2 atm and 35°C	36
0.28	1.48	7.5	0.33	—	—		37
0.30	1.40	8.0	—	12	0.8	Lexan PC resin operated at 25°C	38

1 barrer = 10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹.

imprints during thermal treatment and N₂ is more sensitive to different casting solvents.

Khulbe et al.¹⁵ worked with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) membranes prepared by using the 2% (w/v) solvents carbon disulfide, benzene, 1,1,2-trichloroethylene, toluene, chlorobenzene, and bromobenzene. They reported that the permeability increased and the selectivity (O₂/N₂ and CO₂/CH₄) decreased with the increase in the boiling points of the solvents. In addition, they observed that the surface tension and viscosity of the solvents used for casting the PPO dense membrane affect the performance of the membrane and the state of the polymer in the membrane depends on the type of the solvent used for casting.

Robeson et al.¹⁶ investigated poly(trimethylsilylpropyne) (PTMSP) membranes that show surprisingly high permeability values. Hexane, toluene, THF, chloroform, and chloroform/acetonitrile were the solvents used for the casting solution. During the experiments they observed an increasing trend in the permeability of PTMSP as a function of the solubility parameter of the casting solvent. The poor solvents result in higher permeabilities whereas the selectivities showed only slight differences.

Moe and coworkers¹⁷ studied the effects of film history on gas transport in a fluorinated aromatic polyimide. They concluded that the residual DMAc solvent present in the films produces complexities in the permeation behavior of helium and carbon dioxide. The CO₂ permeabilities were higher and those of helium were lower in a film containing 8 wt % residual DMAc than in an annealed film containing <1 wt % DMAc. Significant differences in the performance of the membranes were also observed between films prepared using the blade-casting and drop-casting techniques.

In this study dense homogeneous membranes of poly(bisphenol A carbonate) (PC) were prepared because of its commercial availability and suitability for investigating preparation parameters. The permeability values of various gases were reported for dense homogeneous PC membranes in numerous studies,^{17–19,21–35} and these are listed in Table I. The reported values for some gases differ significantly. Only a few of these differences may be attributed to the difference in gas permeation measurement parameters such as the temperature, pressure, and differences between commercial types of PC. Probably most of them are caused by the differences in the membrane prepara-

tion parameters such as the type and concentration of the casting solvent, the solvent evaporation temperature and period, and the annealing temperature and period. Unfortunately, in many studies, these values were not even reported. Therefore, we decided to investigate these parameters to find the reasons for the differences in the permselectivities and to understand the importance of different preparation parameters on the performance of dense homogeneous membranes. In addition to gas permeation measurements to understand the effects of the residual solvent and thermal history on the membrane performance, thermal gravimetry analysis (TGA) and mass spectrometry (MS) were used.

EXPERIMENTAL

The PC was purchased from Aldrich, and it has a glass-transition temperature (T_g) of 150°C and a molecular weight of 64,000. The two solvents that were used, chloroform and methylene chloride, were also purchased from Aldrich. All of the chemicals were analytical grade and were used without further purification. Argon, CH₄, CO₂, H₂, N₂, and O₂ were used in the measurements of pure gas permeabilities and were obtained from local companies.

Dense homogeneous flat sheet PC membranes were prepared by using two different casting techniques. Membranes were prepared by simply pouring a solution of PC on the surface of a glass plate and allowing it to dry in an oven at a preadjusted temperature for a specific time (100°C for 10–30 min). Then the film was removed from the surface of the glass plate and further annealed at a preadjusted temperature for different periods (50°C for 8–154 h). In the blade-casting technique, films were obtained by automatic casting on a glass plate at a specific thickness as described previously.^{2,18,20} The casting solution was obtained by dissolving PC in chloroform (CH₃Cl) and methylene chloride (CH₂Cl₂) in different compositions (3–15%, w/v). The final thicknesses of the membranes were in the range of 30–50 μm.

The apparatus used in the determination of the permeability coefficients of single gases was according to ASTM D 1435-82, and the measurements were carried out using a constant volume, variable pressure technique in a permeation cell.^{2,18,20} The penetrant gas taken from the gas cylinder flowed into the gas tank at around 40 psig while the low-pressure side is at atmospheric pressure. A permeating gas flowing into the permeate side increased the pressure that was transmitted to a data acquisition board by a pressure transducer, and pressure versus time data were recorded by a computer. Prior to each measurement, both high- and low-pressure purge valves were opened and the membrane cell was degasified by applying a vacuum.

TABLE II
Permeability Data for Dense Homogenous Flat Sheet PC Membranes

Gas	Permeability (barrer)			
	1st Run	2nd Run	3rd Run	4th Run
Ar	0.60	0.59	0.58	0.58
CH ₄	0.34	0.33	0.33	0.33
CO ₂	5.65	5.54	5.53	5.52
H ₂	8.64	8.35	8.13	7.86
N ₂	0.26	0.25	0.24	0.23
O ₂	2.92	2.76	2.59	2.44

The PC is 7% PC/CH₃Cl dried at 100°C for 30 min and annealed at 50°C for 24 h.

The permeabilities of the gases were evaluated using eq. (1), which is a combined form of Fick's and Henry's laws.

$$J_i = P_i \Delta P / \delta \quad (1)$$

where J_i is the flux, P_i is the permeability, ΔP is the pressure difference across the membrane, and δ is the thickness of the membrane.

The ideal separation factor (σ_{ij}) is determined by using the individual permeation rates of single gases, which is expressed as

$$\sigma_{ij} = P_i / P_j \quad (2)$$

The membranes were analyzed by a Dupont TG analyzer (model 951) to determine the amount of residual solvent. The heating rate was 10°C/min under a N₂ atmosphere. A Hewlett-Packard mass selective detector (model 5973) was used to detect the residual solvent in the membranes.

RESULTS AND DISCUSSION

To check the membrane preparation procedures, the gas permeation setup, and the methodology, a series of reproducibility experiments was carried out. The observed relative error for the permeability of the membranes with the same procedure for different casting times was 3–6%. When the selectivities of this type of membrane were calculated, the relative error was in the range of 6–9%. These results were within the limits of the membrane performance errors found in the literature^{9,10} and the permeability and selectivity values of the same membrane for four runs are tabulated in Tables II and III. When these membranes were retested for their performances after 6 months, reproducible results were obtained and the relative error was also in the range of 3–5%; therefore, no aging effect was observed. It is important to have long-term stability for the membranes, and these

TABLE III
Selectivity for N₂ Data for Dense Homogenous Flat Sheet PC Membranes

Gas	$\alpha (X/N_2)$			
	1st Run	2nd Run	3rd Run	4th Run
Ar	2.34	2.39	2.41	2.43
CH ₄	1.33	1.35	1.39	1.40
CO ₂	22.0	22.3	22.6	23.1
H ₂	33.6	33.5	33.3	33.3
O ₂	11.3	11.1	10.6	10.2

The PC is 7% PC/CH₃Cl dried at 100°C for 30 min and annealed at 50°C for 24 h.

membranes showed this stability after a long period of time.

With a PC concentration of 7% (w/v) chloroform,²⁰ the first parameter that was examined in this study was the evaporation period. The cast films were allowed to dry at 100°C for 10 and 30 min and no annealing was applied to these membranes. The results of the permeability and selectivity measurements are tabulated in Table IV, and the membranes that were allowed to dry for 10 min have slightly higher selectivities and slightly lower permeabilities. Some loosening in the membrane structure was observed for the latter gas permeation runs with the same membranes. When the period of the solvent evaporation was further increased, the membranes became fragile and fractured, so no permeation measurement could be carried out.

The investigation was continued by studying the effects of the annealing temperature and the period. For the annealing step we decided to decrease the temperature to 50°C because of fracture formation when long solvent evaporation periods were used. Annealing was applied at this temperature and workable membranes were obtained (8-h annealing). Table V shows that membranes that were allowed to dry for 10 min followed by 8-h annealing have lower selectivities than the ones that were not annealed (Table IV). In contrast, when membranes dried for 30 min were annealed for the same period, the selectivity values of

TABLE IV
Permeability and Selectivity Data for Unannealed Dense Homogenous Flat Sheet PC Membranes.

Gas	Permeability (barrer)		$\alpha (X/N_2)$	
	10-min 1st Run	30-min 1st Run	10-min 1st Run	30-min 1st Run
Ar	0.74	0.74	2.51	2.00
CH ₄	0.43	0.41	1.50	1.10
CO ₂	7.50	8.06	22.7	21.9
H ₂	9.21	11.1	29.5	30.1
N ₂	0.33	0.37	—	—
O ₂	3.35	4.24	11.7	11.5

The PC is 7% PC/CH₃Cl dried at 100°C for 10 and 30 min.

TABLE V
Selectivity Data for Annealed Dense Homogenous Flat Sheet PC Membranes as Function of Evaporation Time

Gas	$\alpha (X/N_2)$			
	10-min 1st Run	10-min 2nd Run	30-min 1st Run	30-min 2nd Run
Ar	2.03	2.00	2.32	2.22
CH ₄	1.03	1.03	1.35	1.29
CO ₂	19.7	19.5	22.1	20.8
H ₂	24.6	26.1	33.3	30.6
O ₂	9.1	9.79	9.61	9.54

The PC is 7% PC/CH₃Cl dried at 100°C for 10 and 30 min and annealed at 50°C for 8 h. for 10 and 30 min and annealed at 50°C for 8 h.

these membranes increased. This observation also shows that the effect of annealing on the separation performance is a function of the solvent evaporation period. When the performance values of further gas permeation runs with the same membrane were measured, the loosening of the membrane continued.

The above preliminary experiments and few other studies exist in the literature.^{19,28,33} In order to see the effects of further annealing on the membrane performance, the membranes were annealed for 24, 72, and 154 h. The permeabilities of H₂ and CO₂ [Fig. 1(a)] and Ar, CH₄, and N₂ [Fig. 1(b)] gases for different annealing periods are shown in Figure 1. The permeabilities were decreased when the annealing was continued for 72 h; after this period, the permeabilities almost remained constant, even after 154 h. The ideal selectivity values show the same behavior, but an increase was observed with further annealing (Table VI). The trends in the permeabilities and the selectivities are more evident with H₂ and CO₂. The former has the smallest kinetic diameter and the latter may interact with the membrane. Another effect of increasing the annealing period is that the loosening of the membrane ceases after 24-h annealing, and the permeability and selectivity values stay constant for the latter runs (Tables II, III).

The other important parameter that was investigated in this study was the casting solution composition. To see the effects of the PC composition on the membrane separation performance, we cast 3, 5, 7, 8.5, 10, 12, and 15% (w/v) PC on a glass plate by the drop-casting technique. For membranes with 10, 12, and 15% PC composition, workable membranes could not be obtained with this method. The thickness of the films could not be arranged by the drop-casting method; with higher concentrations, we obtained thicker films that fractured. This problem was solved by using an automatic film applicator during casting. Additionally, to compare the two methods, a casting solution composition of 7% was used and no differences were observed for the permeability and selectivity values

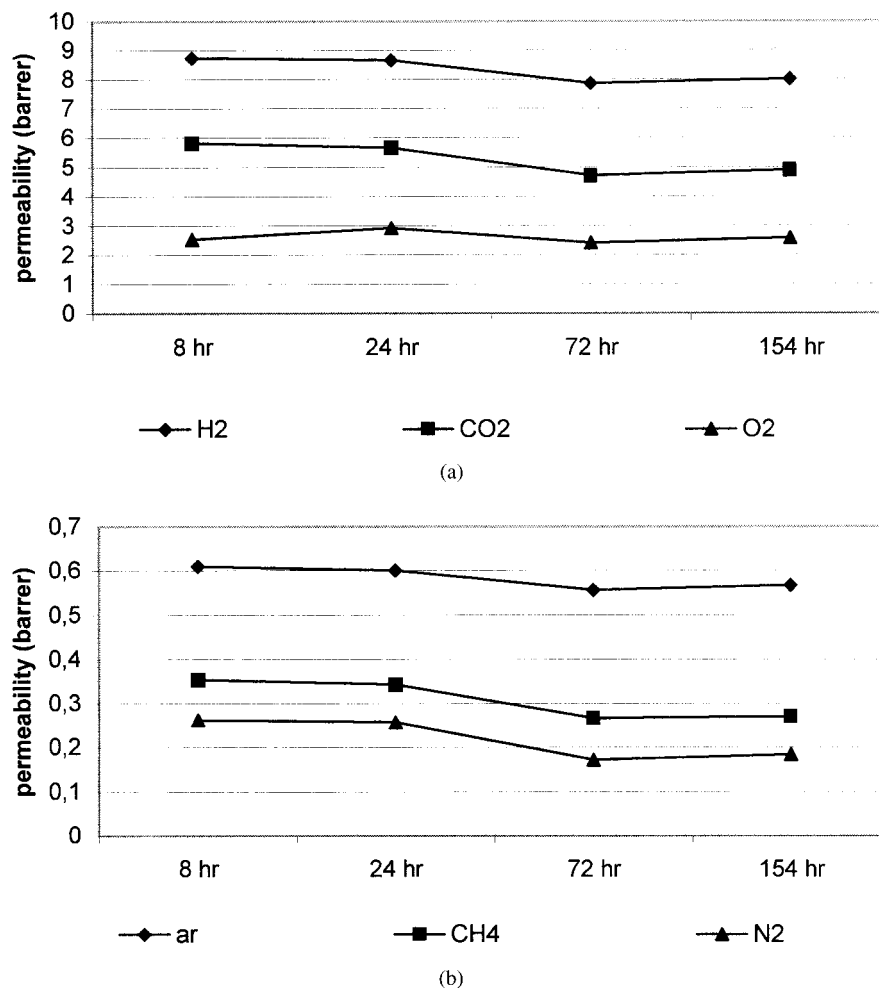


Figure 1 The permeabilities of (a) H₂, CO₂, and O₂ and (b) Ar, CH₄, and N₂ at various annealing periods for 7% PC dried at 100°C for 30 min and annealed at 50°C.

(Table VII). The blade-casting method is not a suitable method for lower concentrations because of the less viscous behavior of the solution; thus, a 7% PC composition was the only one that could be used for a comparison of the two casting techniques. This result indicates that the use of different casting methods did not affect the transport properties for dense homoge-

neous PC membranes prepared under these specific conditions.

As Figures 2(a,b) reveals, the permeabilities significantly decrease as the PC composition is increased, a trend that is observed for all gases. By increasing the

TABLE VI
Selectivity for N₂ Data for Dense Homogenous Flat Sheet PC Membranes

Gas	$\alpha (X/N_2)$			
	8 h	24 h	72 h	154 h
Ar	2.32	2.34	3.23	3.06
CH ₄	1.35	1.33	1.55	1.46
CO ₂	22.1	22.0	27.3	26.4
H ₂	33.3	33.6	45.7	43.3
O ₂	9.61	11.4	13.9	13.8

The PC is 7% PC/CH₃Cl dried at 100°C for 30 min and annealed for different periods.

TABLE VII
Permeability and Selectivity Data for Dense Homogenous Flat Sheet PC Membranes Cast by Two Techniques

Gas	Permeability (barrer)		$\alpha X/N_2$	
	Drop Cast	Knife Cast	Drop Cast	Knife Cast
Ar	0.60	0.61	2.34	2.46
CH ₄	0.34	0.34	1.33	1.36
CO ₂	5.66	5.67	22.0	22.8
H ₂	8.65	8.50	33.6	35.2
N ₂	0.26	0.25	—	—
O ₂	2.92	2.90	11.4	11.6

The PC is 7% PC/CH₃Cl dried at 100°C for 30 min and annealed at 50°C for 24 h. for 30 min and annealed at 50°C for 24 h.

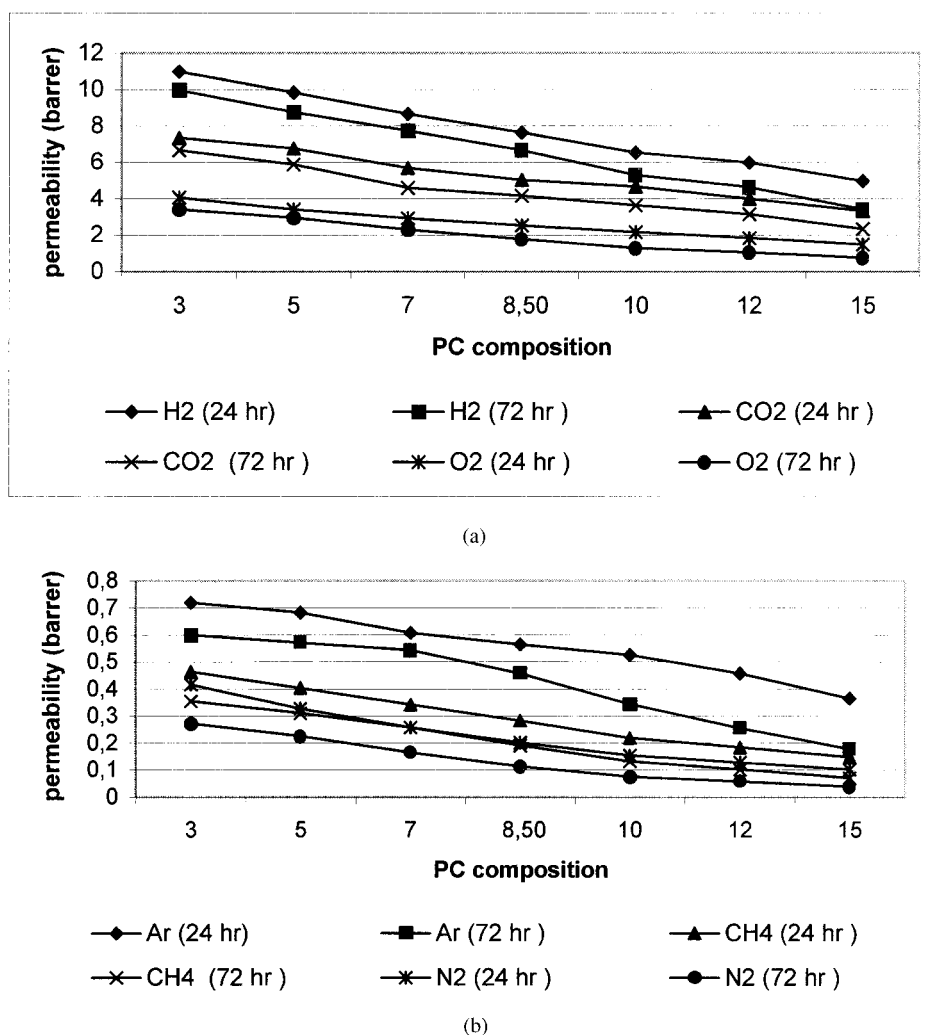


Figure 2 The permeabilities of (a) H₂, CO₂, and O₂ and (b) Ar, CH₄, and N₂ at various PC compositions dried at 100°C for 30 min and annealed at 50°C for 24 and 72 h.

annealing period from 24 to 72 h for all compositions, the same trend is observed for the permeability values; but this time the permeabilities are lower compared to the 24-h annealed ones. When the selectivities of these membranes are considered (Table VIII), they increase with the increasing PC composition and the ones annealed longer have the highest selectivities. A possible reason for this change in the selectivities and permeabilities may be that increasing the PC composition and annealing period leads to denser structures and the amount of solvent evaporated affects the imprinted structure left behind. The effect of the casting solution composition on the performance is a very important observation; and, to our knowledge, no information relating to this effect on membrane performance was previously reported.

To investigate the effect of the solvent-polymer interaction, methylene chloride (CH₂Cl₂) was used as the second solvent. The effect of annealing was first investigated on the membranes prepared in methyl-

TABLE VIII
Selectivity Data for Dense Homogenous Flat Sheet PC Membranes for Different PCs Cast with Chloroform

Gas	$\alpha (X/N_2)$						
	3%	5%	7%	8.5%	10%	12%	15%
Ar							
24 h	1.72	2.07	2.34	2.79	3.44	3.57	3.59
72 h	2.19	2.54	3.31	4.05	4.58	4.64	4.71
CH ₄							
24 h	1.11	1.23	1.33	1.41	1.43	1.44	1.46
72 h	1.31	1.38	1.57	1.69	1.76	1.81	1.88
CO ₂							
24 h	17.6	20.6	22.0	24.9	30.3	31.3	32.5
72 h	24.9	26.4	28.0	36.9	48.5	55.0	61.2
H ₂							
24 h	26.3	30.0	33.6	37.8	42.6	46.7	48.6
72 h	36.7	38.9	47.1	58.8	70.3	81.0	89.4
O ₂							
24 h	9.74	10.4	11.4	12.6	14.2	14.4	14.6
72 h	12.6	13.1	14.0	15.8	17.1	18.3	19.7

The PC is dried at 100°C for 30 min and annealed for 24 and 72 h.

TABLE IX
Permeability Data for Dense Homogenous Flat Sheet PC Membranes for Different PCs Cast with Methylene Chloride

Gas	Permeability (barrer)						
	3%	5%	7%	8.5%	10%	12%	15%
Ar							
24 h	0.35	0.34	0.33	0.32	0.31	0.31	0.30
72 h	0.34	0.33	0.32	0.31	0.31	0.30	0.29
CH ₄							
24 h	0.24	0.22	0.20	0.18	0.17	0.16	0.14
72 h	0.23	0.21	0.19	0.17	0.16	0.15	0.13
CO ₂							
24 h	3.60	3.49	3.36	3.22	3.10	2.97	2.85
72 h	3.37	3.25	3.09	2.95	2.84	2.67	2.56
H ₂							
24 h	5.78	5.61	5.42	5.25	5.08	4.92	4.82
72 h	5.43	5.26	5.12	4.92	4.72	4.58	4.46
N ₂							
24 h	0.19	0.18	0.16	0.15	0.14	0.12	0.11
72 h	0.18	0.16	0.15	0.13	0.12	0.11	0.09
O ₂							
24 h	2.05	1.94	1.85	1.74	1.62	1.50	1.41
72 h	1.92	1.80	1.70	1.52	1.48	1.35	1.25

The PC is dried at 50°C for 30 min and annealed at 50°C for 24 and 72 h.

ene chloride and the separation performance experiments were done with 8-, 24-, 72-, and 154-h annealing periods. The solvent evaporation temperature had to be lowered to 50°C when methylene chloride was used to prevent an excessively rapid removal of the solvent. The permeability and selectivity values showed the same trend for all gases, but this time the effect of the annealing period was much lower when this solvent was used. This observation indicates that the effect of the thermal history on the transport properties strongly depends on the casting solvent.

The casting solution composition was also examined with the membranes cast from a solution of methylene chloride and PC. The permeability and corresponding selectivity values are given in Tables IX and X, respectively. Note that the ones cast from a solution of chloroform have higher permeabilities [Fig. 3(a)] and higher selectivities [Fig. 3(b)] than the ones where methylene chloride is used as the solvent. When chloroform is used as the solvent, the permeabilities of the CO₂ gas show a decrease with respect to an increasing PC composition; in addition, the corresponding selectivities of CO₂/N₂ show an increase whereas the performance of the ones cast from methylene chloride are found to be only slightly affected by the composition change. For higher compositions the permeability and selectivity values approach each other. The same trends in separation performance were observed for all the other gases under study.

Chloroform is known as the theta solvent of PC, and its boiling point is 61.15°C and its molar volume is 85

TABLE X
Selectivity Data for Dense Homogenous Flat Sheet PC Membranes for Different PCs Cast with Methylene Chloride

Gas	α (X/N ₂)						
	3%	5%	7%	8.5%	10%	12%	15%
Ar							
24 h	1.76	1.87	2.01	2.14	2.28	2.49	2.78
72 h	1.84	1.95	2.10	2.34	2.42	2.60	2.97
CH ₄							
24 h	1.20	1.22	1.23	1.23	1.23	1.27	1.30
72 h	1.23	1.20	1.25	1.29	1.30	1.34	1.34
CO ₂							
24 h	18.4	19.2	20.2	21.0	22.1	23.8	25.9
72 h	18.4	19.2	20.3	22.2	22.4	23.8	26.4
H ₂							
24 h	29.5	30.8	32.6	34.3	36.3	39.3	43.8
72 h	29.7	31.1	33.7	36.9	37.2	40.8	45.9
O ₂							
24 h	10.4	10.7	11.1	11.4	11.6	12.0	12.8
72 h	10.5	10.7	11.2	11.4	11.7	12.1	12.9

The PC is dried at 50°C for 30 min and annealed at 50°C for 24 and 72 h.

m³/mol whereas the boiling point of methylene chloride is 44°C and its molar volume²⁵ is 64 m³/mol. This shows us that the interactions of the solvent molecules with the permeant are dependent on its physical properties, which may strongly affect the separation performance of the membranes.

One other possibility may be the special property of chloroform, which is that it can form hydrogen bonds with the matrix polymer. The chains in the membrane matrix may stay far away from each other because of these hydrogen bonds. When further annealing was applied, the matrix becomes rather free of solvent molecules and the chains tend to come nearer, leading to a permeability decrease with an increasing annealing period. This is not valid for methylene chloride,

TABLE XI
Permeability Data for Dense Homogenous Flat Sheet PC Membranes

Gas	Chloroform			Methylene Chloride		
	3%	7%	12%	3%	7%	12%
Ar						
P (barrer)	0.37	0.36	0.35	0.36	0.39	0.33
CH ₄						
P (barrer)	0.15	0.14	0.13	0.14	0.13	0.12
CO ₂						
P (barrer)	3.60	3.46	3.33	3.49	3.35	3.24
H ₂						
P (barrer)	5.18	5.02	4.85	5.11	4.94	4.82
N ₂						
P (barrer)	0.11	0.10	0.09	0.11	0.09	0.09
O ₂						
P (barrer)	1.61	1.48	1.35	1.55	1.43	1.34

The PC is dried at 180°C for 30 min. P, permeability.

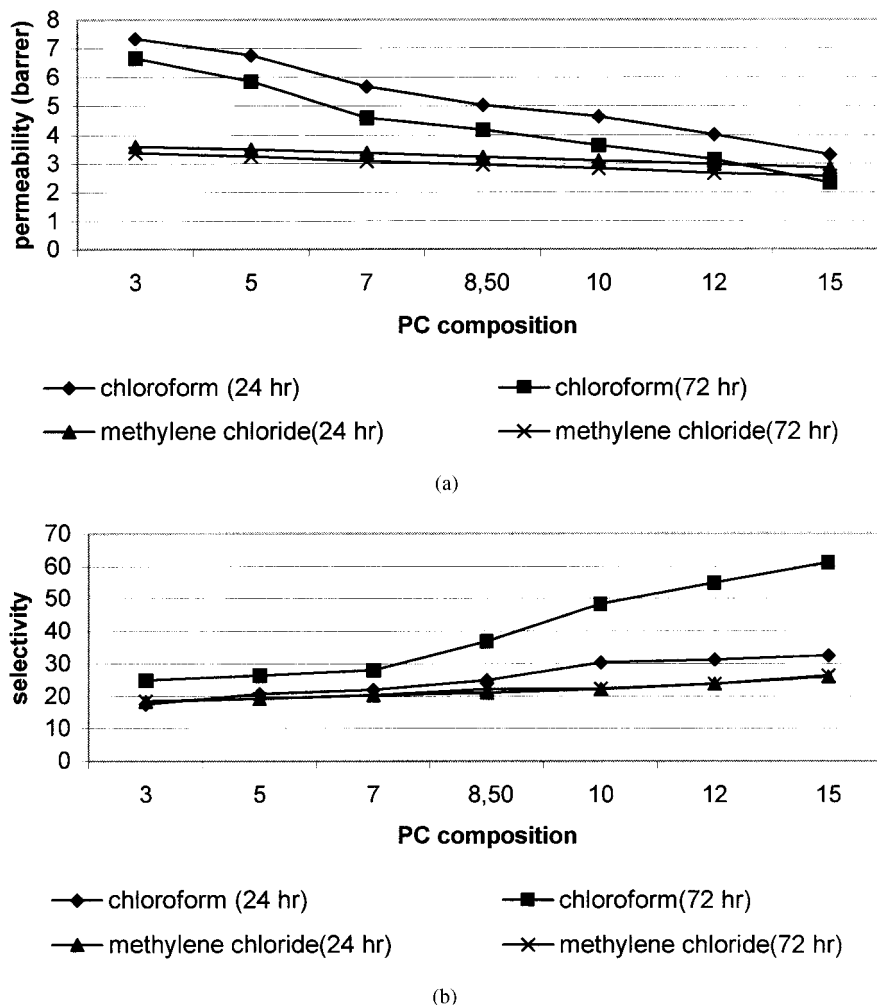


Figure 3 The (a) permeabilities and (b) selectivities of CO₂ for membranes cast with different solvents at various PC compositions dried at 100 and 50°C for 30 min and annealed at 50°C for 24 h.

and the permeability and selectivity results support this idea.

To investigate the effect of the solvent type and composition on the membrane performance when evaporation is carried out above the $T_{g'}$, we prepared membranes with different solvent types and compositions by drying them at 180°C for 30 min. The permeability results given in Table IV clearly show that, when the films were dried above the $T_{g'}$, the solvent type and composition have no effect on the membrane performance. The observed permeabilities are much lower compared to the literature values and to the values obtained when an interacting solvent (chloroform) was used with a sub T_g film formation temperature. Because the membrane is formed above the $T_{g'}$, chains would have time to relax and pack more closely; therefore, a much denser structure would form and lower permeabilities were observed.

In order to understand the importance of the effect of the solvent, membranes in which no solvent was used were selected for comparison. PC pellets were

directly pressed and membranes with higher thicknesses (100 μm) were obtained. The permeability and selectivity values of these membranes are given in Table XII. When compared with the previously cast ones, the membranes with higher compositions tend to behave similar to the pressed ones. From this observation it is concluded that the effect of the type of the solvent is less important at high polymer compositions.

TABLE XII
Permeability and Selectivity for N₂ Data for Dense homogenous Flat Sheet PC Membranes

Gas	Permeability (barrer)	α (X/N ₂)
Ar	0.39	3.54
CH ₄	0.16	1.49
CO ₂	3.73	34.2
H ₂	4.46	48.1
N ₂	0.11	—
O ₂	1.63	14.9

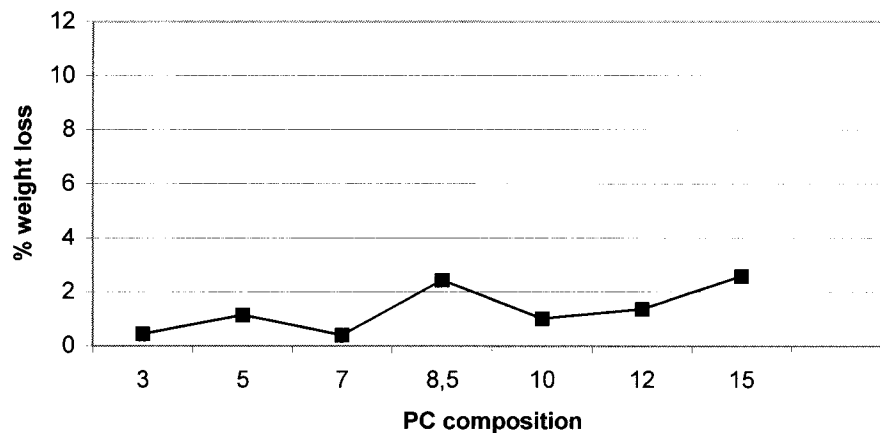


Figure 4 The percentage weight loss from TGA thermograms as a function of the annealing period for 7% PC cast with chloroform and dried at 100°C and annealed at 50°C.

From the separation performance of the membranes, we observed that the type and composition of the solvent strongly affects the permeation mechanism. To investigate whether any solvent remained in the membrane matrix, TGA measurements were done for all types of membranes. The TGA thermograms show that the weight losses are in the range of 0.5–3% at the examined temperature, but there is no direct correlation of these with the permeabilities and selectivities as seen in Figure 4. There is also no direct relationship between the degree of plasticization attributable to the residual solvent and the transport properties. Therefore, the structures formed after solvent evaporation and annealing strongly determine the performance of these membranes.

In addition, in order to be sure whether these losses are due to solvent molecules, MS was used and chloroform peaks were determined. These results show that the solvent molecules are captured in the membrane matrix; and, although these molecules are found in very small amounts, they strongly affect the membrane performance. The TGA thermograms also show that the weight loss begins at the glass-transition temperature of the PC. At this temperature the chains begin to relax and solvent molecules can easily leave the matrix.

When the separation performance is compared with the values found in the literature (Table I), some values are within the range; however, some are much lower or higher because of the different preparation procedures. The selectivities and permeabilities could be modified by changing the solvent evaporation temperature or period, the annealing temperature or period, and the casting solution composition. Thus, the separation performance values strongly support this observation and the results of the studies on the membranes in which no solvent was found and the ones that were annealed above the T_g are other confirming evidence. The films obtained from different solution

casting compositions show different permselectivities but similar trends according to their casting solvents, which is due to the different interactions occurring between the membrane matrix and the solvent molecules.

CONCLUSION

The permeation and separation performances of PC membranes are examined in relation to different preparation parameters. The formation of the final structures of the membranes vary according to their thermal history, casting type, and casting solvent; thus, their transport properties are also affected by these parameters.

The solvent evaporation temperature and period were the parameters investigated in prior studies. We concluded that annealing should be applied for membranes that do not show loosening of the structure. The other impressive observation is that the effect of annealing on the performance is a function of the drying period.

The second parameter was the annealing period. Increasing this period enhanced the selectivities till a point (72 h) where they became stable. Because of the interaction between the solvent molecules and the matrix, similar thermal histories can result in different membrane performance.

The other important parameters examined were the PC composition (w/v) in the casting solution and the solvent used to dissolve the polymer. The permeabilities showed a decrease whereas the selectivities increased with the increasing PC composition. When the results of the membranes that have different residual solvents in their matrix were compared, we observed that the performance depended on the physical properties of the solvents. A higher molar volume and higher boiling point result in higher permeabilities. In addition, specific interactions like hydrogen bonding

may also occur between the solvent molecules and the membrane matrix.

The casting solvent is yet another important factor to determine the transport properties, especially if an interaction occurs in the matrix. Thus, solvent-free membranes were compared with the ones cast from solution. The permeability and selectivity values of these membranes were close to the membranes that have the highest polymer composition. Drying and annealing above the T_g can destroy the imprints of the structure. Even if the casting solvents and the compositions of the membranes were different, the performance values were very similar. The TGA and MS studies show that the solvent molecules cannot be totally eliminated and a small amount of residual solvent may strongly affect the membrane.

Long-range permeability measurements show that the values remain constant after a 6-month period. This is a striking point in the sense that the effect of the solvent and membrane thermal history on the permselectivity performance is still valid even after 6 months. The imprints left in the matrix and the chain structure formation throughout the preparation period strongly affect the transport properties.

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