

CO₂ Selectivity of a new PDMS/PSf Membrane Prepared at Different Conditions

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Abstract

Effect of water/solvent mixtures as coagulation medium with differing solvent content, coagulation bath temperature (CBT) and different coagulants on the gas permeation performance of polysulfone (PSf) membrane were investigated. The CO₂/CH₄, H₂/CO₂ and CO₂/N₂ separation performance of membranes were studied by a constant pressure gas permeation experimental set up. The PSf membrane prepared at the CBT of 25°C (10-45°C range) showed the best gas separation performance with ideal selectivities of 43.9 and 39.8 for CO₂/N₂ and CO₂/CH₄, respectively, and permeance of 21.5 GPU for CO₂ at P=10bar. By increasing of the DMAc solvent into the gelation bath, ideal selectivities of CO₂/CH₄ and CO₂/N₂ have been reduced dramatically from 39.8 to 12.6 and 43.9 to 14.5, respectively at T=25°C and P=10bar. Using methanol as a coagulant resulted in less selective membrane compared with ethanol and water. But, the H₂ and CO₂ permeances were about 3 and 9 times more than those of ethanol and water coagulants, respectively. The coated membranes were given different heating temperature to investigate the suppression of undesirable CO₂ plasticization. The membranes were stabilized against CO₂ plasticization after heat-treatment process.

Keywords: Polysulfone; PDMS/PSf membrane; Synthesis parameters; CO₂ separation

Introduction

Membrane separation has been the technology of interest in the natural gas sweetening. They have also been used in the removal of CO₂ in landfill gas recovery processes and removal of CO₂ in enhanced oil recovery applications (EOR). At present, natural gas is a vigorous energy and it is also produced in large quantity and it often contains excess CO₂. The content of CO₂ must be diminished to meet the pipeline specification, i.e., 2mol% or less [1]. It was reported that separation processes using asymmetric polymeric membranes assist in the reduction of CO₂ concentration for upgrading low-quality natural gas [2,3]. Hydrogen can be used as one of the promising sources of energy for space heating, electric power generation, and transportation fuel. These potential uses have resulted in a huge increase in hydrogen demand. Separation of hydrogen from nitrogen in ammonia purge gas streams was the first large-scale commercial application of membrane gas separation. The process, launched in 1980 by Monsanto, was followed by a number of similar applications, such as hydrogen/methane separation in refinery off-gases [4]. The other major current application of H₂ separation membranes is the separation of hydrogen from methane in ammonia plants. During the production of ammonia from nitrogen and hydrogen, methane enters the reactor as an impurity with the hydrogen. So the methane impurity accumulates until it represents as much as 15% of the gas in the reactor. To control the concentration of these components, the reactor must be continuously purged. The hydrogen lost with this purge gas can represent 2-4% of the total hydrogen consumed. These plants are very large, so recovery of the hydrogen for recycle to the ammonia reactor is economically worthwhile. Hence it is crucial to use a membrane system for recovery of hydrogen from an ammonia plant purge gas stream. It is also worth noting that hydrogen recovery has been among the first commercial applications of membranes in the field of gas separation [5]. Coated membranes are increasingly fascinating due to their advantages such as: use of highly permeable polymers, high permeation flux and cost-effectiveness when the materials are costly and ease of being made defect free. Coated membrane comprised of

a sealing layer and separation film meets these requirements. Besides this, coated membrane provides a flexible approach of membrane compared with integrally skinned asymmetric membrane. This is due to the fact that the material of its coated layer is often different from the separation film [6]. Traditionally, coated membrane is prepared by dip-coating a suitable selective membrane with a thin layer of polymer functioning as the sealing layer [6-8]. Polydimethylsiloxane (PDMS) is the most commonly used rubbery membrane material. Its glass transition temperature (T_g) is among the lowest values recorded for polymers (-123°C) indicating a very flexible polymer backbone with long-range segmental motion [9]. PSf was selected because of its satisfactory gas permeabilities and acceptable permselectivities, and widespread use as a commercial polymer. Its relative low cost and mentioned properties established polysulfone (PSf) as the choice for use as a proper glassy polymer for the fabrication of CO₂ or H₂ separation membrane [10]. Marchese et al. [11] showed that composite membranes with appropriate H₂ separation performance can be obtained by flooding for a short time (1 min) the surface of an asymmetric polysulfone membrane with a solution of 6% Sylgard 182 in cyclohexane. They achieved the ideal separation factors of 43.24 and 34.04 for H₂/N₂ and H₂/CH₄, respectively. Peng et al. [12] reported that the permeance of hydrogen through PDMS/PSf composite membranes was fairly good (62.94 GPU) and the selectivities of H₂/N₂ and H₂/CH₄ are 22 and 20.4, respectively which is less than the ideal selectivity illustrated in the literature. Moreover, Ahn et al. [13] have shown a remarkable enhancement in H₂ gas permeability of polysulfone (11.8

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to 22.7 barrer) by introducing nonporous nanosized silica particles in the matrix of PSf membrane. They achieved to the selectivity of 33.88, 36.61 for H₂/N₂ and H₂/CH₄, respectively. Recently, Weng et al. [14] prepared nanocomposite membranes using MWCNTs with PBNPI as the polymer matrix. They extended this approach and demonstrated that at high MWCNTs concentrations, the permeabilities of H₂ and CH₄ improved significantly from 4.71 to 14.31 and from 0.7 to 1.78 barrer, respectively and they also cited that the selectivity of H₂/CH₄ reached to 8.04. Shao et al. [15] fabricated cross-linked organic-inorganic reverse-selective membranes containing poly(ethylene oxide) (PEO) in situ by using functional oligomers (O,O'-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol: Jeffamine® ED-2003) with a high content of PEO and epoxy-functional silanes (3-glycidyloxypropyltrimethoxysilane: GOTMS). They reported that the organic-inorganic hybrid membrane with 90 wt% of ED-2003 demonstrates an appealing CO₂ permeability of 367 Barrer with an attractive CO₂/H₂ selectivity of 8.95 at 3.5 atm and 35°C. Shao et al. [16] also studied the cross-linking effects using the same diamine and examined the separation performance of resultant 6FDA-durene and Matrimid membranes. They inferred that, for Matrimid membranes, the diamino cross-linking enhances the selectivity of H₂/CO₂, H₂/N₂ and O₂/N₂, and decreases the CO₂/CH₄ selectivity. Shao et al. [17] modified polyimide membranes by using of 1,3-cyclohexanebis(methylamine) (CHBA) as a new cross-linking agent and thermal annealing. They observed that thermal annealing not only improves CO₂/CH₄ selectivity of the cross-linked membranes but also greatly enhances the plasticization resistance by the formation

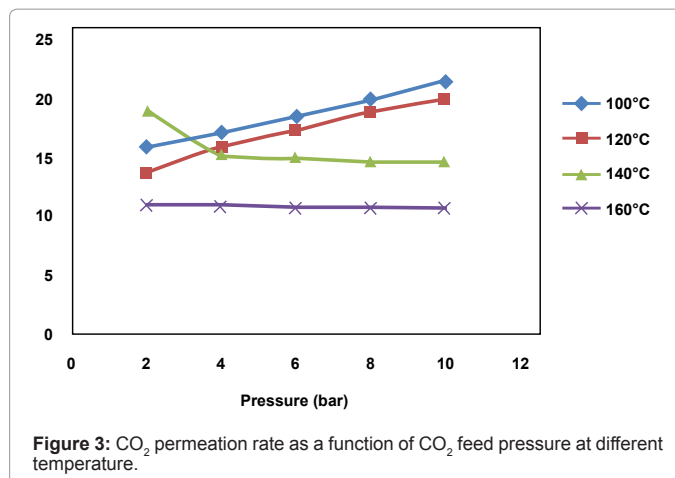


Figure 3: CO₂ permeation rate as a function of CO₂ feed pressure at different temperature.

of charge transfer complexes (CTCs). Shao et al. [18] employed 6FDA-durene as a polymeric precursor to study the properties of membranes from polymeric, to intermediate and further to carbon stages. They found that the maximum permeability for light gases (H₂, He and CO₂) occurs in the carbon stage (around 550°C), which is due to the accelerated decomposition and pore evolution and the maximum permeability for medium gases (O₂, N₂ and CH₄) happens in the intermediate stage (around 475 °C), which should be attributed to the increased chain mobility around the high T_g.

In this study, CO₂/CH₄, CO₂/N₂ and H₂/CO₂ (instead of H₂/CO) selectivities dependence of the PSf membrane to the coagulant type was studied, for the first time. Ideal selectivities of H₂/CO₂, CO₂/CH₄ and CO₂/N₂ were obtained after coating of PSf by PDMS.

Experimental

Materials and module

Polysulfone (PSf(Ultrason-6010)) was supplied by BASF Corporation as polymer for preparation of the membrane casting solutions. Commercially available DMAc (99.5% purity) and tetrahydrofuran (THF) (99% purity) were used as solvents without further purification. The organic non-solvents used are methanol (MeOH) (99.85% purity), ethanol (EtOH) (99.5% purity), and deionized water which were purchased from Merck. n-hexane (as solvent with purity 99%) were supplied by Merck. PDMS (viscosity 5000mPa s), tetraethylorthosilicate (TEOS as crosslinker with purity 98%), dibutyltin dilaurate (DBTDL as catalyst with purity 98%) were also purchased from Beijing Chemical Company, China. Hydrogen, carbon dioxide, nitrogen and methane were purchased from Union Carbide with high purity (99.99%) and used in the pure gas permeation experiments. The dead-end membrane cells made from stainless steel (grade 316) were used to carry out the experiments. The schematic view of manufactured membrane module is shown in Figure 1. The membranes were housed in the cells that consisted of two detachable parts. Rubber O-rings were used to supply a pressure-tight seal between the membranes and the cells. The membranes had an effective area of approximately 15.7 cm² totally.

Membrane preparation

Asymmetric polysulfone flat sheet membranes were prepared by casting solution generally consisted of polysulfone (polymer), DMAc (less volatile solvent), tetrahydrofuran (THF) (more volatile solvent) and ethanol (EtOH) (non-solvent). Casting was performed at 298

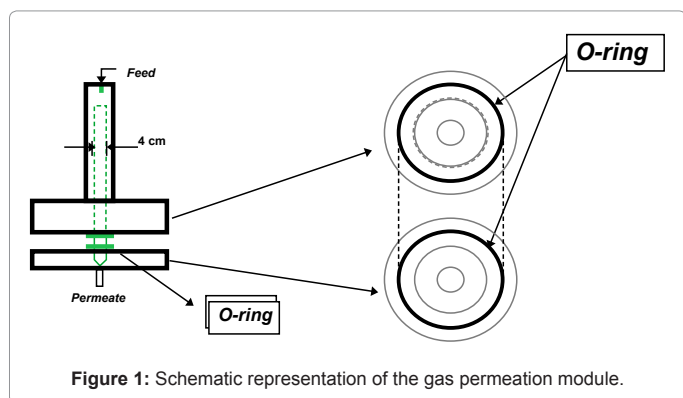


Figure 1: Schematic representation of the gas permeation module.

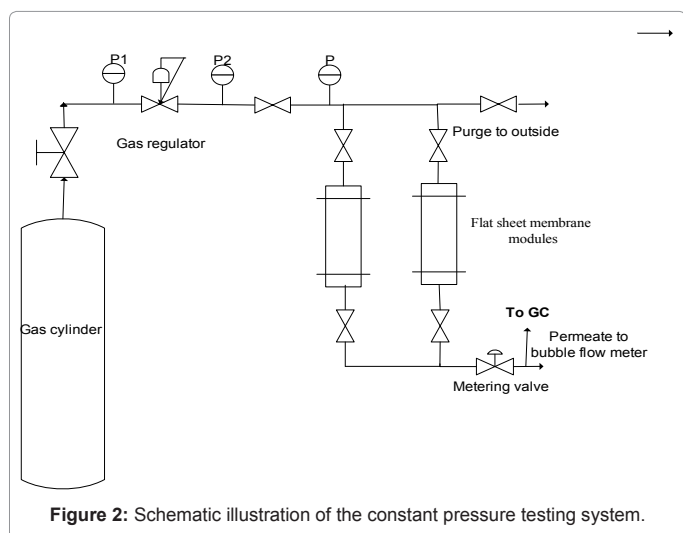


Figure 2: Schematic illustration of the constant pressure testing system.

K in air using a film extender. Membranes were cast at a designated wet thickness (200µm) onto a glass plate. Then, forced-convective evaporation was induced by blowing an inert nitrogen gas stream across membrane surface for 20s before immersion in a coagulation bath and then immediately immersed in the coagulant bath (immersion precipitation method). The water in the membrane was further replaced with ethanol by immersing the membrane for 24 h in aqueous solutions of ethanol with progressively higher ethanol concentrations. Four solutions with different ethanol contents of 25, 50, 75 and 100 vol. % were prepared for this purpose. Then the membrane was immersed in hexane for 24 h in order to extraction of ethanol before it was air dried.

Coating: PDMS, crosslinking agent TEOS, and catalyst DBTDL were mixed in n-hexane for 30 min at 70°C under stirring according to a 10/1/0.2 weight ratio. Prior to casting, the prepared asymmetric PSf membrane was put on the surface of water in a basin. Excess water was wiped off quickly with a filter paper. Then the coating solution was cast on the PSf membrane impregnated with deionized water and these membranes were put under a hood overnight in order to eliminate the solvent by evaporation at ambient temperature. Then the coated membrane was treated for 60 min at 100-160°C in a vacuum oven to complete the crosslinking and reduction of undesirable plasticization effects caused by CO₂ molecules.

Gas permeation measurement

As shown in Figure 2, a constant pressure system was used

Gelation bath composition	Permeance (GPU ^a)			Selectivity	
	CO ₂	CH ₄	H ₂	CO ₂ /CH ₄	H ₂ /CO ₂
0 vol.% DMAC, 100 vol. wt% deionized water	21.5	0.54	25	39.81	1.16
40 vol. % DMAC, 60 vol. % deionized water	10.25	0.36	12.1	28.47	1.18
80 vol.% DMAC, 20 vol. wt% deionized water	5.01	0.27	6.2	18.56	1.24
90 vol.% DMAC, 10 vol. wt% deionized water	2.90	0.23	3.7	12.61	1.28

Temperature: 25°C, feed pressure: 10 bar
^aGPU = 10⁻⁶ cm³ (STP) / (cm² s cmHg)

Table1: Gas permeance and CO₂/CH₄ and H₂/CO₂ selectivities of PDMS/PSf composite membranes (different gelation bath composition).

Gelation bath composition	Permeance (GPU ^a)		Selectivity
	CO ₂	N ₂	CO ₂ /N ₂
0 vol.% DMAC, 100 vol. wt% deionized water	21.5	0.49	43.88
40 vol. % DMAC, 60 vol. % deionized water	10.25	0.34	3015
80 vol.% DMAC, 20 vol. wt% deionized water	5.01	0.25	20.04
90 vol.% DMAC, 10 vol. wt% deionized water	2.90	0.20	14.50

Temperature: 25°C, feed pressure: 10 bar
^aGPU = 10⁻⁶ cm³ (STP) / (cm² s cmHg)

Table2: Gas permeance and CO₂/N₂ selectivity of PDMS/PSf composite membranes (different gelation bath composition).

CBT	Permeance (GPU ^a)		Selectivity
	CO ₂	N ₂	CO ₂ /N ₂
5°C	15.5	0.59	26.27
25°C	21.5	0.49	43.88
50°C	18.5	0.97	14.55
80°C	16.0	1.1	14.55

Temperature: 25°C, feed pressure: 10 bar
^aGPU = 10⁻⁶ cm³ (STP) / (cm² s cmHg)

Table 3: Gas permeance and CO₂/N₂ selectivity of PDMS/PSf composite membrane using deionized water as coagulant (different CBT).

CBT	Permeance (GPU ^a)			Selectivity	
	CO ₂	CH ₄	H ₂	H ₂ /CO ₂	CO ₂ /CH ₄
5°C	15.5	0.63	20.5	1.32	24.6
25°C	21.5	0.54	25	1.16	39.81
50°C	18.5	1.1	22.8	1.23	16.82
80°C	16	1.6	21	1.31	10.00

Temperature: 25°C, feed pressure: 10 bar
^aGPU = 10⁻⁶ cm³ (STP) / (cm² s cmHg)

Table 4: Gas permeance and CO₂/CH₄ and H₂/CO₂ selectivities of PDMS/PSf composite membrane using deionized water as coagulant (different CBT).

Coagulant	Permeance (GPU ^a)			Selectivity	
	CO ₂	CH ₄	H ₂	H ₂ /CO ₂	CO ₂ /CH ₄
Deionized water	21.5	0.54	25	1.16	39.81
Ethanol	62.35	2.05	71	1.14	30.41
Methanol	189.2	8.09	217.5	1.15	23.39

Temperature: 25°C, feed pressure: 10 bar
^aGPU = 10⁻⁶ cm³ (STP) / (cm² s cmHg)

Table 5: Gas permeance and CO₂/CH₄ and H₂/CO₂ selectivities of PDMS/PSf composite membranes (different coagulants).

Coagulant	Permeance (GPU ^a)		Selectivity
	CO ₂	N ₂	CO ₂ /N ₂
Deionized water	21.5	0.49	43.88
Ethanol	62.35	1.97	31.65
Methanol	189.25	7.94	23.83

Temperature: 25°C, feed pressure: 10 bar
^aGPU = 10⁻⁶ cm³ (STP) / (cm² s cmHg)

Table 6: Gas permeance and CO₂/N₂ selectivity through PDMS/PSf composite membranes (different coagulants).

Membrane type	Permeance or permeability				Selectivity	Ref.
	CO ₂	CH ₄	N ₂	H ₂	H ₂ /CO ₂ , CO ₂ /N ₂ , CO ₂ /CH ₄	
Silicone-coated PSf	6.85 ^a	0.47 ^a	0.37 ^a	16	2.34, 18.52, 14.57	[11]
PDMS/PSf	---	3.09 ^b	2.87 ^b	62.94 ^b	-----, -----, -----	[12]
PSf/Silica (85/15 vol.%)	12.9 ^a	0.62 ^a	0.67 ^a	22.7 ^a	1.76, 19.25, 20.81	[13]
PBN/PI (15 wt.%)	---	1.78 ^a	---	14.31 ^a	-----, -----, -----	[14]
Present work	21.5 ^b	0.54 ^b	0.49 ^b	25 ^b	1.16, 43.88, 39.81	

^abarrer (10⁻¹⁰ cm³ (STP)cm/cm² s cmHg)
^bGPU

Table 7: A comparison between the present work and the other studies.

for H₂, CO₂, N₂ and CH₄ gases permeance experiments using an upstream pressure 10 bar while the downstream pressure was effectively atmospheric. Gas permeation tests were performed with two permeation cells. The experiments were performed after a period of equilibration of 30 min. The permeate volumetric flow rate was measured by means of a soap bubble flowmeter reading to 0.05 and 1 cm³. In case of flat-sheets, membrane cells with area of 15.7 cm² were used. The downstream side was always purged with the test gas prior to the permeation measurement. The permeance (*P*/*L*) and selectivity ($\alpha_{(A/B)}$) were calculated viz.

$$\left(\frac{P}{L}\right)_i = \frac{Q_i}{A \times \Delta p_i} \quad (1)$$

$$\alpha_{(A/B)} = \frac{(P/L)_A}{(P/L)_B} \quad (2)$$

Where *Q_i* is volumetric flow rate of gas *i* at permeate outlet at standard temperature and pressure, Δp is the transmembrane pressure difference, and A is the membrane active surface area.

Results and Discussion

Effect of the gelation bath solvent content

Table 1 and Table 2 show the effect of DMAc concentration in the coagulation bath on the permeance of hydrogen, methane, carbon dioxide and nitrogen gases and H₂/CO₂, CO₂/CH₄ and CO₂/N₂ ideal selectivity of prepared membranes at 10 bar. The results denote a general decline in gas permeances with an increase in concentration of the solvent in the coagulation bath. It can be found that the decrease in gases permeance of membrane commensurate with kinetic diameter of gas molecules. In other words, gases with larger kinetic diameter experience less decrease in permeance with the increase of solvent content. In addition, as shown in Table 1 and Table 2, single gas permeances of CH₄ and N₂ through PDMS/PSf composite membrane are far lower than those of H₂ and CO₂ owing to their weak adsorption affinity and slow diffusion compared with H₂ and CO₂ molecules [19]. Increasing of the solvent into the gelation bath is more complex for CH₄ and N₂ permeances: in the first case the solvent tends to increase surface defects that causes to increase the permeation of CH₄ [20,21]. Additionally, solvent causes to delayed demixing mechanism which decrease highly the number of finger voids and eventually tends to decrease the gas permeances. Wijmans et al. [22] and Reuvers et al. [23] similarly, observed which adding of solvent in the coagulation bath prevents the formation of a skin layer and some finger like pores can reach to the surface. So with declining of skin layer, ideal selectivity will be also diminished. As reported in Table 1 and Table 2 by increasing of the solvent into the gelation bath, ideal selectivities of CO₂/CH₄ and H₂/N₂ have been reduced from 39.81 to 12.61 and 43.88 to 14.5, respectively.

Effect of coagulation bath temperature (CBT)

The influence of the coagulation bath temperature on the flat separation performances were also investigated. Table 3 and Table 4 show gas permeances and ideal selectivity of H₂/CO₂, CO₂/CH₄ and CO₂/N₂ for PDMS/PSf membranes fabricated at the different gelation bath temperatures. Comparing the selectivity data obtained from the prepared membrane at the different coagulation temperature (5–25°C) revealed that H₂ and CO₂ gas permeances slightly increase while CH₄ and N₂ gas permeances decrease. In contrast, CH₄ and N₂ gas permeances increased while H₂ and CO₂ permeances decreased for the membranes which prepared at CBT of 25–80°C. Hence, the permeance of low-sorbing penetrant (H₂), which do not plasticize the composite PDMS/PSf membrane is higher than CH₄ and N₂ gas permeances which this phenomenon can be due to the following facts; The solubility of hydrogen, nitrogen and methane in PDMS/PSf composite membrane is very low. According to the solution–diffusion theory, the experimental results illustrate that the gas permeation process through the composite membranes is dominantly controlled by the diffusivity of those gases in the membranes. However, the diffusion of those gases (hydrogen, nitrogen and methane) is determined by the diameter of gas molecular. The diameter of gas molecular is the smallest, so the diffusivity is the largest [24]. Therefore, permeance of hydrogen is higher than those of nitrogen and methane. Regarding the depicted data in Table 3, Table 4, it can be interpreted that the membranes prepared at the coagulation bath temperatures of 25°C exhibit optimum CO₂/N₂ and CO₂/CH₄ separation performance if the possible defects of the dense layer in polysulfone substrate can be filled well through coating a PDMS layer (optimum CBT may be 10 to 45°C).

Influence of coagulant type

The gas permeances and the average selectivities of H₂/CO₂, CO₂/

CH₄ and CO₂/N₂ for the membranes prepared in the water, ethanol and methanol coagulation bath are shown in Table 5 and Table 6 (each test was repeated for 5 times and average value has been presented). By comparing the data depicted in these tables, one can see that using of methanol as a coagulant resulted in less selective membranes (23.39 and 23.83 for CO₂/CH₄ and CO₂/N₂ selectivities) compared with ethanol (30.41 and 31.65) and water (39.81 and 43.88), while the average H₂ and CO₂ permeances were about 3 and 9 times more than those of ethanol and water coagulants, respectively. This rising trend can be interpreted as follows: The gas transport properties of PDMS/PSf membrane is strongly associated with a substantial change of free volume (i.e., quantity of nanospace) caused by changing of coagulants. Ultimately, more spacious pathways and an increase in total free volume from both inefficient chain packing density and the presence of void volume, results in increases in diffusion coefficient and thus leading to the increase in permeance [25]. Considering the results in Table 5 and Table 6, the similar trends in permeances of CH₄ and N₂ gases of membranes made by coagulant water (15 and 16 times less than methanol, respectively) can be attributed to the combinatory effects the configuration changes in the polymeric structure of membranes. A question may arise why the gas permeances of membrane made by water coagulant is less than those of ethanol and methanol. It is worthwhile to mention that the effect of water coagulant on gas permeance decay of membrane is probably due to the tighter interstitial spaces among the chains and restriction in vibration and mobility of polymer chains. As a result, diffusion of penetrant gas molecules through the membrane is hindered and gas permeances decrease. In agreement with a similar report [26], a declining trend is observed for the CO₂/CH₄ and CO₂/N₂ selectivities of membranes made by ethanol and methanol coagulants compared with water as shown in Tables 5 and 6. We also believe that with increasing boiling points of coagulants water (100°C) > ethanol (78.1°C) > methanol (64.7°C), the amounts of macrovoids, free volume, defects and permeances of H₂, CO₂, CH₄ and N₂ reduce in different level in a such way that the CO₂/CH₄ and CO₂/N₂ selectivities and the thickness of effective skin layer increase. Table 7 summarizes a comparison between the present work and the other studies presented in the published earlier articles for evaluation of membrane performance. However, in most of them, it can be said that the CO₂/CH₄ and CO₂/N₂ selectivities in the present study is higher than those of previously reported in the literature [11–14]. Furthermore, the comparatively higher selectivities of CO₂/CH₄ and CO₂/N₂ than those of reported in the literature might be due to the determination of the appropriate parameters in synthesis of defect free composite membrane.

Suppression of plasticization by heat-treatment technique

Plasticization is the major problem faced by CO₂-selective polymeric composite membrane which is a pressure-dependent phenomenon. The increase in gas permeance of a membrane with increasing feed gas pressure is attributed to CO₂-induced plasticization of the polymer matrix [27]. This plasticizing action of CO₂ decreases the ability of the membrane to separate molecules on the basis of size, thereby causing the reduction in selectivity.

One of the important and simple methods to suppress CO₂ plasticization and achieve better composite membrane performance is heat-treatment technique which is caused a densification of the polymer matrix and results in a reduction of chain mobility and simultaneously prevents the membrane plasticization. The PDMS/PSf composite membranes developed in this study were given various heating temperatures (100–160°C) in order to investigate the possibilities of suppressing CO₂ plasticization.

From Figure 3, the CO₂ permeation rate of treated membranes at 100 and 120°C still show an increase up to 10 bar feed pressure because the polymer chains possess an enhanced mobility after exposure to CO₂ molecules. However, these heat treatments are considered not sufficient to prevent plasticization completely. At 140 and 160°C permeance of CO₂ slightly decrease with increasing pressure. When the permeances as a function of feed pressure do not increase anymore, which implies a suppression of the chain flexibility, one can define such method as successful [28]. Therefore, these treatments were efficient in stabilizing the membrane material.

Conclusions

The effect of different water/solvent ratio as coagulation medium, CBT and different coagulation medium on the gas separation property of polysulfone membranes has been successfully investigated. The results indicated that the CO₂/CH₄, CO₂/N₂ and H₂/CO₂ ideal selectivities and the H₂, CO₂ permeances decreased by the increasing of concentration of the solvent in the coagulation bath. The membranes prepared at the CBT of 25°C (10-45°C range) showed the best CO₂/CH₄ and CO₂/N₂ ideal selectivities about 39.81 and 43.88, respectively. With increasing boiling points of coagulants, CO₂/CH₄ and CO₂/N₂ ideal selectivities increased while the gas permeances were decreased. The membranes were stabilized against CO₂ plasticization by giving the membranes a treatment of 140-160°C.

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