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Effect of Synthesis Parameters on Structural Characteristics of Polysulfone Membrane and its Gas Separation Properties

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Abstract

In this study the effects of water/solvent mixture as coagulation medium with different solvent content, coagulation bath temperature (CBT) and coagulant type on the performance, morphology and thermal stability of polysulfone membranes were investigated. SEM and TGA techniques were used to characterize the fabricated membranes. Based on the obtained SEM images, decreasing of water/N,N-dimethyl acetamide (DMAc) ratio as coagulation medium from pure water to mixture of 90 vol.% DMAc and 10 vol.% water, resulted in completely disappearing of macrovoids. Gas permeation test results showed that by addition of solvent into the coagulation bath, H_2/CH_4 and H_2/N_2 selectivities (permselectivities) reduced dramatically from 46.3 to 16.1 and 51.0 to 18.5, respectively. By the way, reducing the CBT from 80°C to 5°C led to elimination of macrovoids as well as attaining high thermal stability. As an interesting result, the membrane prepared at the CBT of 25°C showed the best gas separation performance with permselectivities of 46.3 and 51.0 for H_2/CH_4 and H_2/N_2 respectively, and H_2 permeance of 25 GPU. Using methanol as coagulant resulted in less selective membrane compared with those prepared using ethanol and water. On the other hand, the H_2 permeance of the former case was about 3 and 9 times more than those prepared using ethanol and water as coagulant, respectively. Obtained membrane with methanol revealed the lower thermal stability than those of ethanol and water.

Keywords: H_2 separation; Polysulfone; Composite membrane; Gas permeation

Introduction

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 [1]. Currently, commercially available separation processes for steam reforming unit are pressure swing adsorption, amine absorption and absorption using aqueous solution of potassium carbonate which are highly energy intensive [2-4]. Membrane separation technology is a simple and low-energy method and has received global attention as a promising technology for gas separation and purification. It is also worthy noting that hydrogen recovery has been among the first commercial applications of membranes in the field of gas separation [5]. It should be noted that hydrogen is a small molecule and non-condensable gas, which is highly permeable compared to all other gases. This is particularly true for glassy polymers primarily used to make hydrogen - selective membranes. Since, gas diffusion coefficient decreases with an increase in penetrant molecule size [6], differences in molecular size can result in different gas permeation rates through polymers. In comparison with pure polymers, composite (coated) membranes have individual advantages such as: high permeation flux with the selectivity of the base polymer. Coated membranes comprised of a thin coating layer and support substrate. Composite membrane provides a flexible approach of membrane fabrication compared with integrally skinned asymmetric membranes. This is due to the fact that the material of its separation layer is often different from the substrate [7]. Traditionally, composite membrane is prepared by dip-coating a suitable substrate with a thin layer of polymer [7-9]. Since, PDMS is the most commonly used rubbery membrane material; it was used as coating layer. Its glass transition temperature is among the lowest values recorded for polymers (−123°C) indicating a very flexible polymer backbone with long-range segmental motion [10]. PSf was selected as the base polymer because of its acceptable gas separation performance and its widespread use as a commercial polymer. The relative low cost of PSf and its mentioned properties established it as the choice for using as a proper glassy polymer for the fabrication of H_2 separation membrane [11].

Marchese et al. [12] showed that composite membranes with appropriate H_2 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 H_2/N_2 and H_2/CH_4, respectively. Peng et al. [13] reported that the permeance of hydrogen through PDMS/PSf composite membranes was fairly good (62.94 GPU) and the selectivities of H_2/N_2 and H_2/CH_4 are 22 and 20.4, respectively which is less than the ideal selectivity illustrated in the literature. Moreover Ahn et al. [14] have shown a remarkable enhancement in H_2 gas permeability of polysulfone (from 11.8 to 22.7 barrer) by introducing nonporous nanosized silica particles in the matrix of PSf membrane. They attained the 33.88 and 36.61 for H_2/N_2 and H_2/CH_4 selectivities, respectively. Recently, Weng et al. [15] 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 H_2 and CH_4 improved significantly from 4.71 to 14.31 and 0.7 to 1.78 barrer, respectively. They also cited that the selectivity of H_2/CH_4 reached to 8.04.

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One of the main objectives of this study is to investigate the effect of coagulation bath temperature (CBT) on the morphology of PSf membrane and the focus is on the CBT in which the macrovoids are disappeared. As a new work, the best solvent/coagulant ratio in which macrovoids disappear was also inspected. In this study, the dependency of H_2/CH_4 and H_2/N_2 selectivities of the PSf membrane to the coagulant type was also studied for the first time. Ideal selectivities of H_2/CH_4 and H_2/N_2 were obtained after coating of PSf by PDMS. The new prepared PSf/PDMS composite membranes were characterized by several techniques. To our best knowledge, this is the first study which is focusing on the exploitation of unique effect of different synthesis parameters on the H_2 separation properties of PSf/PDMS composite membrane for the development of specialty membranes for H_2 separation and purification.

Experimental

Materials and membrane module

Polysulfone (PSf-Ultrason-6010) was supplied by BASF Corporation as polymer for preparation of the membrane casting solutions. Commercially available DMAc and tetrahydrofuran (THF) were used as solvents. The applied organic non-solvents were methanol (MeOH), ethanol (EtOH) and deionized water. Methanol and ethanol were purchased from Merck. For the preparation of PDMS solution, n-hexane (as solvent) was supplied by Merck. PDMS (viscosity: 5000 mPa.S), tetraethylorthosilicate (TEOS as cross linker) and dibutyltin dilaurate (DBTDL as catalyst) were also purchased from Beijing

Figure 1: Schematic representation of the gas permeation cell.

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

Chemical Company, China. All liquid solvents were reagent grade and used without further purification. High purity (99.99%) hydrogen, nitrogen and methane gases were purchased from Union Carbide and used in the pure gas permeation experiments. The dead-end membrane cells made from stainless steel were used to carry out the permeation experiments. The schematic view of manufactured membrane cell is shown in Figure 1.

Membrane preparation

Asymmetric flat sheet polysulfone membranes were prepared by casting solution generally consisted of polysulfone (polymer), DMAc (as less volatile solvent), tetrahydrofuran (THF) (as more volatile solvent) and ethanol (EtOH) (as non-solvent). Casting was performed at 298 K in air using a film extender. Membranes were cast at a designated wet thickness of 200μm onto a glass plate. Then, forced-convective evaporation was induced by blowing an inert nitrogen gas stream across the membrane surface for 20 seconds. Prepared samples immediately immersed in the coagulant bath (immersion precipitation method) after evaporation step. After that, the water in the structure of membrane samples was replaced with ethanol by immersing the samples 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. % in water 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. Hexane was removed by simple evaporation.

Composite membrane preparation

To prepare coating solution, PDMS, TEOS as crosslinking agent and DBTDL as catalyst were mixed in n-hexane for 30 min at 70°C under stirring according to 10/1/0.2 weight ratios. Prior to coating, the prepared PSf membranes were put on the surface of water in a basin to act as the support. Excess water was wiped off quickly with a filter paper. Then the coating solution was cast on the PSf membranes impregnated with deionized water and these membranes were put under a laminar air flow cabinet overnight in order to eliminate the hexane by evaporation at ambient temperature. Then the composite membrane was treated for 1 h at 150°C in a vacuum oven to complete the crosslinking. With this technique, mass transfer resistance due to the intrusion of the PDMS solution into the pores of the substrate during fabrication of the composite membrane could be reduced.

Membrane characterizations

Scanning Electron Microscopy (SEM): The membranes were fractured under liquid nitrogen to give a generally consistent and clean break. The membranes were then sputter-coated with thin film of gold. The membranes were mounted on brass plates with double-sided adhesive tape in a lateral position. Cross-sectional images of the membranes were obtained with a CamScan SEM model LEO1450VP microscope.

Thermo Gravimetric Analysis (TGA): Residual solvent was removed from the test films by drying overnight in a vacuum oven at 70°C. The thermal degradation was conducted by thermo gravimetric analysis (Shimadzu TGA-50/50h). About 2 mg of each sample was loaded in a pre-tarred platinum pan and pre-heated above 120°C to remove moisture. After cooling, the sample was reheated from 25 to 800°C at a rate of 3°C/min.

Gas permeation measurement: As shown in Figure 2, a constant pressure system was used for measurement of the permeation of H_2, N_2 and CH_4 gases through prepared membranes. The upstream pressure
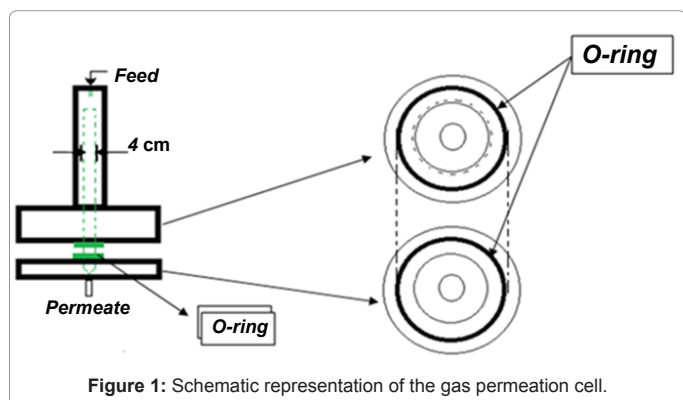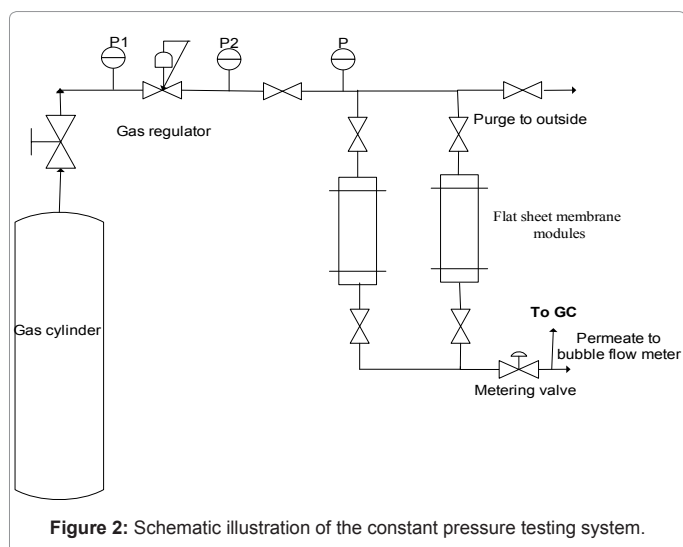
was kept at 10 bar, while the downstream pressure was atmospheric. Gas permeation tests were performed with two permeation cells. The permeation flow rate of each gas was measured by a soap bubble flow meter. It should be noted that the downstream side was always purged with the test gas prior to the permeation measurement.

The permeance (P/ℓ) and selectivity $(\alpha_{A/B})$ of membrane samples were calculated as:

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

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

Where Q_i is volumetric permeation flow rate of ith component at standard temperature and pressure (273 K and 1 bar), Δp_i is the transmembrane partial pressure difference of ith component, and A is the membrane active surface area.

Results and Discussion

Effect of the solvent content of the coagulation bath

The cross-sections of membranes produced from a given casting solution (22 wt.% PSf, 31.8 % DMAc, 31.8 % THF, 14.4 % EtOH) and coagulation baths with varying solvent/water ratios are shown in Figures 3 and 4. As indicated in Figres. 3a to 3d, with increasing the amount of solvent in the coagulation bath, the number of macrovoids in membrane structure decreases. Consequently, the morphology is changed from finger-like to sponge-like structure. As can be seen in Figure 4 (with higher magnification), with increasing the solvent amount in the coagulation bath, the cell size becomes larger. This can be explained as follows: the cells are formed via secondary nucleation and growth mechanism in the polymer-rich phase and growth takes place because of the diffusional flow of solvent from the surrounding polymer solution. A nucleus can only grow if a stable composition is induced in front of it by diffusion. Growth will cease if a new stable nucleus is formed in front of the first formed nucleus. Stropnik et al. [16] presented similar interpretation about cell size variations for several polymeric membranes. The macrovoids are formed via spinodal demixing mechanism and small cells around the macrovoids are formed via secondary nucleation and growth mechanism in the polymer-rich phase [17]. Generally, the formation of macrovoids is a result of the liquid-liquid demixing process, where the nuclei of the polymer-poor phase are also responsible for macrovoid formation. In this way growth of macrovoids occurs and this growth continues until the polymer concentration at the macrovoid/solution interface becomes so high that solidification occurs [18]. In Figure 3c, it can be observed that number of finger-like voids has been decreased considerably. One can see in Figure 3d, finger-like voids have completely disappeared which means that the primary phase separation mechanism is nucleation and growth of polymer-poor phase [16]. In this case, the solidification rate is very slow so that cells can grow and coalesce each other, and results in open and large cellular structure. The surface images of PSf membranes are shown in Figure 5. As can be seen in Figure 5a when pure water was used as coagulant, the surface of the membrane was smooth and there is no pinhole on the membrane surface. On the other hand, in the case of 20/80 mixture of water/DMAc, Figure 5b shows that pores with varying size exist on the membrane surface. The mean pore diameter taken from SEM images is about 112 nm, approximately. Tables 1 and 2 show the effect of DMAc concentration in the coagulation bath on the permeance of hydrogen, methane and nitrogen gases and H_2/CH_4 and H_2/N_2 ideal selectivities of composite 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 the permeance of gases matching 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 Tables 1 and 2,
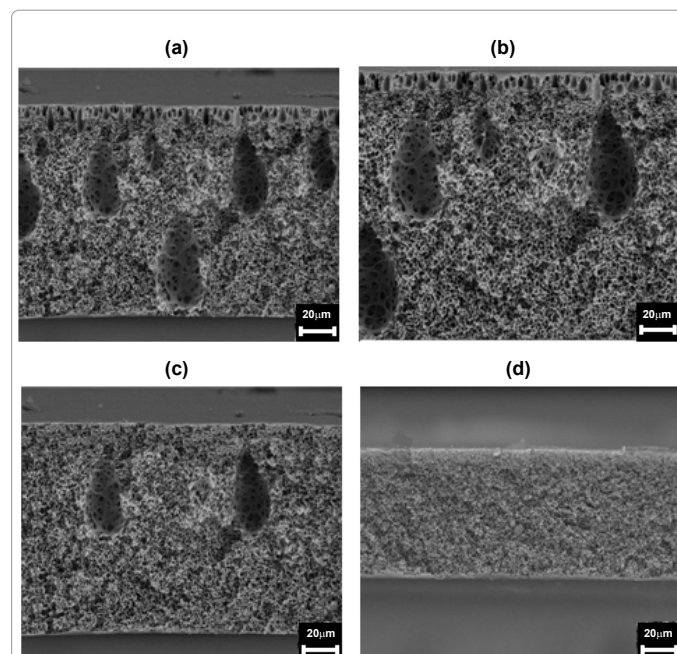

Figure 3: The effect of the solvent concentration in the coagulation bath on membrane structure. Coagulation bath: (a) pure deionized water, (b) 40 vol.% DMAc, (c) 80 vol. % DMAc and (d) 90 vol. % DMAc-10 vol. wt% deionized water.
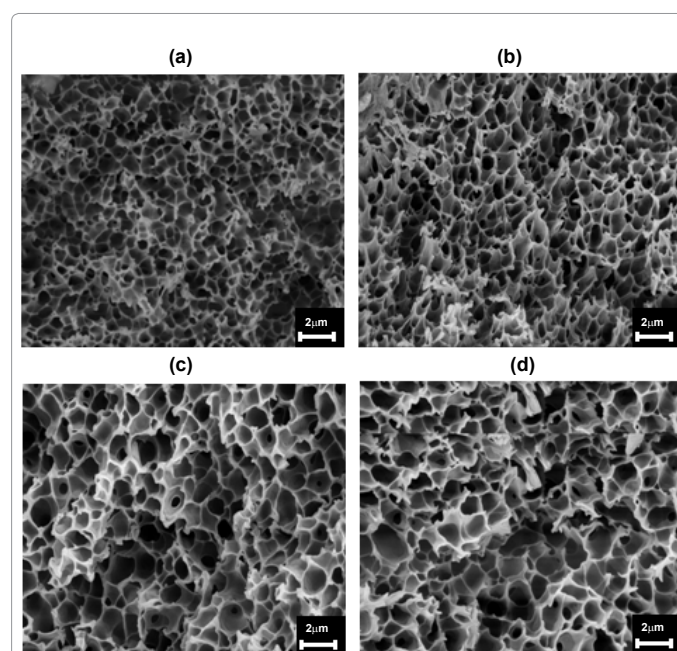

Figure 4: The effect of the solvent concentration in the coagulation bath on membrane structure (with magnification 10000). Coagulation bath: (a) pure deionized water; (b) 40 vol.% DMAc, (c) 80 vol. % DMAc and (d) 90 vol. % DMAc-10 vol. wt% deionized water.
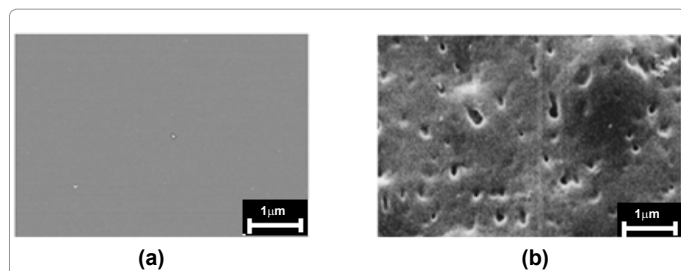
Figure 5: SEM photographs of the surface of PSf membranes. Coagulation bath: (a) pure deionized water (b) 80 vol.% DMAc-20 vol. wt% deionized water.
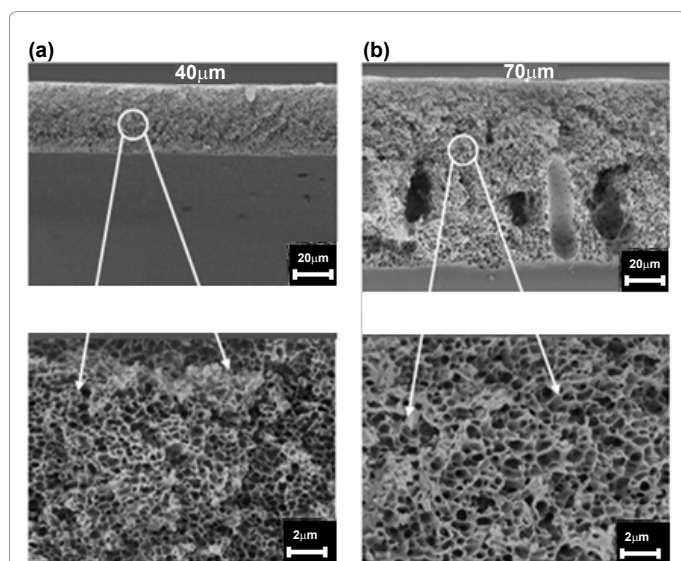

Figure 6: The effect of the coagulation bath temperature on the membrane structure. Coagulation temperature: (a) 5°C, (b) 25°C, (c) 50°C and (d) 80°C.

Gelation bath composition	Permeance (GPU [a])		Selectivity
	H_2	CH_4	H_2/CH_4
0 vol.% DMAc, 100 vol. wt% deionized water	25.0	0.54	46.3
40 vol. % DMAc, 60 vol. % deionized water	12.1	0.36	33.6
80 vol.% DMAc, 20 vol. wt% deionized water	6.2	0.27	16.8
90 vol.% DMAc, 10 vol. wt% deionized water	3.7	0.23	16.1

Temperature: 25°C, feed pressure: 10 bar
[a]GPU = 10^{-6} cm^3 (STP) / (cm^2 s cmHg)

Table 1: Gas permeance and H_2/CH_4 selectivity of PSf /PDMS composite membranes (different gelation bath composition).

Gelation bath composition	Permeance (GPU)		Selectivity
	H_2	N_2	H_2/N_2
Pure deionized water	25.0	0.49	51.0
40 vol. % DMAc, 60 vol. % deionized water	12.1	0.34	35.6
80 vol.% DMAc, 20 vol. wt% deionized water	6.2	0.25	24.8
90 vol.% DMAc, 10 vol. wt% deionized water	3.7	0.20	18.5

Temperature: 25°C, feed pressure: 10 bar

Table 2: Gas permeance and H_2/N_2 selectivity through PSf/PDMS composite membranes (different gelation bath composition).

single gas permeances of CH_4 and N_2 through PSf/PDMS composite membranes are far lower than that of H_2 owing to their weak adsorption affinity and slow diffusion compared with H_2 molecules [19].

Increasing of the solvent into the coagulation bath is more complex

for CH_4 and N_2 gases. In the first case, the solvent tends to increase surface defects that causes the increase in the permeation of CH_4 [20,21]. Additionally, solvent causes delayed demixing which decreases highly the number of finger-like voids and eventually tends to decrease the permeances of gas molecules. Wijmans et al. [22] and Reuvers et al. [23] similarly observed that the addition of solvent into 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 Tables 1 and 2, by increasing the solvent into the coagulation bath, ideal selectivities of H_2/CH_4 and H_2/N_2 have been reduced from 46.3 to 16.1 and 51.0 to 18.5 respectively.

Effect of coagulation bath temperature (CBT)

The effect of the coagulation bath temperature on the structure of flat sheet membranes and separation performance of them were also investigated. As shown in Figures 6a to 6d, with increasing temperature of the coagulation bath from 5°C to 80°C, the cell diameter size increases. Furthermore, the number of macrovoids and membrane thickness are also increased dramatically [24]. This phenomenon can be attributed to the rapid growth of the nucleuses of polymer-poor phase. According to SEM images, it can be observed that at 5°C the macrovoids have been completely removed. This observation can be justified by the reasons of: i) reduction of CBT intensively reduces the mutual diffusivities between the nonsolvent (deionized water) and the solvent (DMAc) in the casting solution during the solidification process, ii) reduction of CBT slows down the growth of primary nucleuses formation after immersion that results in formation of numerous nucleuses in the cast film [25]. The higher number of nucleuses results in suppression of macrovoids, contraction of the polymer chains which eventually led to a restriction in the rotation of PSf segments around the main chain bonds and approximately formation of denser structures (Figure 6a). These findings are in agreement with the other researcher's studies which have been reported in the literature [26]. Tables 3 and 4 show gas permeances and ideal selectivity of H_2/CH_4 and H_2/N_2 for PSf/PDMS composite membranes fabricated at different coagulation bath temperatures.

Comparing the selectivity data obtained from the prepared membranes at low coagulation temperatures (5°C and 25°C) revealed that H_2 gas permeance slightly increases while CH_4 and N_2 gas permeances decrease. In contrast, CH_4 and N_2 gas permeances increased and H_2 permeance decreased for the membranes which prepared at

	CBT	Permeance (GPU[a])	Selectivity
	H_2	N_2	H_2/N_2
5°C	20.5	0.59	34.7
25°C	25.0	0.49	51.0
50°C	22.8	0.97	23.5
80°C	21.0	1.1	19.1

Temperature: 25°C, feed pressure: 10 bar

Table 3: Gas permeance and H_2/N_2 selectivity of PSf/PDMS composite membrane using deioni™zed water as coagulant (different CBT).

	CBT	Permeance (GPU[a])	Selectivity
	H_2	CH_4	H_2/CH_4
5°C	20.5	0.63	32.5
25°C	25.1	0.54	46.3
50°C	22.8	1.1	20.7
80°C	21.0	1.6	13.1

Temperature: 25°C, feed pressure: 10 bar

Table 4: Gas permeance and H_2/CH_4 selectivity of PSf/PDMS composite membrane using deionized water as coagulant (different CBT).

Coagulant	Permeance (GPU[a])		Selectivity
	H_2	CH_4	H_2/CH_4
Deionized water	25.0	2.05	46.3
Ethanol	71.0	2.05	34.6
Methanol	217.5	8.09	26.9

Temperature: 25°C, feed pressure: 10 bar

Table 5: Gas permeance and H_2/CH_4 selectivity through PSf/PDMS composite membranes (different coagulants).

Coagulant	Permeance (GPU [a])		Selectivity
	H_2	N_2	H_2/N_2
Deionized water	25.0	0.49	51.0
Ethanol	71.0	1.97	36.0
Methanol	217.5	7.94	27.4

Temperature: 25°C, feed pressure: 10 bar

Table 6: Gas permeance and H_2/N_2 selectivity through PSf/PDMS composite membranes (different coagulants).

Membrane type		Permeance or permeability			Selectivity		Ref.
		H_2	CH_4	N_2	H_2/CH_4	H_2/N_2	
Silicone-coated PSf		16[a]	0.47[a]	0.37[a]	34.04	43.24	[26]
PSf /PDMS		62.94[b]	3.09[b]	2.87[b]	20.4	22	[27]
PSf/Silica (85/15 vol.%)		22.7[a]	0.62[a]	0.67[a]	36.61	33.88	[28]
PBN/PI (15 wt.%)		14.31[a]	1.78[a]	- - - -	8.04	- - - -	[29]
Present work		25[b]	0.54[b]	0.49[b]	46.3	51.0	

[a]barrer (10^{-10} cm³ (STP)cm/(cm² s cmHg)
[b]GPU

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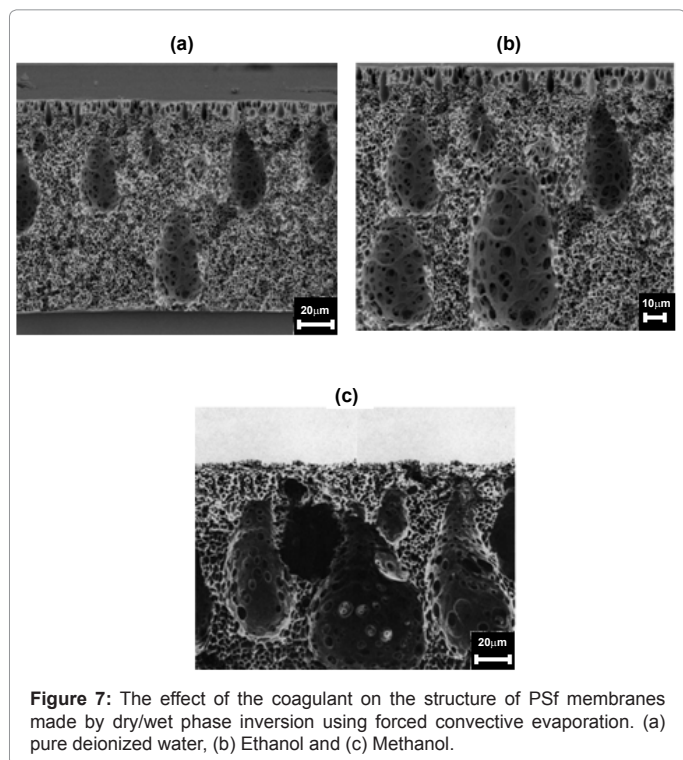

Figure 7: The effect of the coagulant on the structure of PSf membranes made by dry/wet phase inversion using forced convective evaporation. (a) pure deionized water, (b) Ethanol and (c) Methanol.

higher CBTs (25, 50 and 80°C). Hence, the permeance of low-sorbing penetrant (H_2), which do not plasticize the composite PSf/PDMS membrane is higher than those of CH_4 and N_2 gases. This phenomenon can be attributed to the following facts. The solubility of hydrogen,

nitrogen and methane in PSf/PDMS composite membrane is very low. According to the solution–diffusion mechanism, the experimental results illustrates that the gas permeation process through the composite membranes is dominantly controlled by the diffusivity of used gases in the membranes. However, the diffusion of those gases (hydrogen, nitrogen and methane) is determined by the molecular diameter of gases. The molecular diameter of gas is the smallest, so the diffusivity is the largest [27]. Therefore, permeance of hydrogen is higher than that of nitrogen and methane. Regarding the depicted data in Tables 3 and 4, it can be interpreted that the membranes prepared at the coagulation bath temperatures of 25°C exhibit the optimum H_2 separation performance if the possible defects of the dense layer in polysulfone substrate can be filled well through coating with a PDMS layer.

Influence of coagulant type

The scope of this section is to establish relationships between different organic quench media and water for a given casting solution and the resulting morphologies. As can be seen in Figures 7 and 8, the membranes made by the coagulation bath of methanol resulted in asymmetric structure with thin, but microporous skin layers supported by substructure containing more finger-like macrovoids and large cellular structure compared with water and ethanol as coagulants. According to Figure 9, it can be found that the presence of methanol as a drastic coagulant lowers the effective thickness of the skin layer in comparison with water and ethanol (from 400nm to 300nm).

Furthermore, high density, high nodules agglomeration and high intermolecular polymer chain packing density can be achieved by using coagulant in the order of methanol<ethanol< water. According to the SEM images taken from the surface of membranes (Figure 10), one can see that when water was used as coagulant, the surface of the membrane is smooth, and there is no clear pore in the surface. When ethanol was used as coagulant, pinholes with nearly 20μm in diameter appear on the membrane surface sparsely.
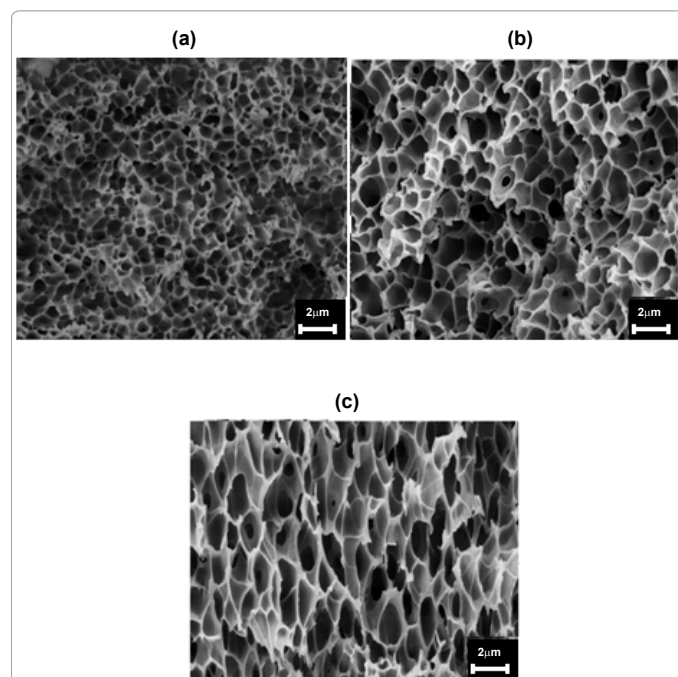

Figure 8: The effect of the coagulant on the structure of PSf membranes made by dry/wet phase inversion using forced convective evaporation. (a) pure deionized water, (b) Ethanol and (c) Methanol (with magnification 10000).
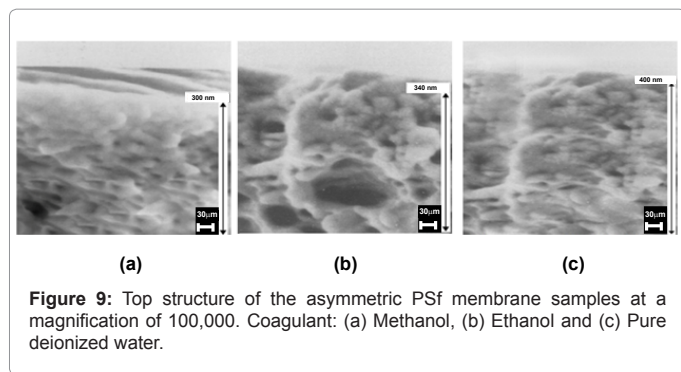
Figure 9: Top structure of the asymmetric PSf membrane samples at a magnification of 100,000. Coagulant: (a) Methanol, (b) Ethanol and (c) Pure deionized water.
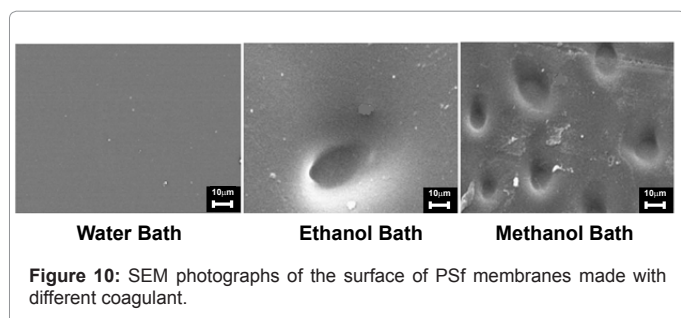

Figure 10: SEM photographs of the surface of PSf membranes made with different coagulant.
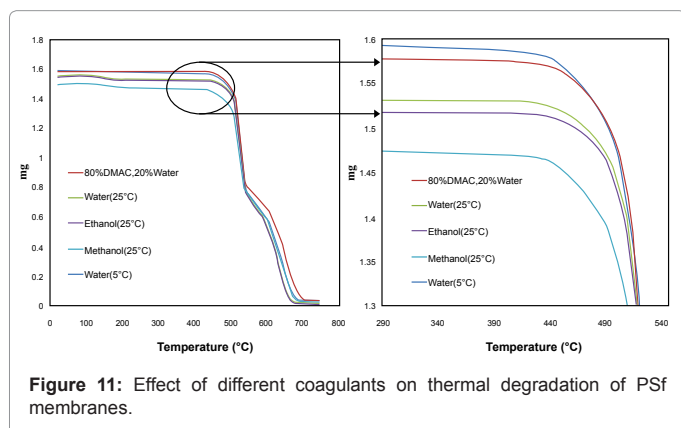

Figure 11: Effect of different coagulants on thermal degradation of PSf membranes.

In the case of using methanol as coagulant, it causes the appearance of higher number of pinholes with diameter of 10μm on the surface. The gas permeances and the average selectivity of H_2/CH_4 and H_2/N_2 for the membranes prepared in the water, ethanol and methanol coagulation bath are presented in Tables 5 and 6 (each test was repeated for 5 times and the average value has been presented). By comparing the data depicted in these tables, one can see that using methanol as coagulant, resulted in less selective membrane (26.9) in comparison with ethanol (34.6) and water (46.3), while the average H_2 permeance was 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 PSf/PDMS composite 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 permeances of gases [28]. Considering the results in Tables 5 and 6, the similar trends in permeances of CH_4

and N_2 gases for membranes made by water as coagulant (15 and 16 times less than that of methanol, respectively) can be attributed to the combinatory effects the configurational changes in the polymeric structure of membranes. A question may arise why the H_2 permeance of membrane made by water as coagulant is less than that of ethanol and methanol. It is worthwhile to mention that the effect of water as 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 permeance decreases. In agreement with a similar report [29], a declining trend is observed for the H_2/CH_4 and H_2/N_2 selectivities of membranes made by ethanol and methanol as coagulant in comparison with water, as shown in Tables 5 and 6. We also believe that with increasing the boiling points of coagulants (water: 100°C > ethanol: 78.1°C > methanol: 64.7°C), the numbers of macrovoids, the amount of free volume, defects and permeances of H_2, CH_4 and N_2 reduce in different level in a such way that the H_2/CH_4 H_2/N_2 selectivities and the thickness of effective skin layer increase.

Table 7 presents a comparison between the obtained results in present work and the other studies presented in the published earlier articles for evaluation of the membrane performance. As can be seen, the H_2/CH_4 and H_2/N_2 selectivities in the present study is higher than that previously reported in the literature [12–15]. Furthermore, the comparatively higher selectivities of H_2/CH_4 and H_2/N_2 than that reported in the literature might be due to the determination of the appropriate parameters in synthesis of defect free composite membranes.

Effect of coagulation bath parameters on the thermal properties

Thermo-gravimetric analysis was carried out on the polymers synthesized here to examine their thermal stability. The TGA curves for PSf membranes made by different coagulants are shown in Figure 11. As indicated in this figure, with decreasing the temperature of the coagulation bath containing deionized water and increasing of solvent/water ratio in the coagulation bath (80%vol. DMAc) thermal stability of membranes increases. By using different coagulants, thermal stability of membranes can also improve. As can be resulted in TGA curves, the existence of methanol, ethanol and water as coagulants increased thermal stability of PSf membranes, respectively. We believe that these can be due to the following facts: A reduction in CBT results in the shrinking of the polymer chains after immersion of the cast film and also, a reduction in CBT results in denser structures with augmented intermolecular polymer chain packing density. Clearly, the compactness of polymer chains, along with denser structures and higher chain packing density, led to a restriction in the rotation of PSf segments around the main chain bonds and, thus, higher thermal stability.

Effective parameters on the thermal stability of PSf membranes are high effectiveness thickness and high intermolecular polymer chain packing density. As interpreted in the previous section by using methanol, ethanol and water as coagulants, density, thickness, agglomeration of nodules and also intermolecular polymer chain packing density increased respectively. Thus it can be expected that thermal stability of membranes also be increased.

Conclusion

The effect of different water/solvent ratios as coagulation medium, CBT and different coagulation medium on the morphology, thermal stability and gas separation property of polysulfone membranes has

been successfully investigated. The results revealed that the H_2/CH_4 and H_2/N_2 ideal selectivities and the H_2 permeance decreased by the increasing of concentration of the solvent in the coagulation bath. The case of 20/80 vol. % mixture of water/DMAc as coagulant also showed that pores with varying size exist on the membrane surface and in the case of 10/90 vol.% mixture of water/DMAc, finger-like macrovoids disappeared completely. By increasing temperature of the coagulation bath from 5°C to 80°C the cell diameter size, macrovoids and membrane thickness were increased. The membranes prepared at the CBT of 25°C showed the best H_2/CH_4 and H_2/N_2 ideal selectivities about 46.3 and 51.0 respectively. As a result, at CBT of 5°C macrovoids were completely removed. With increasing boiling points of coagulants, H_2/CH_4 and H_2/N_2 ideal selectivities increased while the H_2 permeance was decreased. TGA curves showed that membrane made at 5°C of coagulation bath had a high thermal stability while the membranes prepared by using methanol as coagulant showed the lower thermal stability.

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