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MODIFICATION OF PSf MEMBRANE NANOSTRUCTURE USING DIFFERENT FABRICATION PARAMETERS AND INVESTIGATION OF THE CO_2 SEPARATION PROPERTIES OF PDMS-COATED PSf COMPOSITE MEMBRANES

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Abstract - The effects of preparation parameters on the performance and morphology of polydimethylsiloxane/ polysulfone (PDMS/PSf) membranes were investigated. The PDMS layer is mainly used for sealing the defects of the PSf selective layer. The membrane morphologies were characterized by using scanning electron microscopy (SEM). The CO_2/CH_4 separation performance of membranes was studied by a pure gas permeation experimental set up. According to the SEM results, decreasing the water/N,N-dimethylacetamide (DMAc) ratio as the coagulation medium from pure water to mixture of 90 vol.% DMAc and 10 vol.% water resulted in complete disappearance of macrovoids and also a lowering of the membrane selectivity. Permselectivity results showed that the ideal CO_2/CH_4 separation factor of the membranes was improved by the presence of the non-solvent additive to the polymer solution. It was also observed that reduction of the coagulation bath temperature (CBT) led to elimination of macrovoids which affect gas separation performance. Using methanol as a coagulant resulted in a less selective membrane compared with ethanol and water as coagulants and the CO_2 permeance was about 3 and 9 times greater than with ethanol and water as coagulants, respectively.

Keywords: Preparation parameters; PDMS/PSf membrane; Coagulation medium; CBT; CO_2 separation.

INTRODUCTION

High concentrations of greenhouse gases such as CO_2 in the atmosphere cause the main environmental problem associated with global warming and acid rain formation. Besides, elimination of carbon dioxide from fuel gases results in a higher caloric value. Thus, separation of CO_2 from gas mixtures seems to be essential (Thambimuthu *et al*., 2005; Herzog *et al*., 2000; Abu-Zahra *et al*., 2009).

Polymeric membranes have been the technology of interest for gas separation processes like those mentioned above. These kinds of membranes have been used to remove CO_2 in landfill gas recovery processes, biogas purification, natural gas sweetening, etc. (Basu *et al*., 2010; Brunettia *et al*., 2010; Ren *et al*., 2012). Polymer-based membranes have become more competitive in comparison to the traditional separation processes such as amine scrubbing and cryogenic separation (Olajire, 2010; Klara and Srivastava, 2002; Liu and Shi, 2010; Anderson *et al*., 2006). At present, natural gas is the most important source of energy; it is also produced in large quantity and it often contains excess CO_2. The content of CO_2

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*To whom correspondence should be addressed must be diminished to meet the pipeline specification, i.e., 2 mol% or less (Baker, 2004). It was reported that separation processes using asymmetric polymeric membranes assist in the reduction of the CO_2 concentration for upgrading low-quality natural gas (Bhide and Stern, 1993a; Bhide and Stern, 1993b).

Gas separation by composite membranes is increasingly fascinating due to their advantages over integrally skinned asymmetric membranes such as: use of highly permeable polymers, high permeation flux, cost-effectiveness when the materials are costly and ease of being made defect free (Chung *et al*., 1999).

Coated membranes comprised of a sealing layer and separation film meet these requirements. Besides this, coated membranes provide a flexible approach to membrane fabrication. This is due to the fact that the material of the coating layer is often different from the selective film. Traditionally, coated membranes are prepared by dip-coating a suitable selective membrane with a thin layer of polymer functioning as the sealing layer (Chung *et al*., 1999; Henis and Triboldi, 1981; Feng and Huang, 1997).

Highly permeable polymer can be used to prepare a defect-free selective top-layer. In this way, membrane selectivity increases significantly, with almost no reduction in permeability (Peter and Peinemann, 2009). PDMS is the most commonly used rubbery membrane material for the above purpose. 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 (Brandrup *et al*., 1999). The PDMS membranes synthesized up to now and evaluated in gas separation applications were in the form of a single layer (Choi *et al*., 2007; Raharjo, 2007) or of a composite with a macroporous support (Wu, 2006; Yeow, 2002), or a mixed matrix (Kim *et al*., 2004). As a glassy polymer, PSf has some favorable characteristics such as wide operating temperature limits; maximum and optimum physical properties such as strength and flexibility; good toughness; easy fabrication in a wide variety of configurations and modules and relative low cost, which make it suitable for gas separation processes (Xu and Qusay, 2004; Shi *et al*., 2007; Rafiq *et al*., 2012). The fabrication parameters of PSf, significantly affect its morphology and separation performance.

Wang *et al*. (2002) reported that adding non-solvent additives into the casting solution can decrease the dissolving power of the solvent and therefore increase the polymer-polymer interaction. Adding a non-solvent additive to the PSf polymer solution augments the tendency of polymer chains to adopt a more tightly coiled conformation. From the other point of view, when non-solvents are added to the polymer solution, polymer solidification can swiftly occur at the membrane surface and, accordingly, membranes with a thin skin layer and a more uniform structure can be formed (Wang *et al*., 1995).

Wijmans *et al*. (1983) investigated the effect of coagulation bath composition on the structural characteristics of cellulose acetate (CA) membranes and found that small amounts of solvent in the coagulation bath can promote instantaneous liquid-liquid phase separation. The existence of a thick dense skin is also associated with instantaneous liquid-liquid phase separation. A high concentration of solvent in the bath results in the transition from instantaneous to delayed formation which causes the formation of a microporous structure without a dense skin.

The effect of CBT variation on the structural parameters of CA membranes was studied by Smolders *et al*. (1992). They found that the increase of CBT causes the formation of macrovoids and a more porous structure. The coagulation medium is another important synthesis parameter which can exert drastic effects on the resulting structures of membranes made by phase inversion processes (Banks and Sharples, 1966; Saler *et al*., 1974; Strathmann, 1985; Mulder *et al*., 1985; Wijmans *et al*., 1985; Bottmo *et al*., 1985).

In this study, the effect of coagulation bath temperature, the solvent/coagulant ratio, the coagulant type and the presence of non-solvent in the casting solution on the morphology of composite PDMS/PSf membranes was studied. Moreover, prepared membranes were subjected to gas separation tests to evaluate the performance of the resultant membranes.

EXPERIMENTAL

Materials and Module

Polysulfone (PSf Ultrason-6010) was supplied by BASF Corporation as the polymer for preparation of the membrane casting solutions. Commercially available DMAc and tetrahydrofuran (THF) were used as solvents for polysulfone, the organic non-solvents used were methanol (MeOH), ethanol (EtOH) and deionized water, which were purchased from Merck. n-Hexane (as solvent) was supplied by Merck. PDMS (viscosity 5000 mPas), tetraethylorthosilicate (TEOS as crosslinker), and dibutyltin dilaurate (DBTDL as catalyst) were purchased from Beijing Chemical Company, China. All liquid solvents were reagent grade and used without further purification. CO_2 and CH_4 gas cylinders were purchased from

Technical Gas Services. The dead-end membrane cells, made from stainless steel (grade 316), were used to carry out the experiments. The schematic view of the manufactured membrane module is shown in Fig. 1. The membranes were placed 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 cm^2.

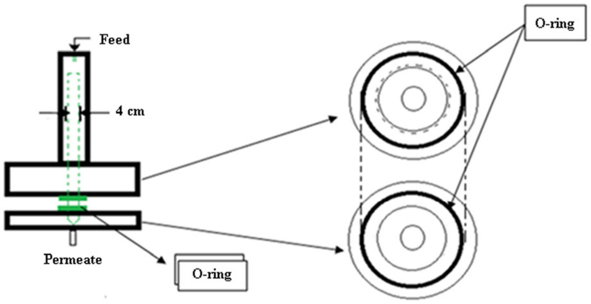


Figure 1: Schematic view of the gas permeation module.

Membrane Preparation

Asymmetric PSf flat sheet membranes were prepared by casting. The 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 K in air using a casting blade. Membranes were cast at a designated wet thickness (200µm) onto a polished glass plate. Then, forced-convective evaporation was induced by flowing an inert nitrogen gas stream across the membrane surface for 20s before immersion in a coagulation bath and then it was 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 (25, 50, 75 and 100 vol.%) were prepared for this purpose. Then the membrane was immersed in hexane for 24 h in order to extract the ethanol before it was dried with air.

Composite Membrane Preparation

10 g PDMS, 1 g of the crosslinking agent TEOS, and 0.2 g of the catalyst DBTDL were mixed in 40 g of n-hexane for 30 min at 70 °C under stirring. The coating solution was then cast on the PSf membranes and they were put under a hood overnight in order to eliminate the solvent by evaporation at ambient temperature. As prepared, the membranes were treated for 1 h at 150 °C in a vacuum oven to complete the crosslinking. A typical cross-sectional SEM image of the PDMS/PSf membrane is shown in Fig. 2. As can be observed, the asymmetric PSf membrane contains a thin selective layer with a thickness of approximately 2µm and a highly permeable coated layer with a thickness of 10µm. The total thickness of the PSf membrane, including the top and porous layers, is about 120 µm.

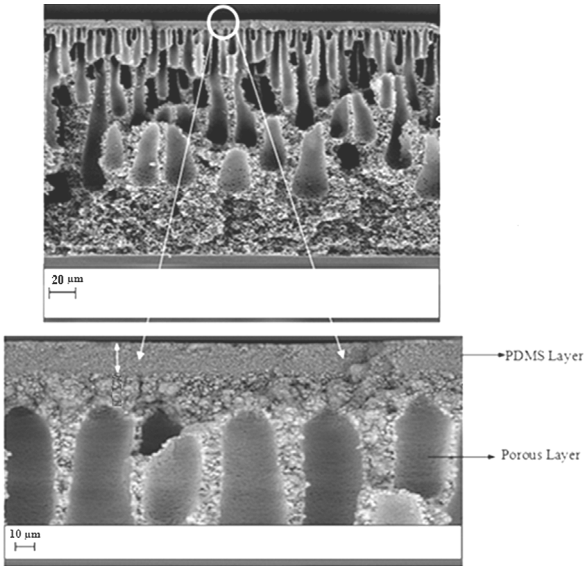


Figure 2: Cross-sectional SEM image of the PDMS/ PSf composite membrane.

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 a 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 Cam Scan SEM model LED 1450 VP microscope (LEO, Germany).

Gas Permeation Measurements

A constant pressure system was used for the gas permeation experiments as shown in Fig. 3. Gas permeation tests were performed by using two permeation cells. Circular coated membrane discs with an effective permeation area of 15.7 cm^2 (membrane area of two cells) were used.

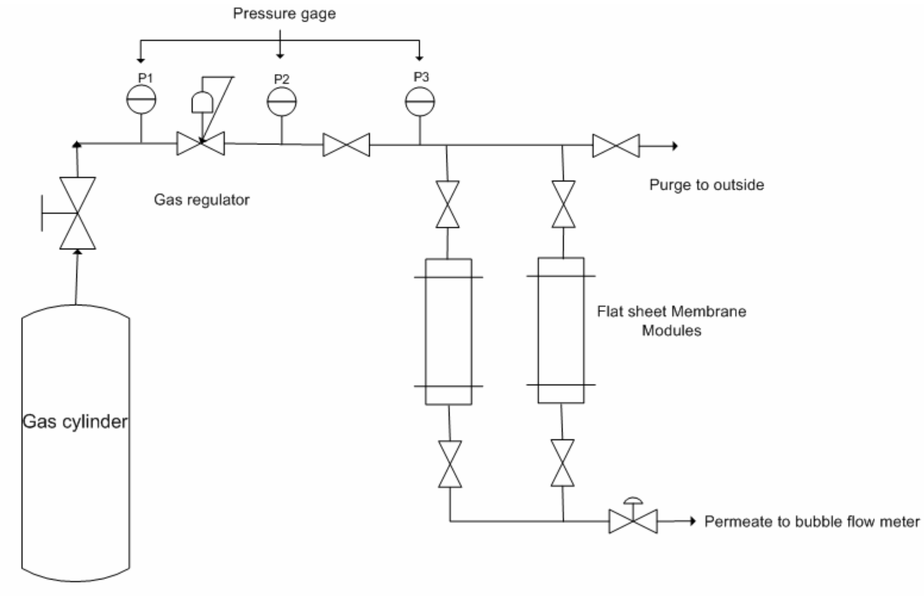


Figure 3: Schematic diagram of the constant pressure testing system

The permeation rates were measured by a bubble flow-meter. The CO_2/CH_4 separation experiments were conducted at room temperature (25 °C) and 4 bar pressure. The gas permeates were collected at ambient pressure. Each test was repeated 3 times and the average value is presented.

According to Pesek and Koros (1993), asymmetric membranes are defined to be ‘defect-free’ if the selectivity of a membrane is greater than 80% of the intrinsic value. The intrinsic permeation properties of dense PSf for CO_2 and CH_4 are given in Table 1 (Chern *et al*., 1985).

RESULTS AND DISCUSSION

Effects of the Non-Solvent in the Casting Solution

The optimum non-solvent concentration in the casting solution has to be determined in order to achieve defect-free and ultrathin-skinned asymmetric membranes for gas separation processes. The phase separation is further controlled by the thermodynamic properties of the casting solution and the non-solvent in the coagulant bath. The addition of a non-solvent additive to the polymer solution has been found to play a basic role in the development of polymeric membranes for gas separation. Three different casting solutions were prepared by varying of non-solvent (ethanol) content and were used to study the effect of non-solvent on the membrane properties. In the case of a non-solvent free casting solution, a thick skin covers a porous sublayer with a relatively uniform pore size distribution. The sample obtained in this case is formed by a delayed mechanism of liquid-liquid phase separation (Mulder, 1996). The effect of non-solvent additive on the permeance for methane and carbon dioxide and on the CO_2/CH_4 selectivity at pressure of 4 bar of the composite membranes prepared with different casting solution compositions is depicted in Table 2. As an interesting finding, the selectivity of the synthesized composite membrane surpassed that of the isotropic PSf film reported in Table 1.

Table 1: Intrinsic permeation properties of PSf (Chern *et al*., 1985).

Permeability coefficient (Barrer)		Intrinsic selectivity
CO_2	CH_4	CO_2/CH_4
4.5	0.16	28.1

1Barrer $=10^{-10}$ [cm^3(STP) cm / cm^2s cmHg]

Table 2: Gas permeance and selectivity through PDMS/PSf composite membranes (different casting solution composition)

Sample	Permeance (GPU [a])		Selectivity
	CO_2	CH_4	CO_2/CH_4
22 wt.% PSf, 39 wt.% DMAc, 39 wt.% THF	14.5(±0.04)	0.57(±0.004)	25.4(±0.06)
22 wt.% PSf, 35 wt.% DMAc, 35 wt. % THF, 8 wt.% EtOH	15.4(±0.07)	0.58(±0.005)	26.5(±0.08)
22 wt.% PSf, 31.8 wt.% DMAc, 31.8 wt. % THF, 14.4 wt.% EtOH	17(±0.05)	0.59(±0.007)	28.8(±0.05)

Temperature: 25 °C, feed pressure: 4 bar.

[a] GPU = 10^{-6}cm^3 (STP) / (cm^2 s cmHg).

As can be seen in Table 2, the ideal CO_2/CH_4 separation factor is enhanced from 25 (without ethanol) to 28.8 (14.4 wt.% ethanol) by introducing the ethanol additive. Recently, Aroon *et al.* (2010) reported that, by using 10.7 wt.% ethanol as additive, an ideal selectivity of 5.09 was obtained for CO_2/CH_4 when NMP was used as solvent. They also obtained a selectivity of 12.45 for CO_2/CH_4 with 10 wt.% ethanol as additive in the case of a NMP/ THF mixture as solvent. Considering Table 2, the CO_2 permeance was slightly enhanced from 14.5 GPU to 17 GPU by increasing the amount of the non-solvent. This can be attributed to instantaneous demixing induced by the presence of the non-solvent additive that caused the formation of a thin skin layer. Among these three cases, a casting solution that contains 14.4 wt% ethanol was less defective than other casting solutions. Hence, as a result, increasing the ethanol can increase the coalescence of the polymer chains in the dense layer and thus the formation of a less defective dense layer.

Effect of the Gelation Bath Solvent Content

According to Table 3, the four samples containing different solvent/water ratios were prepared in order to study the effect of solvent content in the gelation bath on the PSf characteristics. The cross-sections of membranes prepared from a given casting solution (22 wt.% PSf, 31.8% DMAc, 31.8% THF, 14.4% EtOH) and gelation baths with varying solvent/water ratios are shown in Fig. 4. As indicated in Figs. 4 (a) to (c), with increasing amount of solvent in the coagulation bath, one observes a decreasing number of macrovoids in membrane structure. Consequently, the morphology changes from a finger-like to a sponge-like structure. As can be seen at higher magnification, with increasing solvent amount in the coagulation bath, the cell size becomes larger. This can be explained as follows: the cells are formed via a 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.* (2002) presented a similar interpretation of cell size variations for several polymeric membranes. The macrovoids are formed via a spinodal demixing mechanism and small cells around the macrovoids are formed via a secondary nucleation and growth mechanism in the polymer-rich phase (Aroon *et al.*, 2010). Generally, the macrovoid formation is a result of the liquid-liquid demixing process, where the nuclei of the polymer-poor phase are responsible for macrovoid formation. In this way, growth of the macrovoids occurs and this growth continues until the polymer concentration at the macrovoid/solution interface becomes so high that solidification occurs (Amirilargani *et al.*, 2009). In Fig. 4 (c), it can be observed that the number of finger voids has decreased notably. In Fig. 4 (d), the finger voids have completely disappeared, which means that the primary phase separation mechanism is nucleation and growth of the polymer poor phase (Stropnik *et al.*, 2002). In this case, the solidification rate is very slow so that cells can grow and coalesce with each other, which results in an open and large cellular structure.

Table 3 shows the effect of DMAc concentration in the coagulation bath on the permeance of methane and carbon dioxide and on the pure gas CO_2/CH_4 separation factor of composite membranes at a pressure of 4 bar. The permeation results showed that the CO_2 permeance was increased by increasing the concentration of the solvent in the coagulation bath. This can be attributed to the delayed demixing induced by the presence of the solvent molecules in the coagulation bath. The effect of variation of the solvent content variation in the gelation bath on the CH_4 permeance behavior of the synthesized membranes can be seen in Table 3 (Kim *et al.*, 1997; Kim *et al.*, 1999). Wijmans *et al.* (1983) and Reuvers *et al.* (1987) similarly observed that, by adding solvent to the coagulation bath, the formation of a skin layer was prevented or some finger-like pores can reach the surface and, consequently, the separation factor diminished. As reported in Table 3, increasing the solvent in the gelation bath, reduced the separation factor for CO_2/CH_4 from 28.8 to 19.

Table 3: Gas permeance and selectivity through PDMS/PSf composite membranes (different gelation bath composition); casting solution composition: 22 wt.% PSf, 14.4 wt.% ethanol, 31.8 wt.% DMAc, 31.8 wt.% THF.

Gelation bath composition	Permeance (GPU [a])		Selectivity
	CO_2	CH_4	CO_2/CH_4
0 vol.% DMAc, 100 vol. wt% deionized water	17(±0.05)	0.59(±0.007)	28.8(±0.05)
40 vol. % DMAc, 60 vol. % deionized water	20.1(±0.07)	0.72(±0.002)	28(±0.01)
80 vol.% DMAc, 20 vol. wt% deionized water	23.7(±0.03)	1.25(±0.005)	19(±0.02)
90 vol.% DMAc, 10 vol. wt% deionized water	25.9(±0.06)	1.41(±0.003)	18.4(±0.03)

Temperature: 25 °C, feed pressure: 4 bar

[a] GPU = 10^{-6} cm^3 (STP) / (cm^2 s cmHg).

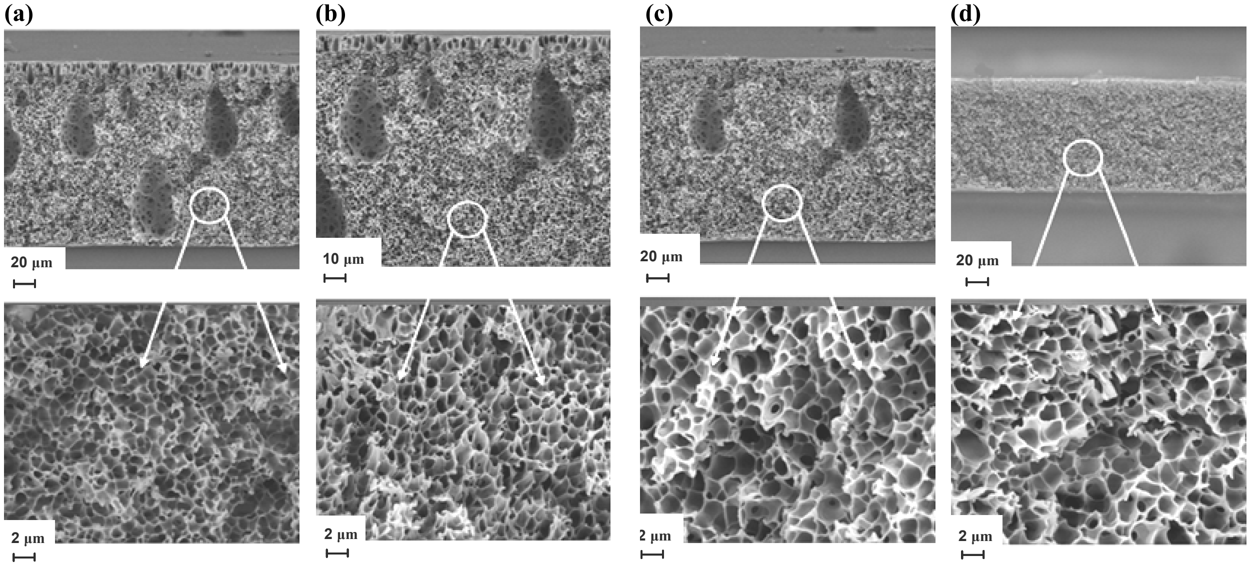


Figure 4: The effect of DMAc/deionized water vol% as coagulation bath on the membrane structure (CBT: 25 °C): (a) 0:100; (b) 40:60 (c) 80:20 (d) 90:10. The PSf casting solution consisted of: 22 wt.% PSf, 14.4 wt.% ethanol, 31.8 wt.% DMAc, 31.8 wt.% THF.

Effect of Coagulation Bath Temperature (CBT)

The influence of the coagulation bath temperature in the range from 5 °C to 80 °C on the flat sheet membrane structures and separation performances was also investigated. The upper and lower limits were selected based on the gelation bath freezing temperature and the PSf softening temperature, respectively. As shown in Figs. 5 (a) to 5 (d), increasing the coagulation bath temperature, increased the cell diameter. Furthermore, the amount of macrovoid and the membrane thickness are also increased dramatically (Han and Nam, 2002). This phenomenon can be explained by the rapid growth of the nuclei of the polymer-poor phase. According to the SEM images, it can be observed that, at the temperature of 5 °C, the macrovoids have been completely removed. This observation can be justified by the following. Reducing the CBT levels strongly reduces the mutual diffusivities between the nonsolvent (deionized water) and the solvent (DMAc) in the casting solution during the solidification process. In addition, reduction of CBT slows down the growth of the primary nuclei formed after immersion, which results in the formation of numerous nuclei in the cast film (Barzin *et al.*, 2005). The high amount of nuclei results in the suppression of macrovoids and in compactness of the polymer chains, which eventually leads to a restriction in the rotation of PSf segments around the main chain bonds and the formation of denser structures (Fig. 5 (a)). These findings are in agreement with other studies reported in the literature (Smolders *et al.*, 1992). Table 4 shows gas permeances and the separation factors for CO_2/CH_4 for PDMS/PSf coated membranes fabricated at the different gelation bath temperatures. Comparing the selectivity data obtained for the membranes prepared at the different coagulation temperatures (5–80 °C) revealed that the CO_2 and CH_4 gas permeances were increased. Among the CBTs studied here, the membranes prepared at the coagulation bath temperature of 25 °C exhibited optimum gas separation performance, which means that the amount of pinholes in the selective skin layer was negligible.

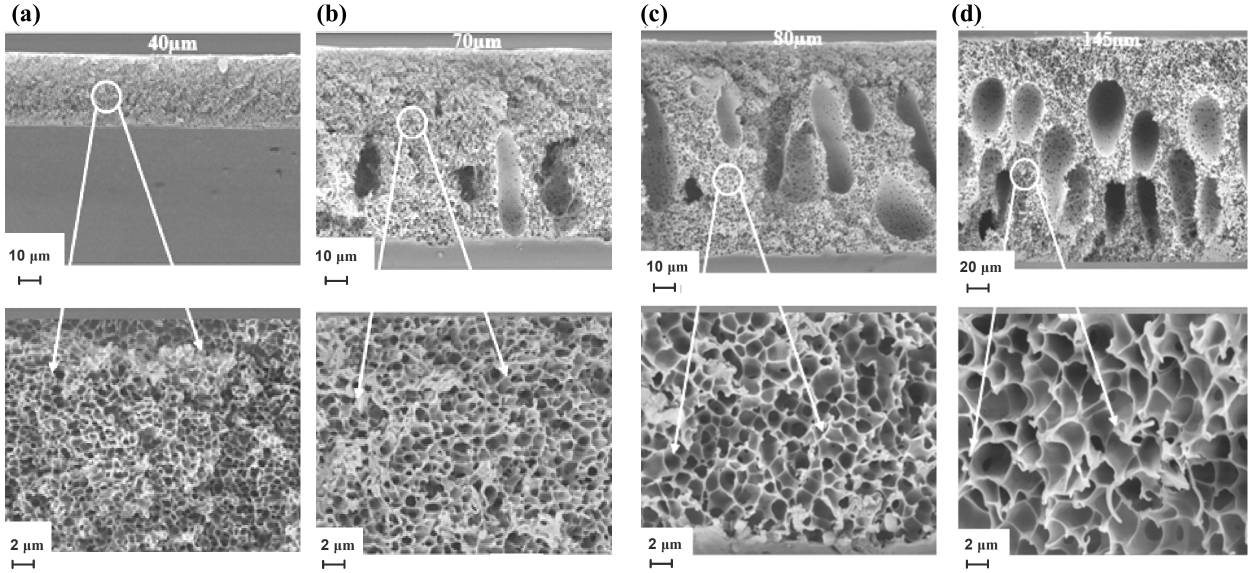


Figure 5: The effect of the coagulation bath temperature on the membrane structure, deionized water bath temperature: (a) 5 °C; (b) 25 °C; (c) 50 °C; (d) 80°C; the PSf casting solution consisted of: 22 wt.% PSf, 14.4 wt.% ethanol, 31.8 wt.% DMAc, 31.8 wt.% THF.

Table 4: Gas permeance and selectivity of PDMS/PSf composite membranes using deionized water as coagulant (different CBT); casting solution composition: 22 wt.%PSf, 14.4 wt.% ethanol, 31.8 wt.% DMAc, 31.8 wt.% THF.

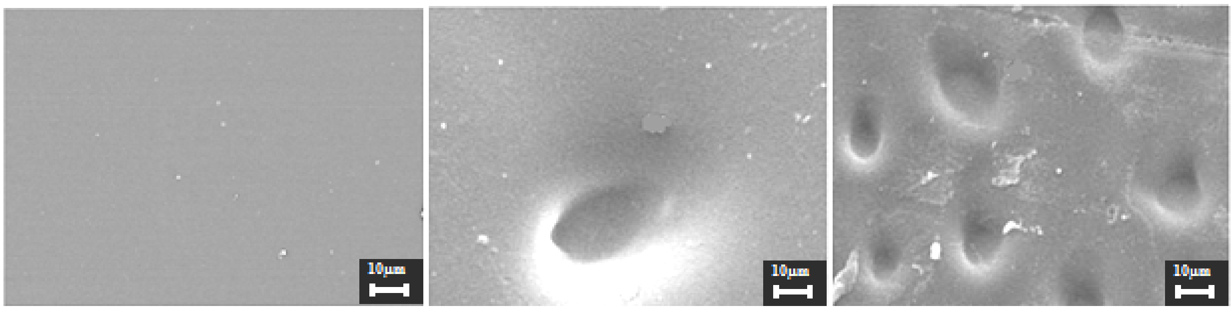
CBT (°C)	Permeance (GPU [a])		Selectivity CO_2/CH_4
	CO_2	CH_4	
5	13.9 (±0.06)	0.55(±0.007)	25(±0.06)
25	17(±0.05)	0.59(±0.007)	28.8(±0.05)
50	19.98(±0.04)	1.17(±0.003)	17(±0.07)
80	22.95(±0.07)	1.76(±0.004)	13(±0.05)

Temperature: 25 °C, feed pressure: 4 bar

[a] GPU = 10^{-6} cm^3 (STP) / (cm^2 s cmHg).

Influence of Coagulant Type

The scope of this section is to establish relationships between different organic quench media and water for a given casting system and the resulting morphologies. According to the SEM images taken of the surface (Fig. 6) of the membranes, one can see that when water was used as the coagulation bath, the surface of the membrane was smooth with no clear pores. When ethanol was used as the coagulation bath, pinholes appeared sparsely on the membrane surface, while the use of methanol as coagulant caused the appearance of a large amount of pinholes on the surface. The gas permeances and the selectivities for CO_2/CH_4 of the membranes prepared in the water, ethanol and methanol coagulation baths are shown in Table 5. By comparing the data depicted in this table, we can see that using of methanol as the coagulant resulted in a less selective membrane (23) compared with ethanol (28) and water (28.8), while the CO_2 permeance was about 3 and 9 times greater than with ethanol and water as coagulants, respectively. These results are in agreement with Pinnau *et al.* (1992) observation for N_2/O_2. A question may arise as to why the CO_2 permeance of membranes made with methanol as coagulant is higher than with ethanol and water. We believe that CO_2 molecules are adsorbed at a high level on the skin layer surface and can then diffuse through the dense layer; therefore, the CO_2 permeance is governed by the skin layer thickness. Whenever the thickness of the dense skin layer decreases, the permeance of CO_2 increases.



Water Bath **Ethanol Bath** **Methanol Bath**

Figure 6: SEM photographs of the surface of PSf membranes made with different pure coagulants (CBT: 25 °C). PSf casting solution composition: 22 wt.% PSf, 14.4 wt.% ethanol, 31.8 wt.% DMAc, 31.8 wt.% THF.

Table 5: Gas permeance and selectivity through PDMS/PSf composite membranes (different coagulants); casting solution composition: 22 wt.% PSf, 14.4 wt.% ethanol, 31.8 wt.% DMAc, 31.8 wt.% THF.

Coagulant	Permeance (GPU [a])		Selectivity CO_2/CH_4
	CO_2	CH_4	
Deionized water	17(±0.05)	0.59(±0.007)	28.8(±0.05)
Ethanol	45.6(±0.07)	1.62(±0.008)	28(±0.09)
Methanol	145.4(±0.04)	6.31(±0.02)	23(±0.04)

Temperature: 25 °C, feed pressure: 4 bar

[a] GPU = 10^{-6} cm^3 (STP) / (cm^2 s cmHg).

CONCLUSIONS

The effect of non-solvent additive (ethanol), different water/solvent ratios as the coagulation medium, CBT and different coagulants on the morphology and gas separation property of PDMS/PSf membranes has been successfully investigated. The results revealed that the CO_2/CH_4 separation factor and the CO_2 permeance were increased by the addition of a non-solvent additive. The CO_2/CH_4 separation factor decreased upon increasing the concentration of the solvent in the coagulation bath. With a 20/80 vol. % mixture of water/DMAc as coagulant, pores of varying sizes existed on the membrane surface and, in the case of a 10/90 vol. % mixture of water/DMAc, the finger voids disappeared completely. By increasing the coagulation bath temperature, the cell diameter, the macrovoids and the membrane thickness were increased. By using different coagulants (differing in their boiling points), the CO_2/CH_4 separation factor and the CO_2 permeance were changed notably.

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