Comparing Different Methods of Fabricating Polysulfone Membranes for CO_2/CH_4 Separation

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Abstract

The present study investigated the fabrication of polysulfone (PSU) gas separation membranes using various solvents and methods. Membranes were prepared via the dry-wet method and dry casting. Following the dry casting method, two different solvents such as N-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF), were utilized. DMF resulted in membranes with higher permeability. The membrane fabricated by PSU (20 wt%) and DMF (80 wt%) through dry casting provided optimal results in terms of permeability and selectivity. The carbon dioxide permeability of this membrane was 3.63 barrer with the carbon dioxide/methane selectivity of 18.25. The mentioned membrane also accounts for the best selectivity among the membranes prepared by dry-wet and dry casting methods.

Keywords: Polysulfone, Gas separation, Carbon dioxide, Methane, Permeability, Selectivity

1 Introduction

Conventional methods for separating carbon dioxide from methane include chemical conversion to other compounds, adsorption on solids, and absorption in liquid solvents [1]. These processes consume a lot of energy, require significant investment, and take considerable space [1]. The separation of gasses using the membrane process is an alternative option that is cost-effective in energy consumption [2]. However, to compete with conventional technologies, it is necessary to develop membranes and modules that can process large gas volumes. In other words, to reduce the size and number of membrane modules, high carbon dioxide permeability is expected from the membrane and the process itself [2]. Despite many advances in this field, the need for suitable materials to make high permeability membranes is still evident.

Membranes used to separate carbon dioxide mixed with methane are usually made of glassy polymers, such as polysulfone (PSU) [3-7], poly(vinyl chloride) (PVC) [8-10], cellulose acetate (CA) [11-19], poly(ether sulfone) (PES) [20-23], polyimide [24-27], and polycarbonate [28, 29], because of the high selectivity of carbon dioxide compared to methane in these membranes. Regardless of mechanical strength, chemical resistance and durability are essential criteria for selecting membranes in the gas separation process [30].

In general, two types of PSU membranes are used to separate carbon dioxide and methane, including dense and asymmetric membranes. Three dry, wet, and dry-wet methods are applied to

make dense and asymmetric membranes. In the dry method, the polymer solution is cast on a suitable plate, and the solvent is allowed to evaporate. PSU membrane fabricated by dry methods has a dense structure. In the wet method, the composition of the polymer solution is similar to the dry method. Before precipitation of the polymer layer in the non-solvent bath, solvent evaporation is performed to concentrate the outer part of the polymer layer. These membranes are often so defective that they cannot be used in gas separation without post-processing. One of the most popular membrane processing methods in this field is the use of a coating layer. In the dry-wet method, two solvents are used: a more volatile solvent and a less volatile solvent, which show different tendencies towards non-solvent. First, the polymer film is evaporated by convective flow and then immersed in the coagulation bath [31].

A review of previous research shows that to make gas separation PSU membranes with an asymmetric structure, including an ultra-thin and flawless selective layer, it is necessary to induce the convective evaporation of solvent [31]. According to these studies, two solvents, dimethylacetamide (DMAC) and N-methyl-2-pyrrolidone (NMP), can be used as the less volatile solvents in this regard. However, most gas separation articles have used DMAC [32, 33]. In these articles, the best results have been obtained using PSU, DMAC, tetrahydrofuran (THF), and ethanol with a composition of 22, 31.8, 31.8, and 14.4 wt%, respectively [31, 34]. Pesek and Koros [35] used DMAC and NMP as the less volatile solvents, THF as the volatile solvent, and ethanol as non-solvent to fabricate the PAU membranes used in gas separation. After casting, the solution was subjected to convective evaporation, after which the resulting film was immersed in a water bath. The researchers reported that if NMP was used instead of DMAC, optimal results would be obtained at different concentrations of the components. The difference in the performance of DMAC and NMP solvents is because NMP is a stronger solvent for PSU than DMAC, and therefore more ethanol is needed to bring the solution to the biphasic boundary.

The influence of solvents on the properties of PSU gas separation membranes was studied before; however, none of the previous studies investigated the effect of different procedures for the fabrication of such membranes. In the present study, PSU membranes were fabricated through the dry-wet method and dry casting. The effect of the membrane fabrication method and the solvents was studied by examining the morphology of membranes and their performance in gas permeation experiments.

2 Materials and methods
2.1 Materials
Polysulfone (PSU) and N-methyl-2-pyrrolidone (NMP) were obtained from BASF and Daejung, respectively. Dimethylformamide (DMF), dimethylacetamide (DMAC), tetrahydrofuran (THF), and ethanol (Eth) were purchased from Merck. Carbon dioxide and methane were provided by Khorakyan Oxygen CO.

2.2 Membrane preparation
To prepare the polymer solutions, the desired amount of polymer was added to the pure solvent or a specific combination of solvent/non-solvent. The solution was then stirred for 18 hours at 30 °C on a magnetic stirrer. The resulting homogeneous solution was kept stagnant for 20 minutes to prevent defect formation in the membrane. Dry-wet and dry methods were used to make the membranes.

2.2.1 Dry-wet method

A literature review shows that DMAC was used to form most gas separation membranes through the dry-wet method [32, 33]. The best results were obtained using solutions consisting of PSU, DMAC, THF, and ethanol with a composition of 22, 31.8, 31.8, and 14.4 wt%, respectively [31, 34]. However, solution preparation based on the mentioned composition led to the coagulation of the polymer solution. According to the observations, during the solution preparation process, the solution consisting of polymer, DMAC, and THF was completely homogeneous, but when adding ethanol and increasing the ethanol concentration to more than 14% by weight, the solution was coagulated. Therefore, solution composition was changed to 22, 32, 32, and 14% by weight for PSU, DMAC, THF, and ethanol. After casting the solution at 250 μm, the nitrogen flow passed above the solution for 1 minute, and when the solution became cloudy, the mirror with the solution on it was immersed in a water bath at 25 °C. The resulting membrane had a very low permeability at 2.02 GPU and 0.91 GPU for CO_2 and CH_4, respectively, and a very low CO_2/CH_4 selectivity at 2.22. Changes in pressure and duration of nitrogen flow had little effect on improving results.

In the continuation of the membrane fabrication process, NMP was used as the non-volatile solvent. Previous studies have shown that if NMP is used instead of DMAC, it is necessary to increase the concentration of ethanol because NMP is a stronger solvent for PSU and therefore requires more ethanol as the non-solvent to bring it to the two-phase boundary [35]. Accordingly, the best composition of the polymer solution was reported as 22, 29, 29, and 20% by weight for PSU, NMP, THF, and ethanol, respectively [35]. However, the addition of more than 16% by weight of ethanol resulted in the coagulation of the solution. Therefore, the ethanol concentration was not increased to more than this amount. Table 1 shows the fabrication conditions of two selected samples made using NMP.

Location of Table 1

2.2.2 Dry casting

In this method, after preparing the polymer solution, the solution was cast, and the resulting polymer layer was first placed in an oven at 65 °C for 24 hours to precipitate the polymer. The residual solvent was then evaporated in a vacuum oven at 70 °C for 4 hours.

Fabrication of PSU membranes by dry casting was conducted by two procedures. In the first method, 10 g of PSU solution in 10% by weight was prepared. Due to the low viscosity of this solution, it was not possible to cast it with a film applicator, and therefore the solution was poured into a petri dish. In the second method, a solution with a PSU concentration of 20% by weight was prepared and cast at 250 μm thickness. In both methods, two types of solvents, NMP and DMF, were used to determine the appropriate solvent. Table 2 shows the fabrication conditions of some of the best membrane samples prepared by dry casting.

Location of Table 2

2.3 Investigation of membrane morphology

The cross-sectional morphology of PSU membranes was examined by scanning electron microscopy (LEO 1450 VP, made in Germany). Prior to imaging, the specimens were coated with a gold-palladium sputter coater (SC7620, UK). For cross-sectional imaging, the samples were fractured in liquid nitrogen before coating.

2.4 Gas separation experiments

The permeability of pure CH_4 and CO_2 gases at ambient temperature and the constant pressure of 8 bar was investigated by a device designed and constructed for this purpose. The PSU membranes were cut as needed and placed inside a membrane cell with an effective surface area of 15.3 cm^2. After establishing the gas flow at the desired pressure, the permeate flow was measured by a bubble flowmeter.

Membrane permeability for each gas was calculated by the following equation [36]:

$$P_i = \frac{Q_i}{\Delta P_i A}$$ (1)

In this regard, Q_i is the volumetric flow rate of gas i (cm^3/s) at standard temperature and pressure, ΔP_i is the pressure difference between the two sides of the membrane (cmHg), and A is the effective membrane area (cm^2). The permeability of each gas was reported in terms of barrer (one barrer is 10^{-10} cm^3 (STP).cm/(cm.s.cmHg)).

The ideal selectivity of pure gas (α_{ij}) was calculated using the following equation [36]:

$$\alpha_{ij} = \frac{P_i}{P_j}$$ (2)

Experiments were performed first with CH4 and then with CO2 for all membranes. In each experiment, membrane permeability was recorded at 30-minute intervals until a constant value was reached. It should be noted that the experiments were repeated three times for each membrane code, and the average results were reported.

3 Results and discussion

3.1 Dry-wet method

As stated in section 2, using DMAC as the solvent did not lead to acceptable membrane performance. Table 3 shows the pure gas permeability test results for two selected samples made using NMP as the solvent. As shown in Table 1, both membranes were fabricated by convective evaporation and then precipitation in a water bath. Regarding Table 2, the Dry-wet-1 membrane cast at 250 μm provided very low CO_2 permeability but showed acceptable selectivity. In order to improve the flux, different durations and different flow rates of nitrogen flow were investigated, but the results did not improve. Membrane fabrication at a lower thickness (Dry-wet-2) resulted in a significant improvement in flux, but on the other hand, membrane selectivity was severely reduced. Fig. 1 shows the SEM image of the Dry-wet-2 membrane. It is clear that this membrane consists of a dense layer on a porous support. The support cavities start at the bottom and end in several macropores at the top, and finally, the dense selective layer is seen on top of the support. The cross-sectional image of this membrane is expected to provide a high flux due to its relatively thin selective layer and porous support and a high selectivity due to the dense structure of the selective layer. However, it is possible that there were defects in the selective layer that led to a decrease in membrane selectivity. According to the results, the membranes prepared by the dry-wet method by neither DMAC nor NMP provided acceptable results.

Location of Table 3
Location of Fig. 1

3.2 Dry casting

PSU membranes were fabricated by dry casting in two ways and by two types of solvents. Table 4 shows the results of gas permeability tests for the membrane samples prepared by dry casting. A comparison of membranes prepared at two polymer concentrations of 10 and 20% by weight (comparison of Dry-1 with Dry-2 and Dry-3 with Dry-4 in Table 4) shows that the solution at a lower concentration led to a membrane with lower permeability. It is due to the presence of more solvent, which requires longer evaporation to precipitate the polymer. As a result, precipitation is slower at lower concentrations, and the density of the polymer chains increases. On the other hand, the use of DMF in comparison with NMP (comparison of Dry-1 with Dry-3 and Dry-2 with Dry-4 in Table 4) shows that DMF resulted in membranes with higher permeability which can be due to its faster evaporation (boiling point: 153 °C) compared to NMP (boiling point: 202 °C), faster precipitation of the polymer and consequently less density of the polymer chains.

Location of Table 4
Location of Fig. 2

According to the results of Table 4, the Dry- 4 membrane provided the optimal results in terms of permeability and selectivity. A comparison of Table 4 with Table 3 also shows that the Dry-4 membrane accounts for the best selectivity among the membranes prepared by both dry-wet and dry methods. Fig. 2 shows a cross-sectional SEM image of the Dry-4 membrane and indicates a very dense structure.

4 Conclusion

PSU membranes were fabricated using various solvents and methods and were examined in gas permeability experiments. Two different methods, including the dry-wet method and dry casting, were investigated. Using DMAC as the less volatile solvent in the dry-wet method did not lead to acceptable membrane performance. Using NMP as the less volatile solvent, the membrane cast at 250 μm provided very low CO_2 permeability but showed acceptable carbon dioxide/methane selectivity. Membrane fabrication at a lower thickness resulted in a significant improvement in flux, but on the other hand, membrane selectivity was severely reduced. Therefore, the membranes prepared by the dry-wet method by neither DMAC nor NMP provided acceptable results. NMP and DMF were applied as two different solvents using the dry casting method, while DMF resulted in membranes with higher permeability. The membrane fabricated by PSU (20 wt%) and DMF (80 wt%) through dry casting provided the optimal results in terms of permeability (3.63 barrer) and carbon dioxide/methane selectivity (18.25).

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Table 1 Membrane fabrication conditions through the dry-wet method using NMP as the solvent

Membrane code	Composition of the casting solution (wt%)				Fabrication procedure
	PSU	NMP	THF	Eth	
Dry-wet-1	22	31	31	16	Casting at 250 μm, 1 min convective evaporation, immersion in the water bath
Dry-wet-2	22	31	31	16	Casting at 200 μm, 1 min convective evaporation, immersion in the water bath

Table 2 Membrane fabrication conditions through dry casting

Membrane code	Composition of the casting solution (wt%)			Fabrication procedure
	PSU	NMP	DMF	
Dry-1	10	90	-	10 g of solution was poured into a petri dish, placed in an oven at 65 °C for 24 hours, and then in a vacuum oven at 70 °C for 4 hours.
Dry-2	20	80	-	The solution was cast at 250 μm, placed in an oven at 65 °C for 24 hours, and then in a vacuum oven at 70 °C for 4 hours.
Dry-3	10	-	90	10 g of solution was poured into a petri dish, placed in an oven at 65 °C for 24 hours, and then in a vacuum oven at 70 °C for 4 hours.
Dry-4	20	-	80	The solution was cast at 250 μm, placed in an oven at 65 °C for 24 hours, and then in a vacuum oven at 70 °C for 4 hours.

Table 3 Gas permeation results using membranes fabricated by the dry-wet method

Membrane code	P_{CO2} (barrer)	P_{CH4} (barrer)	P_{CO2}/P_{CH4}
Dry-wet-1	0.78	0.06	12.93
Dry-wet-2	15.97	7.41	2.15

Table 4 Gas permeation results using membranes fabricated by dry casting

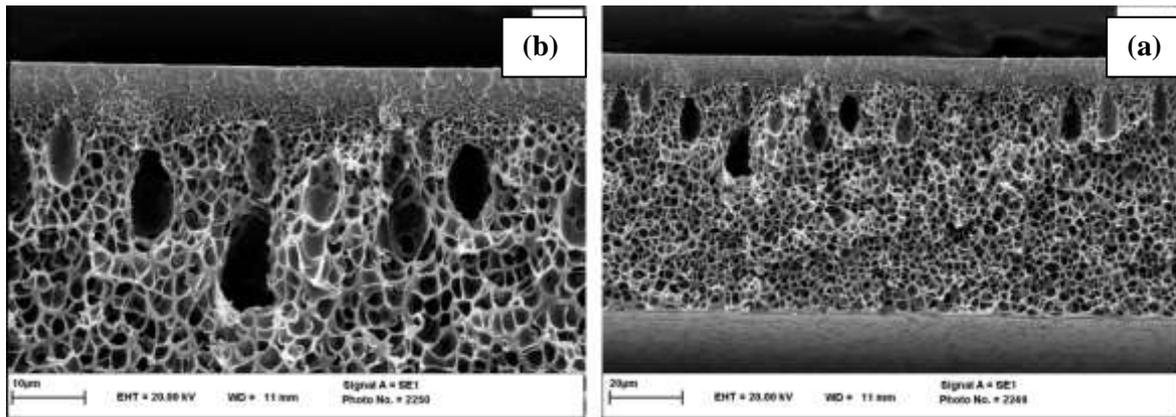| Membrane code	P_{CO2} (barrer)	P_{CH4} (barrer)	P_{CO2}/P_{CH4}
Dry-1	0.30	0.02	16.05
Dry-2	0.90	0.05	17.07
Dry-3	1.56	0.09	16.88
Dry-4	3.63	0.199	18.25

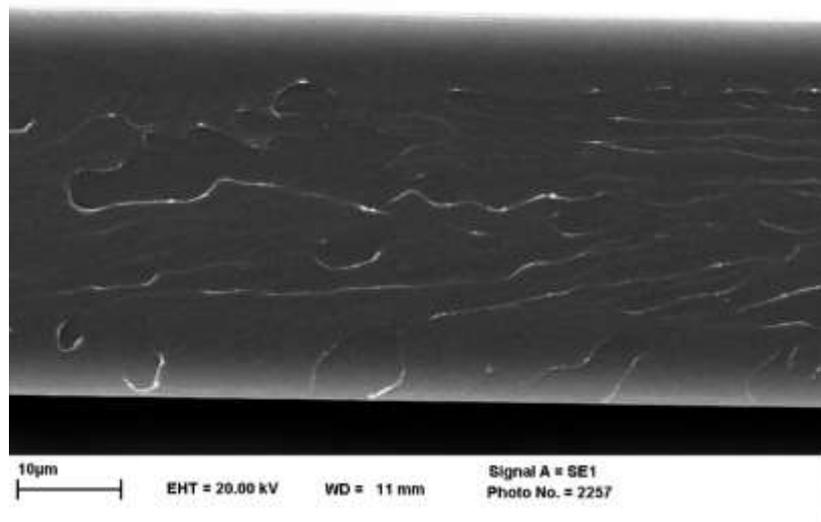Fig. 1 Cross-sectional SEM image of the Dry-wet-2 membrane: (a) total section and (b) top section

Fig. 2 Cross-sectional SEM image of the Dry-4 membrane