Polymer blend membranes for CO2 separation from natural gas

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Abstract: Polymeric membranes are dominantly used in industrial gas separation membrane processes. Enhancement in membranes permeability and/or selectivity is a key challenge faced by membrane researchers. The current work represents the effect of polyetherimide blending on separation performance of polysulfone membranes. Polysulfone/polyetherimide (PSF/PEI) blend flat sheet dense membranes were synthesized and tested for permeation analysis of CO2 and CH4 gases at 6, 8 and 10 bar pressure and 25°C temperature. Morphology and thermal properties of membranes were characterized by field emission scanning electron microscope (FESEM) and thermo gravimetric analysis (TGA) respectively. Blend membranes were dense and homogeneous as deduced from FESEM analysis. Thermal stability of synthesized blend membranes was maintained by blending with PEI as characterized by TGA results. Decrease in permeability of both gases was observed by the addition of PEI due to rigidity of PEI chains. Additionally, selectivity of synthesized blend membranes was enhanced by blending PEI and blend membranes show improved selectivity over pure PSF membrane. This new material has the capability to be used as gas separation membrane material.

1. Introduction

Polymer blends are attractive alternative materials for gas separation membranes as compared to inorganic or mixed matrix membranes due to ease of processing, simplicity and synergetic properties of polymer blends [1]. It is a general requirement for gas separation membranes to have high permeability and high selectivity [2]. However, the typical trade off line known as Robeson upper bound line suggests that increase in permeability is at the expense of selectivity and vice versa [3]. According to solution diffusion model, the permeability of a gas across the membrane is a function of diffusivity and solubility [2]. Thus, by molecular engineering of membrane materials, diffusivity and/or solubility of a membrane for a target gas can be enhanced. Polymer blending of a base material with high glass transition temperature (Tg) rigid polymers provide diffusion selectivity to polymer blend matrix as reported by [1, 4].

Polysulfone is a commodity polymer used for membrane synthesis. It has moderate gas separation performance, good film forming ability and high plasticization resistance [4]. Thermal and chemical

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stability, adequate permeability and selectivity of polyetherimide made it a suitable choice for gas separation membranes. Its reported selectivity for CO₂/CH₄ gas pair is 30-40 [5]. Therefore, blending small amount of PEI in PSF matrix will enhance the selectivity of the resultant blend membrane. The miscibility of PSF/PEI blend was reported in literature [6]. But no study is available in literature for application of PSF/PEI blend as gas separation membranes.

Therefore, the present study reports the blending effect of PEI in base PSF matrix on morphology and gas transport properties of PSF membrane by varying the PEI concentration from 0-3%. The synthesised membranes were characterized and tested for permeation of CO₂ and CH₄ gases at room temperature and 6, 8, 10 bar pressure.

2. Experimental

2.1. Chemicals
Polysulfone (PSF) Udel® P-1800 taken as a base polymer was acquired from Solvay Advanced Polymers, L.L.C, U.S. Polyetherimide (PEI) was obtained from Sigma Aldrich, Germany. 1-Methyl-2-pyrrolidone EMPLURA® (NMP) was used as a solvent and it was obtained from Merck. CO₂ and CH₄ gases with 99.99% purity were purchased from MOX-Linde Gases Sdn. Both polymers were pre dried at 110°C for 24 hours to remove the moisture.

2.2. Membrane Synthesis
Pre-dried polymers (20% w/w) were dissolved in NMP solvent to prepare casting solution in a closed container. The casting solution was stirred for 24 hour at room temperature to completely dissolve the polymers followed by degassing for 30 minutes to remove the air bubbles formed during the mixing process. The casting knife was adjusted at 180 μm opening and the casting solution was poured onto a clean glass plate to cast the membrane films. The casted membranes were isolated in the vacuum oven at 25°C for the first 48 hours. For the next 24 hours, the temperature was raised 20°C for each 2 hours until the temperature reached 65°C which was maintained for 20 hours. After 72 hours of drying process, the membranes were secured.

2.3. Membrane Characterization
The synthesized membranes were characterized by FESEM and TGA in order to investigate the morphology and thermal properties of synthesized membranes.

2.4. Gas Permeation Analysis
The permeability of pure CO₂ and CH₄ gas across the membrane was recorded in the pressure range of 6-10 bar and room temperature. The detailed aspects of membrane permeation unit can be found in our previous work [7]. The CO₂ permeability (P_{CO₂}) was calculated according to the following formula:

\[ P_{CO₂} = \frac{J_{CO₂} \cdot l}{\Delta P_{CO₂}} \]  

where, \( J_{CO₂} \) is flux of CO₂, \( \Delta P_{CO₂} \) is differential partial pressure of CO₂ across the membrane and \( l \) is thickness of membrane. Similarly, permeability of CH₄ can also be calculated using the same formula. Then, the ideal selectivity (\( \alpha \)) of membrane was obtained by dividing the permeability of CO₂ by permeability of CH₄.

\[ \alpha_{CO₂:CH₄} = \frac{P_{CO₂}}{P_{CH₄}} \]
3. Results and Discussion

3.1.1. Membrane Morphology
Morphology of synthesized membranes is shown in Figure 1. PSF membrane has smooth, dense and homogeneous structure. The blend membranes have a similar dense structure with no pore formation. At a magnification of 1000, no cracks or defects are observed in membrane structure at macroscopic level [8]. However, with the increase in PEI content the resultant blend membrane has some irregularities in the cross-section. At the same time, the structure is not phase separated [9]. Thus, higher concentration of PEI would result in partially miscible blend. It is worth mentioning that membrane samples with higher weight percent of PEI were synthesised and it was noticed that the blend was not miscible at concentrations higher than 5 weight percent PEI in PSF matrix and the synthesised membrane samples were not stable. Thus, PEI in lower concentrations (< 5 %) makes miscible or partially miscible blend.

Figure 1. Cross sectional images of (a) PSF, (b) PSF-PEI (99-1), (c) PSF-PEI (98-2) and (d) PSF-PEI (97-3) blend membrane.
3.2. Thermal properties of Membranes
Thermal properties of PSF/PEI blend membranes are portrayed in Figure 2. The first weight loss is observed at 200°C which might be due to trapped solvent. The second weight loss represents the degradation of polymer backbone at 490°C [7]. Blending of PEI does not affect the thermal properties of PSF membranes. Thermal properties of PSF membrane and blend membranes are in agreement with literature [10].

3.3. Gas Permeation Analysis

3.3.1. Effect of blend composition on gas permeability
The blend membranes were tested for gas permeation properties of CO₂ and CH₄ gases for the effect of PEI concentration on gas transport properties of membranes. The experiments were run at 6 bar pressure and 25°C. The permeability of both gases decreases with increase in PEI concentration as can be seen in Figure 3. The decrease in permeability is due to higher glass transition temperature (Tₙ) of PEI polymer which is reported in literature as 217°C [11]. Moreover, PEI has stiff, rigid and compact structure as compared to PSF [1]. Figure 4 shows an opposite trend to membrane permeability and selectivity of blend membranes is improved by increasing PEI concentration. Again, stiffness and rigidity of PEI chains caused the enhanced selectivity.

![Figure 2. TGA curves of synthesized membranes.](image)

![Figure 3. Effect of PEI weight fraction on permeation of CO₂ and CH₄ gases at 6 bar and 25°C.](image)

![Figure 4. Effect of PEI weight fraction on ideal selectivity of blend membranes at 6 bar and 25°C.](image)
3.3.2. Effect of feed pressure on gas permeability

Figure 5 and 6 shows the effect of feed pressure on CO$_2$ and CH$_4$ permeability of blend membranes. The pressure was varied from 6-10 bar. A decreasing trend in permeability of both gases is observed which is known trend for glassy polymers [7]. For both gases, native PSF membrane has the highest permeability. PSF-PEI (97-3) shows the lowest permeability of both gases. The CH$_4$ permeability of blend membranes is significantly lower than CO$_2$ gas due to larger relative size of CH$_4$ gas (3.8 Å) as compared to CO$_2$ gas (3.3 Å).

Shown in Figure 7 is the ideal selectivity of synthesized membranes. The ideal selectivity of blend membranes is increasing with increase in feed pressure. Within this pressure range, no plasticization effect was observed. Unblended PSF membrane has the lowest selectivity. However, by blending with PEI, the resultant selectivity is significantly improved. The stiffness and rigidity of PEI chains impart the diffusion selectivity and sieving ability to blend membrane. The selectivity of native PSF membrane at 10 bar pressure is 11.06 whereas for PSF-PEI (97-3) membrane it is 13.06 which accounts for 10.43 % improvement in ideal selectivity. Thus, the selectivity of PSF membrane can be improved by blending rigid glassy polymers [7]. A similar trend of effect of pressure was observed by [12]. The selectivity of PSF-PEI (97-3) blend membrane falls near attractive region for natural gas processing [13].

![Figure 5. Effect of feed pressure on CO$_2$ permeability of blend membranes.](image)

![Figure 6. Effect of feed pressure on CH$_4$ permeability of blend membranes.](image)

![Figure 7. Effect of feed pressure on ideal selectivity of blend membranes.](image)
4. Conclusion
This study presented the synthesis, characterization and gas permeation properties of polysulfone/polyetherimide (PSF/PEI) blend membranes. The polymer blends were miscible or partially miscible in low PEI concentration (< 5% PEI). The thermal properties of PSF/PEI blend membranes followed the general degradation trend of PSF membranes. Higher concentration of PEI led to decrease in CO$_2$ and CH$_4$ permeability and increase in CO$_2$/CH$_4$ selectivity due to rigidity of PEI chains. Significant improvement is observed in selectivity of PSF/PEI blend membranes. The blend membranes followed the typical behaviour of glassy polymers with respect to effect of feed pressure. This new material has the capability to be used as gas separation membrane material in CO$_2$ separation from natural gas.

5. References
[1] Dorosti F, Omidkhah M R, Pedram M Z and Moghadam F 2011 Chem. Eng. J. 171 pp 1469-1476
[2] Chung T S, Jiang L Y, Li Y and Kulprathipanja S 2007 Prog. Polym. Sci. 32 pp 483-507
[3] Mannan H A, Mukhtar H, Murugesan T, Nasir R, Mohshim D F and Mushtaq A 2013 Chem. Eng. Technol. 36 pp 1838-1846
[4] Rafiq S, Man Z, Maitra S, Maulud A, Ahmad F and Muhammad N 2011 Korean J. Chem. Eng. 28 pp 2050-2056
[5] Arabi Shamsabadi A, Kargari A and Bahrami Babaheidari M 2014 Int. J. Hydrogen Energy 39 pp 1410-1419
[6] White D M, Giles H F, Matthews R O 1983 Google Patents
[7] Mannan H A, Mukhtar H, Othman M R, Shahrun M S and Murugesan T 2015 J. Appl. Polym. Sci., 133 42946
[8] Feng S, Ren J, Li H, Hua K, Li X and Deng M 2013 Journal of Energy Chemistry 22 pp 837-844
[9] Anil Kumar P V, Anilkumar S, Varughese K T and Thomas S 2011 J. Polym. Res. 19 pp 1-12
[10] Rafiq S, Man Z, Maitra S, Muhammad N and Ahmad F 2012 J. Appl. Polym. Sci. 123 pp 3755-3763
[11] Chung T S and Xu Z L 1998 J. Membr. Sci., 147 pp 35-47
[12] Basu S, Cano-Odena A and Vankelecom I F J 2010 Sep. Purif. Technol. 75 pp 15-21
[13] Baker R W and Lokhandwala K 2008 Ind. Eng. Chem. Res. 47 pp 2109-2121

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