Development and performance evaluation of Polydimethyl siloxane/Polysulfone (PDMS/PSF) composite membrane for CO₂/CH₄ separation

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Abstract. Asymmetric polysulfone (PSF) membrane was developed by phase inversion in this study. Polysulfone (PSF) membrane was modified to develop a composite polymeric membrane. Polydimethyl siloxane (PDMS) was used to modify the PSF membrane. PDMS/PSF composite membrane was developed by dip coating of PDMS over PSF. Developed membranes were characterized in terms of membrane morphology by scanning electron microscope (SEM). Micro structure of polysulfone (PSF) membrane confirmed that developed membrane was asymmetric. Dense PDMS coating in microstructure of composite membrane was observed. Membrane swelling experiments were performed by immersing developed membranes in water for specific time period. PDMS/PSF composite membrane resisted water swelling as compared to PSF membrane. Performance of the membrane was evaluated before and after swelling within the pressure range of 2-10 bar. Reasonable decrement in permeance and selectivity was observed after membrane swelling. Thus, membrane swelling affected the separation performance of both PSF and PDMS/PSF composite membrane by decreasing the permeance and selectivity values.

1. Introduction
Membrane technology is one of the most suitable options in removal of carbon dioxide from natural gas [1, 2]. Conventional separation processes used for natural gas processing are absorption, adsorption and cryogenic distillation. All these processes have limitations of high cost and high energy consumption. The advantages in membrane based gas separation are low cost, simple process and high separation efficiency [3]. Polymeric membranes have gained importance because of their excellent separation efficiency in CO₂ removal from natural gas or methane [4]. Due to the excellent thermal and mechanical stability, polymeric membranes can be used in harsh operating conditions or offshore locations [5]. Performance of the polymeric membrane is affected by the problem of swelling in membrane. Swelling can be caused by solvent during membrane synthesis or it can be caused by humidity in feed during the separation process [6]. Swelling affects the separation performance of polymeric membrane by changing its molecular structure [7]. Cross linking and thermal treatment is one of the techniques used to overcome membrane swelling [8]. In the present work, effect of...
membrane swelling on separation performance of composite polymeric membrane was studied. Polydimethyl siloxane/Polysulfone (PDMS/PSF) composite membrane was developed. Polysulfone (PSF) is a glassy polymer with excellent thermal stability and high plasticization resistance [9]. Polydimethyl siloxane (PDMS) is a rubbery polymer having excellent permeability in CO$_2$/CH$_4$ separation [10]. Composite polymeric membrane exhibits good separation performance in CO$_2$/CH$_4$ separation [11]. Madaeni et al. [12] developed a PDMS/PES composite polymeric membrane by dip coating and manual casting of PDMS over PES. Mansoori et al. [13] analyzed the gas permeation properties of PDMS/PSF composite membrane in terms of CO$_2$ permeability and CO$_2$/CH$_4$ selectivity. CO$_2$/CH$_4$ selectivity was reported as 39.81 for PDMS/PSF composite membrane.

2. Experimental
In this work, PDMS/PSF composite membrane was developed by using dip coating method. Membrane morphology was studied by scanning electron microscopy (SEM). Separation performance of the developed membrane was evaluated for pure carbon dioxide and methane at the pressure of 2-10 bar. Permeation experiments were performed under dry and wet conditions. In dry conditions, membrane samples were tested before swelling in membrane. In wet conditions, membrane samples were soaked in water for 5 minutes prior to permeation analysis. Water was used as a swelling agent. Permeation results of both dry and wet conditions were compared to study the effect of water swelling on separation performance of developed composite membrane.

2.1 Chemicals
Commercial grade polysulfone (PSF) Udel ® 1800 was purchased from Solvay Advanced Polymers U.S. Liquid polydimethyl siloxane (PDMS) was purchased from Acros organics, Belgium. Solvents N-methyl-2-pyrrolidone (NMP) and n-hexane were supplied by Merck.

2.2 Membrane Fabrication
Polysulfone (PSF) was in powder form and dried for 24 hours before use. To develop asymmetric polysulfone membrane, a homogeneous casting solution was obtained by adding 20 wt. % of polysulfone (PSF) in NMP solvent, followed by continuous stirring of 24 hours at room temperature. After that, the casting solution was degassed for 2 hours using ultrasonic bath to remove any bubbles formed during stirring. Homogeneous dope solution of PSF was obtained with complete dissolution of polymer in solvent. Membranes were cast on glass plate using casting knife by adjusting the gap opening as 30 microns between knife and glass plate. Cast membranes were placed in non-solvent bath (deionized water) for 24 hours to complete the solvent precipitation. After 24 hours, membranes were removed from glass plates and placed for atmospheric drying of 12 hours. As a last step, after atmospheric drying membranes were dried overnight in vacuum oven at 80 °C.

2.3 Modification to Composite membrane
Composite membrane was developed by dip coating of pure polysulfone membrane. 30 wt. % of PDMS solution was prepared by adding it to n-hexane solvent followed by gentle stirring at room temperature. A homogeneous PDMS solution was obtained. Developed PSF membrane was dip coated for 10 minutes in PDMS solution by immersing the membrane in PDMS solution for the required time period. After that membrane was taken out from PDMS solution and kept for atmospheric drying for four hours. After that, membrane was thermally annealed at temperature of 80 °C for 45 minutes. After thermal treatment, PDMS/PSF composite membrane was cured with complete crosslinking of PDMS and PSF.

2.4 Characterization and performance evaluation
Micro structures of the developed membranes were studied by scanning electron microscopy (SEM). Performance of the developed membrane was evaluated before and after membrane swelling within the pressure ranges of 2-10 bar. Permeance and selectivity results of both the conditions were
compared to study the effect of membrane swelling on separation performance of developed membrane. Performance of the membrane was evaluated by using permeation equipment described by Jusoh et al.[14] in another study. Permeance values for carbon dioxide and methane and CO₂/CH₄ selectivity was estimated by method reported by Rafiq et al. [15].

2.5 Swelling Experiments
Water swelling behavior of developed membrane was studied by soaking the developed membranes in distilled water for 15 minutes. Membrane sample was cut according to the size (1.98 cm) of permeation test cell. Weight of the sample before and after swelling was measured. Swelling degree defines the total water uptake in membrane for that specific time period. Swelling degree was calculated by the following equation reported in [16].

\[
\text{Swelling degree (SD) } \% = \frac{w_2 - w_1}{w_1} \times 100
\]

where \(w_1\) is the weight of dry membrane, while \(w_2\) is the weight of swollen wet membrane.

3. Results and Discussion
PDMS/PSF composite membrane was developed by dip coating of PDMS on PSF. Membrane morphology was studied by scanning electron microscopy (SEM).

3.1 Scanning Electron Microscopy (SEM)

Figure 1. Cross sectional SEM images of (a) PSF membrane (b) PDMS/PSF composite membrane

Figure 1 shows SEM micrographs of developed membrane samples. Cross sectional SEM image (Figure 1-a) of pure polysulfone membrane shows the two layers in membrane morphology. Upper layer is dense layer with porous support layer. This shows that the developed membrane is asymmetric with two different morphologies (dense and porous) [14]. Porous layer shows different pore sizes in membrane morphology, while the uniformity in upper dense layer was observed with no defects. Figure 1(b) shows the cross sectional SEM image of PDMS/PSF composite membrane. Clear difference between the morphology of pure PSF and PDMS/PSF composite membrane can be observed from the SEM micrograph. Composite membrane shows dense morphology. Porous layer completely disappeared due to PDMS coating and pore filling phenomena was observed in case of composite membrane.
3.2 Performance evaluation before swelling

Figure 2 shows the CO₂ and CH₄ permeance of the developed PSF and PDMS/PSF composite membrane. With increase in pressure decrease in both CO₂ and CH₄ permeance was observed. This attributes to the characteristic behaviour of glassy polymers [17].

![Figure 2](image)

**Figure 2.** CO₂ and CH₄ permeance across pressure for PSF and PDMS/PSF composite membrane.

For pure polysulfone (PSF) membrane, CO₂ permeance at 2 bar was calculated as 33.4 GPU but at the pressure of 10 bar permeance decreased to 19.1 GPU. Similar behavior was observed for PDMS/PSF composite membrane that permeance decreases uniformly with increase in pressure. This indicates that there is no plasticization in developed membrane samples [18]. CH₄ permeance also decreases with increase in pressure in case of both pure and composite membrane. Both CO₂ and CH₄ permeance in case of composite membrane is less than the permeance in case of pure polysulfone membrane. This shows that PDMS coating affected the permeance of pure polysulfone membrane. Denser PDMS layer over PSF might be the possible reason for decrease in CO₂ and CH₄ permeance values.

3.3 Degree of swelling

Swelling degree for pure polysulfone membrane was calculated as 157.14%. High swelling degree in PSF membrane indicates that the membrane was completely swollen after immersion in water. However, swelling degree in PDMS/PSF composite membrane was very low (74.5%) as compared to PSF membrane. This indicates that the developed PDMS/PSF composite membrane resisted water and prevented water swelling in membrane. The possible reason of lower swelling degree in PDMS/PSF composite membrane was the water resistant nature of PDMS. Based on results of swelling degree, it can be concluded that PDMS/PSF composite membrane resisted water swelling at atmospheric conditions.

3.4 Performance evaluation after swelling

After swelling experiments, permeation analysis was carried out to check the effect of swelling on separation performance of developed membranes. Figure 3 shows the CO₂ and CH₄ permeance of pure and composite membrane after swelling.
With the increase in feed pressure, decrease in CO\(_2\) and CH\(_4\) permeance was observed for both pure and composite membrane. This indicates that there is no plasticization in membrane at any pressure [18]. If the permeance results for both CO\(_2\) and CH\(_4\) were compared with the results before swelling, then after swelling a remarkable decrease in CO\(_2\) and CH\(_4\) permeance was observed. For example, before swelling the CO\(_2\) permeance in PSF membrane at 10 bar was 19.1 GPU. But after swelling permeance value for same membrane at same pressure decreased to 2.11 GPU. Similarly in case of CH\(_4\) permeance, decrease in permeance was observed as compared to the CH\(_4\) permeance before swelling. Thus, swelling affected the performance of the pure and composite membrane by decreasing CO\(_2\) and CH\(_4\) permeance. Water swelling in membrane caused contraction in membrane pores [20], resulting a remarkable decrease in CO\(_2\) and CH\(_4\) permeance.

3.5 CO\(_2\)/CH\(_4\) selectivity before & after swelling

Figure 4 (a) shows the CO\(_2\)/CH\(_4\) selectivity of pure and composite membrane before swelling. Selectivity was observed to increase with increasing feed pressure. In case of pure polysulfone membrane, maximum selectivity at 10 bar was observed as 4.50. For PDMS/PSF composite membrane at 10 bar selectivity was recorded as 4.69. Permeation results for both PSF and PDMS/PSF composite membrane are in accordance with the dual sorption model for gas separation [19]. Figure 4 (b) shows CO\(_2\)/CH\(_4\) selectivity of developed membranes after swelling. Decrease in selectivity with increasing pressure was observed for PSF and PDMS/PSF composite membrane. This behavior is
opposite as compared to selectivity before swelling. Thus, water swelling in membrane also decreased the separation factor in both PSF and PDMS/PSF composite membrane. Before swelling, selectivity of PSF membrane at 10 bar was 4.50, but after swelling selectivity at same pressure decreased to 1.19. Similarly, for PDMS/PSF composite membrane selectivity before swelling was 4.69 at 10 bar, but after swelling selectivity decreased to 1.00. Based on these results, it can be concluded that water swelling affects the separation performance of membrane adversely by causing a remarkable decrease in separation factor of membrane.

4. Conclusions
PDMS/PSF composite membrane was developed by dip coating of PSF membrane with PDMS. Membrane morphology was studied by scanning electron microscopy (SEM). SEM micrographs reveal that developed membrane is asymmetric having dense and porous layer, while dense morphology for composite membrane was observed. Water swelling in developed membrane was studied by immersing the developed membranes in water for stipulated time period. Swelling degree value indicated that PDMS/PSF composite membrane resisted water swelling up to some extent. Permeation analysis shows that water swelling in membrane affected the separation performance of both PSF and PDMS/PSF composite membrane by decreasing permeance and selectivity.

5. References

[1] Scholes, C.A., G.W. Stevens, and S.E. Kentish, 2012 Fuel 96 pp 15-28
[2] Nasir, R., H. Mukhtar, and Z. Man, 2014 J. Appl. Sci. 14(11) pp 1186-1191
[3] Zhang, Y., Sunarso, J, Liu, S, Wang, R, 2013 Int. J. Greenhouse Gas Control 12 pp 84-107
[4] Ghosal K. and B.D. Freeman. 1994 Polym. Adv. Technol 5(11) pp 673-697
[5] Cui, L., Qiu, W, Paul D. R. and Koros, W. J. 2011Polymer 52(15) pp 3374-3380
[6] Catalano J Myezwa , D. Angelis, Sarti G. C. 2012 Int. J.Hydrogen Energy 37(7) pp 6308-6316
[7] Izák. P. Hovorka S Bartovský T Bartovská L Crespo J G. 2007 J. Memb. Sci. 296(1–2) pp 131-138
[8] Aziz, F. and A.F. Ismail. 2010 Sep. Purif. Technol. 73(3) pp 421-428
[9] H.A. Mannan, Mukhtar H, and T. Murugesan. 2014. Appl. Mech. Mater. 625 pp 172-175
[10] Banihashemi, F., M. Pakizeh, and A. Ahmadvand. 2011 Sep. Purif. Technol.79(3) pp 293-302.
[11] Sadrzadeh M, Amirilargini M, Shahidi K, and Mohammadi T. 2009 J. Memb. Sci., 342(1–2) pp 236-250
[12] Madaeni, S.S., M.M.S. Badieh, and V. Vatangool. 2013 Polym. Eng. Sci. 53 (9) pp 1878-1885
[13] Mansoori SAA, Pakizeh M, and J. A. 2011 J. Memb. Sci. Technol., 1(106)
[14] Jusoh , Lau. K.K, Shariff. A. M. Yeong. Y. F. 2014 Int. J. Greenhouse Gas Control, 22 pp 213-222
[15] Rafiq. S., Man. Z., Maitra. S., Maulud. A., Ahmad. F 2011 Korean J. Chem. Eng, 28(10) pp 2050-2056
[16] Chen. J. Li. J., Lin. Y., and Chen. C. 2009 J. Appl. Polym. Sci. 112(4) pp 2425-2433
[17] Mannan. H.A., H. Mukhtar, and T. Murugesan. 2015 App. Mech. Mat. 699 pp 325-330
[18] Nasir. R., Mukhtar , Man. Z. Dutta , Shahrun Abu Bakar. 2015 J. Memb. Sci. 483 pp 84-93
[19] Nasir. R., Mukhtar, Man. Z., Shahrun Abu Bakar 2015 RSC Advances, 5(75) pp 60814-60822
[20] Farid, O.M. 2010. Ph.D. Thesis. University of Nottingham, United Kingdom.

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