Potential of Polysulfone/Polydimethyl Siloxane Thin Film Composite (PSf-PDMS-TFC) Membrane for CO_2/N_2 Gas Separation

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Potential of Polysulfone/Polydimethyl Siloxane Thin Film Composite (PSf-PDMS-TFC) Membrane for CO_2/N_2 Gas Separation

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Abstract. The capture and storage of carbon dioxide has been identified as one potential solution to greenhouse gas driven climate change. Efficient separation technologies are required for removal of carbon dioxide from flue gas streams to allow this solution to be widely implemented. This study is mainly focusing on the effect of different concentration of polydimethyl siloxane (PDMS) in dip-coating solution on the membrane's performance. The asymmetric thin flat sheet membrane was prepared by dry/ wet phase inversion process consisting 20 %w/v of polysulfone (PSf) as the support layer polymer and 80 %w/v of N- methyl-2-pyrrolidone (NMP) as the solvent. PDMS was coated on the support PSf membrane with the composition of 10, 15 and 20 wt% of PSf in n-hexane respectively. The characterization of morphology of TFC membrane will be conducted by using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR). The membrane's performance and the selectivity of CO_2/N_2 separation will be determined by conducting gas permeation test. The result obtained, show that membrane with highest concentration of PDMS in dip-coating solution give a highest performance in selectivity and unfortunately it contributes to lower permeability. It is vice versa from the membrane without PDMS in the top layer which gives highest value of permeability but lowest in selectivity. From the characterization and permeation test of the membrane, hereby the membrane with highest percentage of PDMS should be selected for the future development of membrane due to its highest value of selectivity which contributes to highest efficiency in separating the gas.

1. Introduction

Enhancements of the greenhouse effect in the worldwide have contributed to the study that can recover this problem. The most abundant greenhouse gas CO_2 has risen from preindustrial levels of 280 parts per million (ppm) to present levels of over 365 ppm [1]. Carbon dioxide, CO_2 arise from different emission sources, particularly flue gas from power stations, steel works and chemical industries. According to the study done by Mitsubishi Heavy Industries, Ltd., 98% of CO_2 emissions are derived from fossil fuel combustion, exhausted to atmosphere by flue gas stacks from furnace boilers, gas

turbines and engine emission. The content of the flue gases that released at atmospheric pressure usually containing Oxygen, Carbon Dioxide, Nitrogen, NO_x, SO_x and dust particulate impurities.

The separation of gas by thin barrier termed as membranes is a dynamic and rapidly growing field, and it has been proven to be technically and economically superior to other emerging technology. Materials for effective separation of gases can follow one of two overall strategies; increasing the rate of diffusion of gases through the polymeric structure and increasing the solubility of gases through the polymeric structure. Unfortunately, there is frequently a trade-off between selectivity and permeability [2]. In preparation of gas and vapour separating membranes, a polymer should have the following intrinsic properties:(1) High selectivity for the components to be separated, (2) High permeability for the permeating components and (3) High life expectance under operating condition such as good thermal, chemical and mechanical stability. In this particular study, PSf and PDMS were selected as a polymer in developing support membrane and thin film due to their great characteristic such as a tough and rigid polymer, high-temperature properties and chemically inert.

2. Methodology

2.1 Chemicals

PSf pellet purchased from Sigma Aldrich (M) Sdn. Bhd. PSf used is without any modification. Anhydrous NMP supplied from Sigma Aldrich (M) Sdn. Bhd was used as a solvent. Water is used as a coagulation medium. CO_2 and N_2 used in permeation test.

2.2 Membranes Preparation

With the amount of 20% PSf pellet, it is been added gradually into beaker contains 80% of NMP solvent and mixed by mechanical stirrer. The mixing step continues for at least 7 to 8 hours till homogenous and clear solution was formed. The dope solution was prepared within a range of temperature between 60^{o}C to 80^{o}C.

2.3 Dope Solution Casting Process

The dope solution was casted on a glass plate by using a glass rod. It is followed by the immersion in a water bath in accordance of dry/ wet phase inversion process. Casting process was conducted at room temperature (30^{o}C±2). The cast membrane was immersed into water to initiate delamination and slightly peel the membrane film from the glass plate. After that the membrane is transferred and immersed into the coagulation medium with water act as a coagulation medium for 1 hour and further dried in the air at room temperature.

2.4 Thin Film Composite Membrane Preparation

The dip-coating solution is prepared by mixing PDMS with n-hexane solvent with stirring. The dip-coating solution is consisting of three different percentages of PDMS which were 10%, 15% and 20% in n-hexane solvent. The prepared asymmetric PSf membranes were placed on a glass plate. The coating solution is placed on the PSf membrane by dropped the PDMS/n-hexane solution on the skin layer of the membrane. PSf membrane is allowed to dry for 5 minutes and cure process is carried out in oven at 60^{o}C for 1 hour.

2.5 Gas Permeation Test

The thin film composite of PSf/ PDMS membrane is tested on pure gas CO_2 and N_2. The pure gas will be tested at pressure in the range of 0.5 bar to 1.5 bar. The time of the first bubble formed and volume difference of the soap water by each membrane was taken.

The gas permeation rate (P) was calculated by using equation as followed:

$$P = \frac{Vl}{At\Delta p}(cm^3(STP)cm)/(cm^2 s.cmHg) \quad (1)$$

The permeance (P/l) was calculated using equation as followed:

$$\frac{P}{l} = \frac{V}{At\Delta p}(cm^3(STP)cm)/(cm^2 s.cmHg) \quad (2)$$

where, V = the volume (cm^3) displaced in time () A = the effective membrane area (cm^2) Δp=The transmembrane pressure expressed in cmHg.

Meanwhile, Selectivity was calculated using this equation:

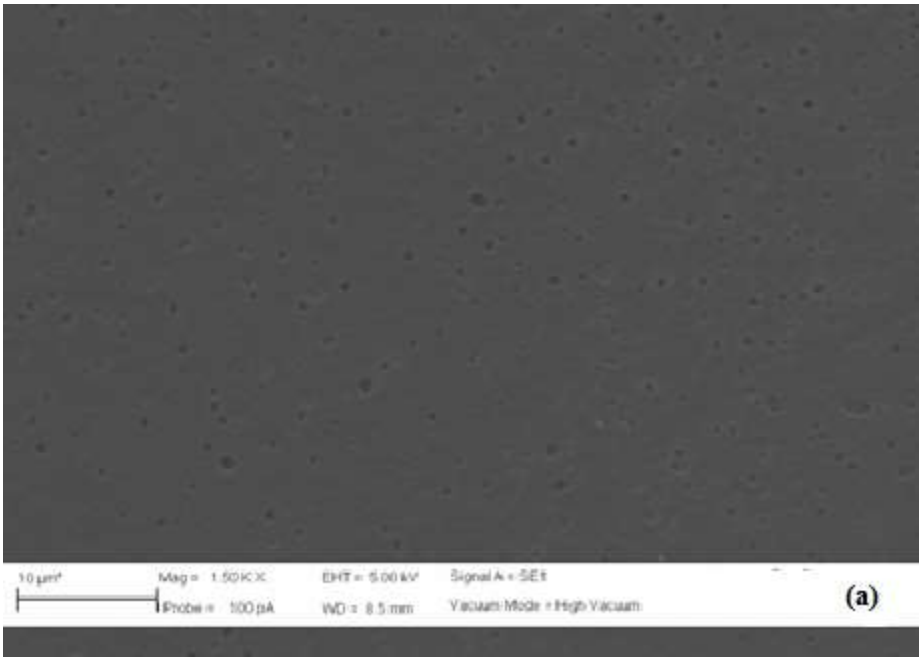
$$\alpha = P_i/P_j \quad (3)$$

P_i = Permeance of one gas component
P_j = Permeance of another gas component

2.6 Membrane Characterization (SEM and FTIR)
The prepared membrane is characterized using two methods which are by using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Radiation (FTIR). There are several parameters that will be evaluated from this study which were morphological studies and effect of concentration of polymer.

3. Results and Discussion

3.1 Effect of Dip Coating Percentage on the Membrane Morphology
Structure of the surface membranes produced from 0%, 10%, 15% and 20% of PDMS are illustrated in Figure 1 (a), (c), (e) and (g) respectively. As shown in the surface structure of the membrane, as the amount of percentage of PDMS increased, a fewer number of macro-voids in the membrane structure are observed. Figures 1(b) illustrate that membrane without dip coating solution figured as finger-like macro-voids. The finger-like macro-voids ends at the top surface of the skin layer, making the surface defective with pin-holes [4]. The enhancement of the PDMS illustrate in Figure 1 (d), (f) and (h) shows that the sub-layer has a nodular structure, diminishing the chance of pin-hole formation at the membrane surface.
In the sequence of Figure 1 (d), (f) and (h), a new selective layer was formed and covered the entire surface pore in order 10%, 15% and 20% of PDMS percentage respectively. The presence of 10% PDMS in the dip coating solution has no obvious effect on the cross section structure of the membranes. Proceeding in increasing the percentage of PDMS results in higher polymer concentration in the upper layer of the membrane forming films and in a denser coating layer with smaller pores in the final membranes.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EHT = 5.00 kV
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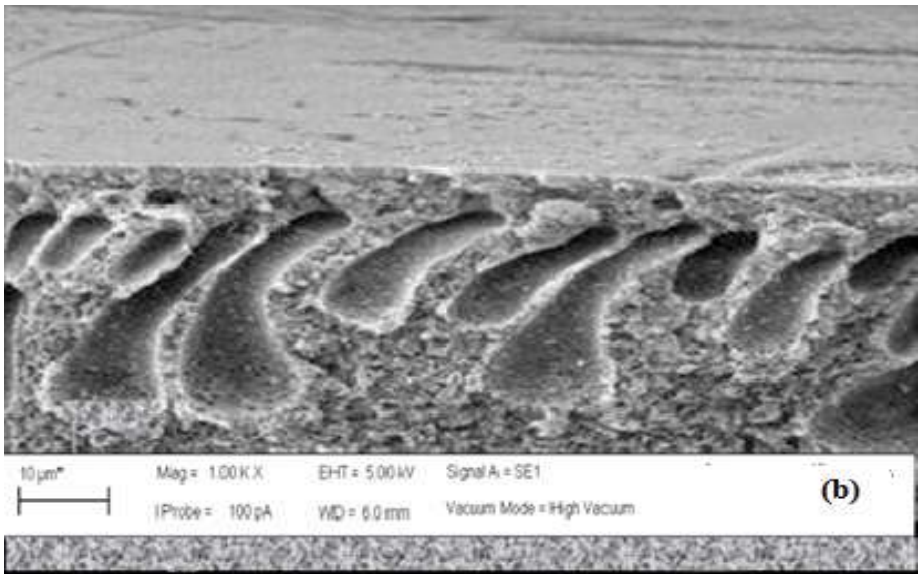
Probe = 100 pA
WD = 8.5 mm
Vacuum Mode = High Vacuum
(a)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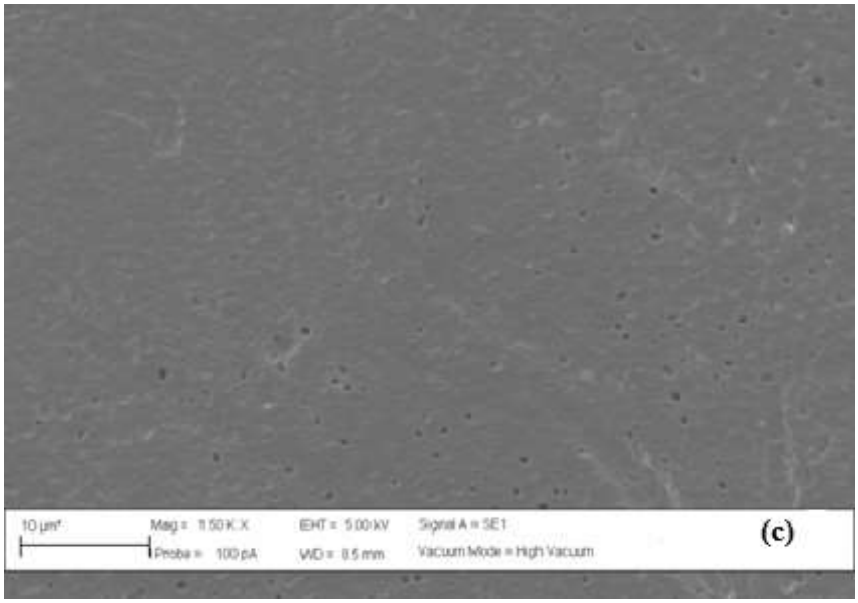
(b)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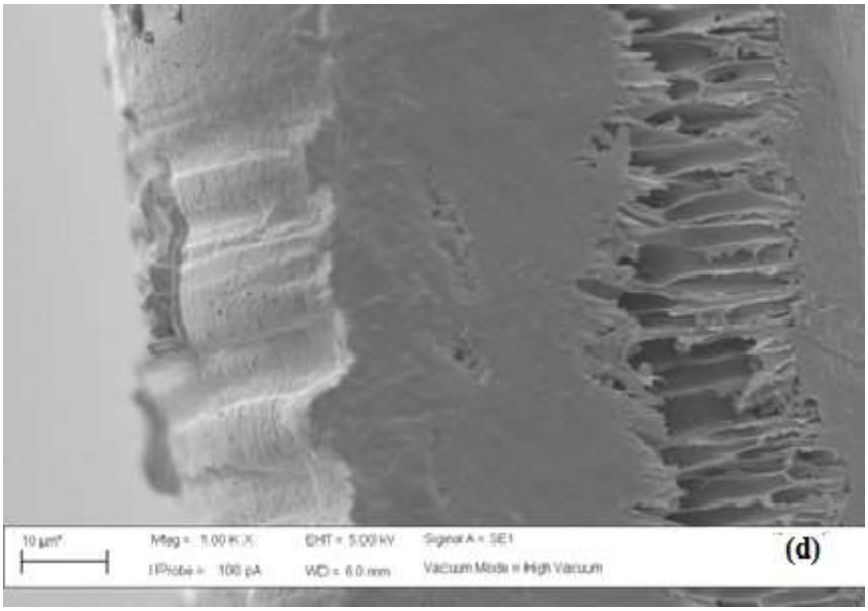
(c)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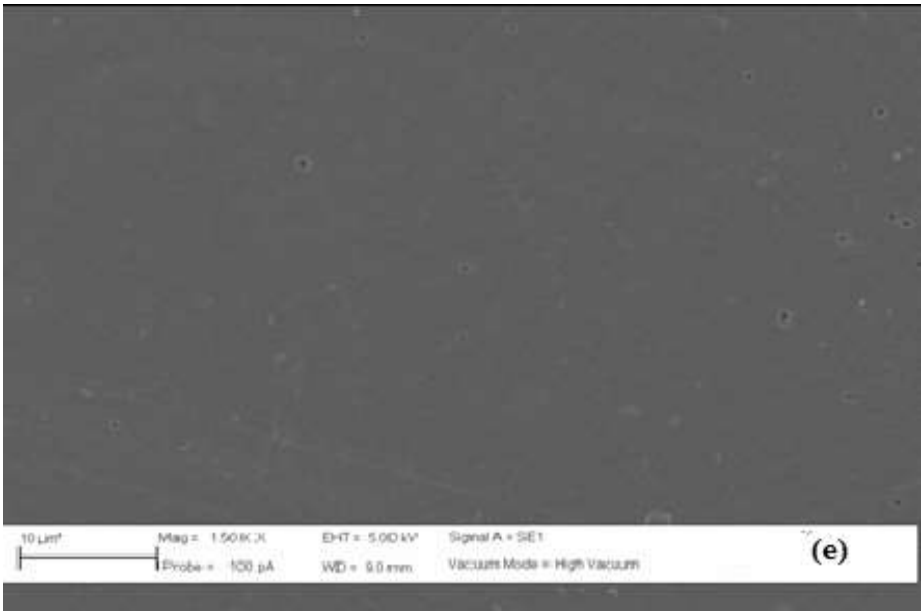
(d)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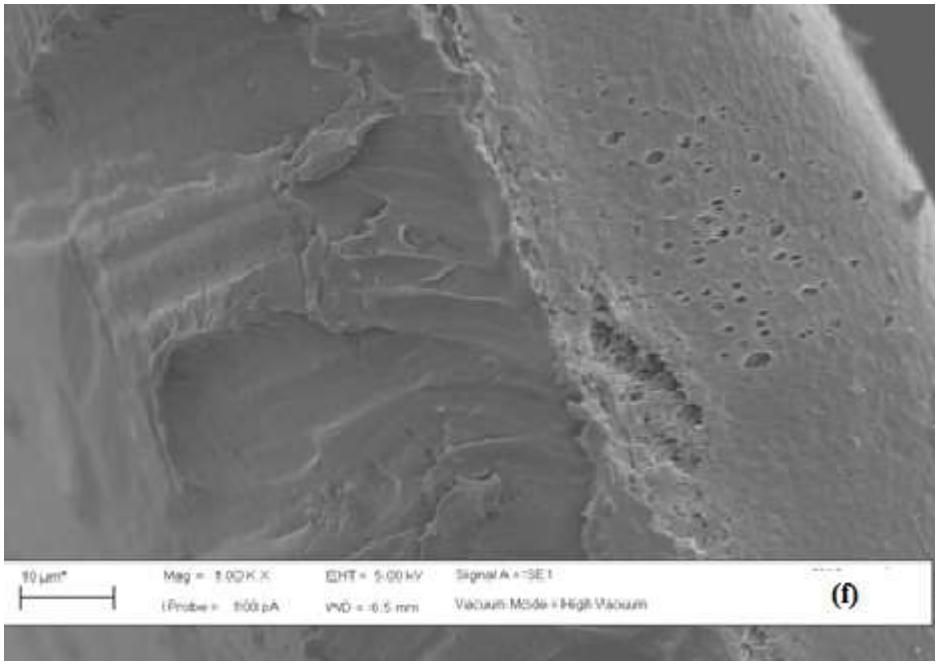
(e)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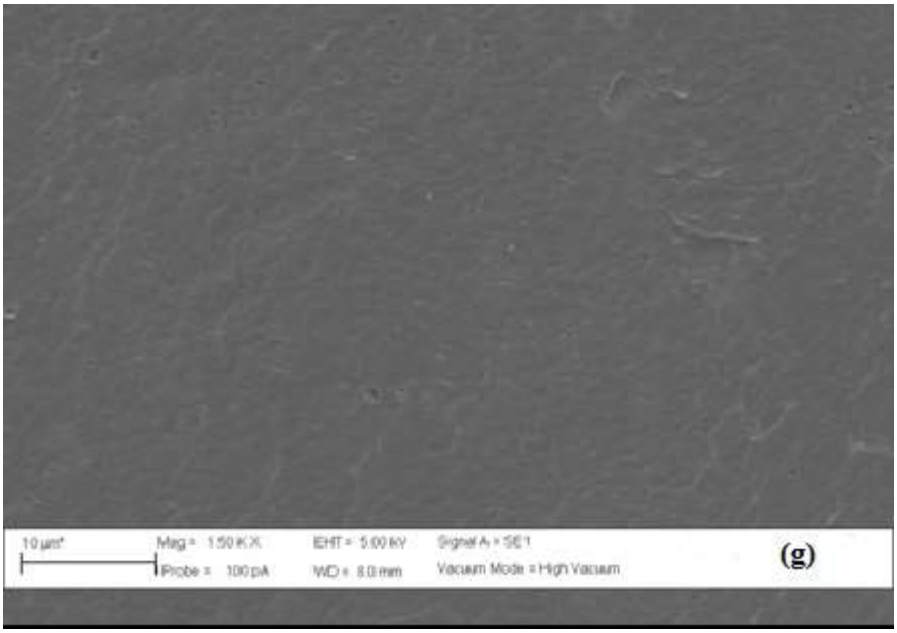
(f)



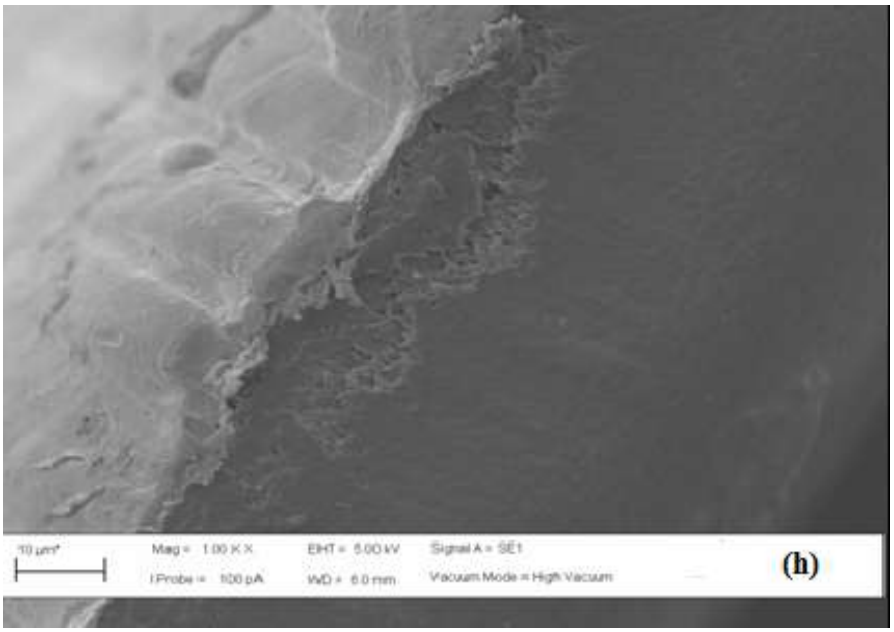


Figure 1. (a) Surface Image of PSf Membrane with 0% PDMS at Magnification 1.50 K X; (b) Cross Section Image of PSf Membrane with 0% PDMS at Magnification 1.00 K X; (c) Surface Image of PSf Membrane with 10% PDMS at Magnification 1.50 K X (d) Cross Section Image of PSf Membrane with 10% PDMS at Magnification 1.00 K X (e) Surface Image of PSf Membrane with 15% PDMS at Magnification 1.50 K X (f) Cross Section Image of PSf Membrane with 15% PDMS at Magnification 1.00 K X (g) Surface Image of PSf Membrane with 20% PDMS at Magnification 1.50 K X (h) Cross Section Image of PSf Membrane with 20% PDMS at Magnification 1.00 K X.

3.2 Effect of Concentration of Top Layer on the FTIR Analysis

FTIR spectra of 0%, 10%, 15% and 20% of PDMS concentration are shown in Figure 2 (a), (b), (c) and (d) respectively. The spectrum indicates the functional groups that presence in the sample, which are siloxane group (Si-O) stretching vibration at 1000-1100 cm^{-1} and sulfone group (S=O) at 1150-1300 cm^{-1}. The changes in the intensity of the sulfone group can be attributed to the consumption of sulfone group due to increasing siloxane group content. The characteristic IR absorption bands for PSf polymer will decrease in the sequence of 0 % > 10 % > 15 % > 20 % of the PDMS solutions. This is the consequence from the siloxane group is taking place of sulfone group in their reaction. The IR spectrum for the PSfs samples prepared with a 0% of PDMS content shows a peak at 1243.85 cm^{-1} indicating the sulfone groups still in the support polymer sample. For PSf samples prepared with 10, 15 and 20% PDMS content, there are no apparent peaks at 1243.85 cm^{-1}, suggesting the sulfone group is reacted with siloxane groups. The Si-O absorption cannot be clearly detected for the polymer samples prepared at 0% PDMS content. For 10, 15 and 20% PDMS the changes in the intensity of Si-O groups were due to the addition of percentage of PDMS.

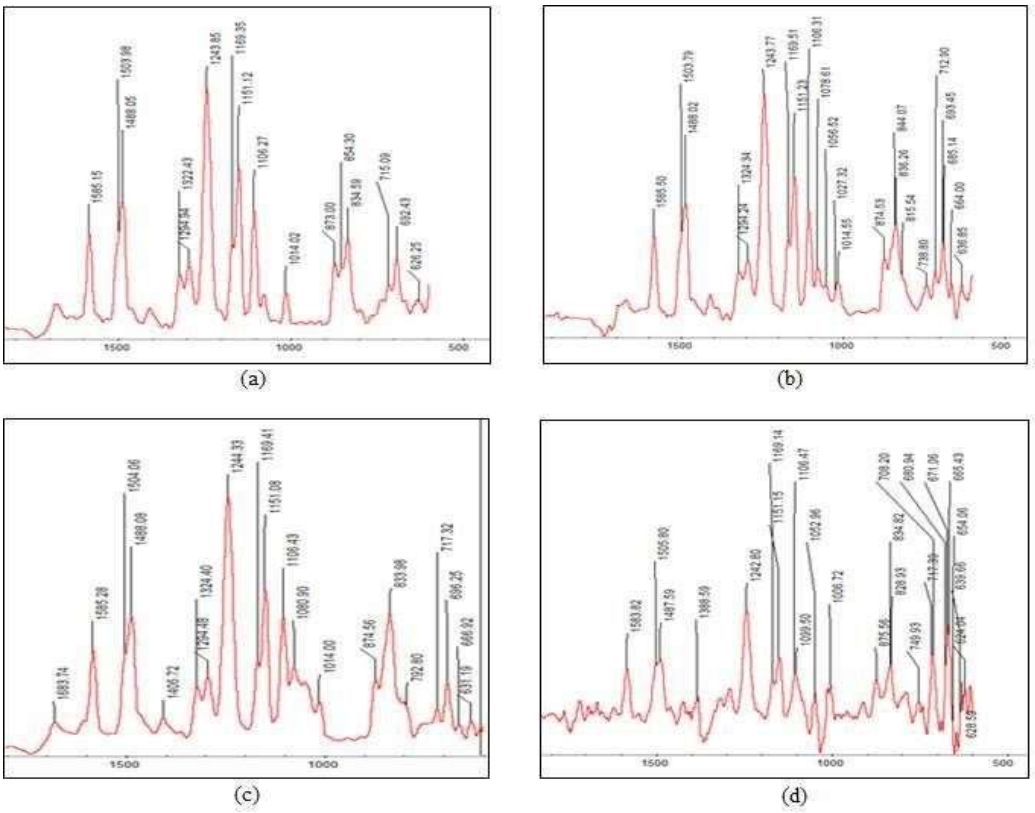


Figure 2. FTIR Absorbance Peak for (a) 0% PDMS of PSf-PDMS Membrane; (b) 10% PDMS of PSf-PDMS Membrane; (c) 15% PDMS of PSf-PDMS Membrane; (d) 20% PDMS of PSf-PDMS Membrane

3.3 Effect of Concentration of Selective Top Layer on the Membrane Performance for Gas Separation

The permeability graph trends obtained in Figure 3 and Figure 4, it is show that the permeability of CO_2 is slightly higher than permeability of N_2 due to kinetic molecular diameter for CO_2 is much smaller which is 3.3 angstroms rather than kinetic diameter of N_2 molecule approximately 3.6 angstroms. CO_2 molecule is easier to pass through the membrane due to its molecular diameter is smaller than N_2 and resulting higher permeability of CO_2 gas [5]. The changes in permeability of single pure gases with change in feed pressure. The decrease in viscosity of polymer for the dip coating solution can allow

higher diffusion of gas rate in sub-layer which makes the permeability of certain gas to be higher. As a result, thin film composite membrane with a thin and porous skin layer and open cell sub-layer will result higher permeability value. Meanwhile, N_2 permeability is slightly increased as well as feed pressure is increase. Feed pressure is acting as a driving force of the N_2 molecule to pass through the membrane. Since larger driving forces were applied to N2 molecule, it will contribute to a lot of N_2 particle will pass through the polymeric membranes then resulting to high permeability value.

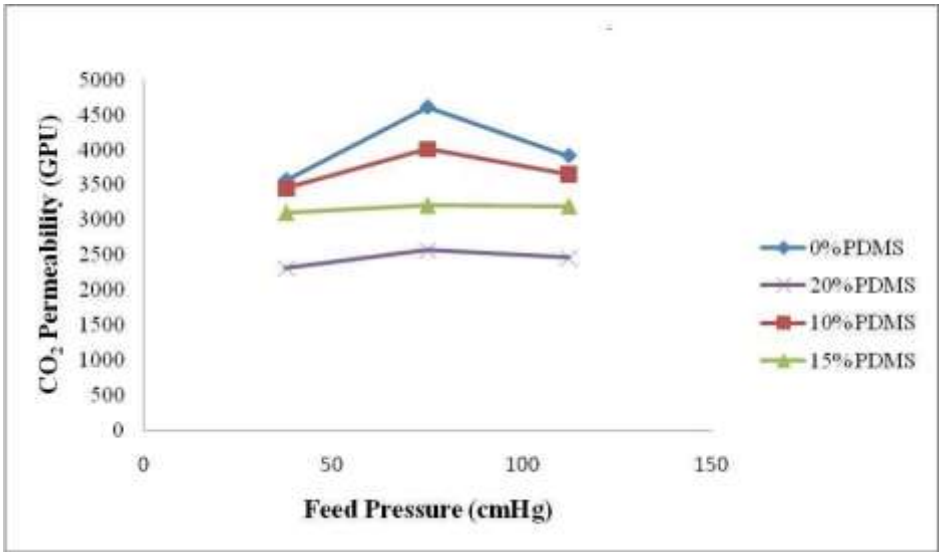


Figure 3. CO_2 Permeability versus Feed Pressure

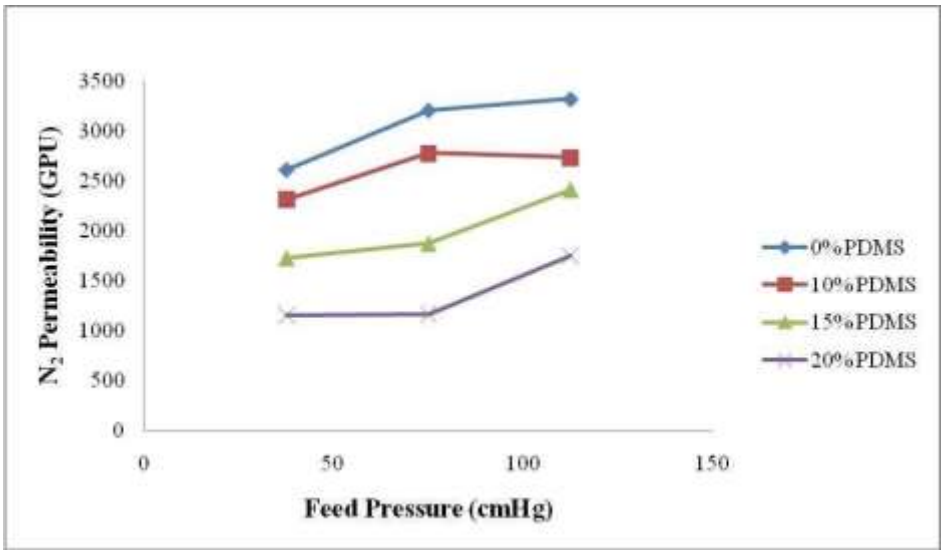


Figure 4. N_2 Permeability versus Feed Pressure

By referring to the Figure 5, the selectivity of the membrane increase with the increase of the percentage of PDMS in the order of 0 % < 10 % < 15 % < 20% of the PDMS concentration. Membrane with concentration 20% PDMS exhibit highest selectivity about 1.57 because increasing the polymer concentration, resulted a denser and thicker skin layer membrane. Furthermore, since the polymer concentration in dip coating solution is increased, it was observed that the skin layer thickness increased while both mean pore size and surface porosity decreased. The uncoated membranes seem to exhibit lowest selectivity probably due to existence of defect (pores) and the enhancement of free volume in the

thin skin layers. The relationship between selectivity and the feed pressure show that with increasing the feed pressure, it is resulted lower selectivity. This is suggesting that when there was large driving force that drive the molecule to pass through the membranes, the efficiency of separating the gas is getting lower hence contribute to the bad performance.

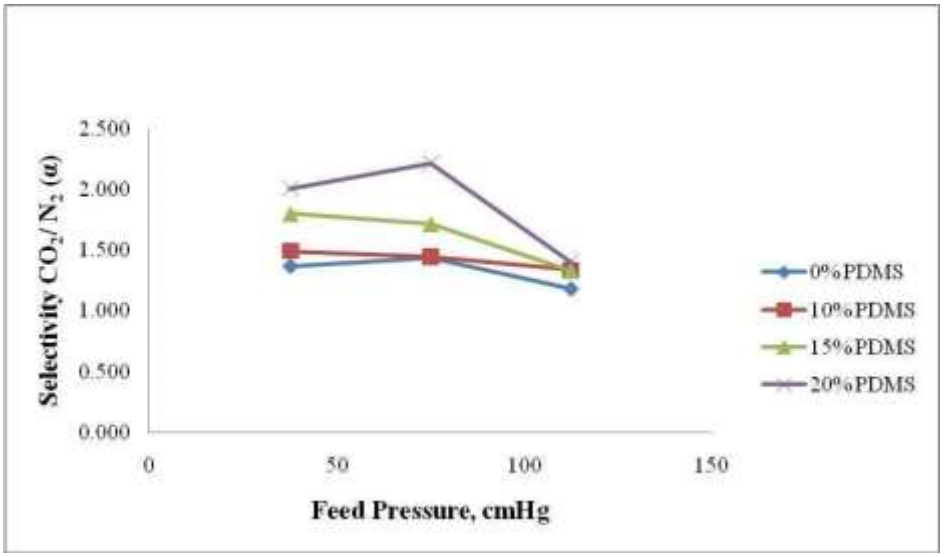


Figure 5. CO_2/ N_2 Selectivity versus Feed Pressure

4. Conclusion

This study successful developed the TFC PVDF/ PEBAX membrane. More sponge-like asymmetric structures were formed across the membrane wall and the macro void formation is suppressed. This is due to the higher viscosity of the casting solution that delayed the phase inversion rate (kinetic effect) which results in a sponge-like structure.

Acknowledgement

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5. References

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