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Influence of PVDF/Pebax TFC Casting Temperature towards CO_2/N_2 Gas Separation

M. S. Abdul Wahab and A. R. Sunarti*

Faculty of Chemical Engineering and Natural Resources, Universiti Malaysia Pahang, Gambang - 26300, Pahang, Malaysia; sunarti@ump.edu.my

Abstract

Objectives: A Thin Film Composite (TFC) membranes has been successfully synthesized via introducing casting temperature adjustment to counter the permeability-selectivity conflict. **Methods:** 15 wt% Polyvinylidene Fluoride (PVDF) was diluted in 85 wt% N-Methyl-2-Pyrrolidone (NMP) and cast on a glass plate at 40°C-80°C. To form the TFC, 3 wt% of Polyether block amides (Pebax 1657) was used as a coating layer on top of the PVDF substrate. **Findings:** The surface roughness of the samples cast at 60°C was measured to be 102.6 nm while the other is less than 100 nm and the CO_2 and N_2 flux was measured to be 749 and 13 barrer respectively with CO_2/N_2 selectivity of 58.54. **Application:** The result has been plot on Robeson 1991 and it fall beyond the upper boundaries, indicate that the future of coating material and casting techniques can be further explored to maximize the limit of material capabilities.

Keywords: Composite Membrane, Coating Method, CO_2/N_2 Separation, PEBAX, PVDF

1. Introduction

Polymeric membrane system possesses several criteria including low capital cost, low energy requirement, high mechanical resistance, energy efficient and ease of operation over conventional separation techniques such as cryogenic distillation and pressure swing adsorption[1]. However, every good in polymeric membranes come with it prices when there is a slight weakness in them which discover for ages and popular said as a trade-off between permeability and selectivity by Robeson's upper bound curves. Figure 1 shown in the upper bound that was plot in 1991 and 2008 where Robeson analysed all available permeation data of polymeric membranes for CO_2/N_2 gas pairs and plotted each membrane's permeability against selectivity for the gas[2].

From the plot, a visible scattered data revealed that there is an upper bound which is the limit of gas polymeric membranes performance for the selectivity-permeability relationship, such that the selectivity decreases linearly with increasing permeability. Since then, the development of polymeric membrane materials that can surpass Robeson's upper bound has been the central topic in polymeric membrane development for gas separation.

Recently, work on membranes matrix modification to enhance the separation efficiency by having several polymeric materials combines with an inorganic porous substance such as Zeolite, Carbon Nano Tube (CNT) and Zeolitic Imidazolate Framework (ZIF) or often called Mixed Matrix Membranes (MMM) and Thin Film Composite (TFC)-multiple layer combination, show a significant improvement, but still have a room for an improvement.

The focus of this work is to study how the surface roughness as a result of different casting temperature influence the separation efficiency of the PVDF/Pebax 1657 TFC and did the involve parameter manage to surpass the Robeson trade-off limits. Few works on casting techniques which involve temperature iteration has shown a significant improvement towards the membranes efficiency but none are specific for CO_2/N_2 Separation. In[3] his work reported that membranes cast at 100°C perform better than that cast at low temperature due to having

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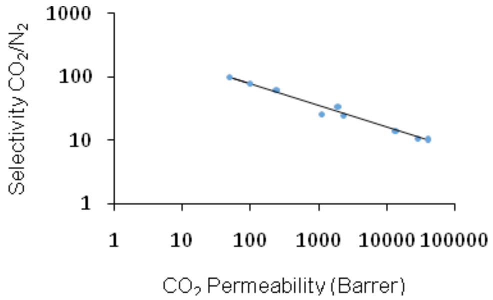

Figure 1. Robeson upper bound of gas selectivity vs permeability

strong mechanical stability. But, by increasing the casting temperature, the membranes might turn out to be brittle. To encounter with the high and low temperature study, Pebax 1657 is chose as a selective layer because of its good CO_2 adsorbent, flexible and high mechanical strength due to nylon 6 contents in the polymer matrix[4].

2. Materials and Methods

Pallet of analytical grade Polyvinylidene Fluoride (PVDF) was purchased from Sigma Aldrich. Pebax 1657 (60% Polyether and 40% polyamide) was purchased from Arkema France. Two solvent used in this study which is ethanol and N-Methyl-2-pyrrolidone for dope preparation was supplied by Fisher Scientific. There are two gases used, 99.99% purified CO_2 and N_2 which will be used for TFC performance study was supplied by Azam Synergy.

Preparation of PVDF substrate was started by diluting 15 wt% PVDF pellet in 85% NMP and uniformly stirred at 80°C for about 7 hours until all the pellets dissolved. The PVDF dope solution was then degassed by leaving at room temperature for 24 hours to achieve bubbles free solution. The solution was cast on a glass plate at room temperature, 40°C, 60°C and 80°C by using automatic casting machine with an adjustable temperature control with thickness of 0.03 mm before submerging in a water bath for 2 hours and then dried at room temperature for 24 hours. 3 wt% of Pebax 1657 was dissolved in the combination of 70/30 ethanol/water at 80 °C for 2 hours until a homogeneous, clear and dilute solution was obtained. This Pebax 1657 coating solution was left at room temperature for 24 hours before it was coated on the PVDF substrate. The dip coating method was used where 5 ml of the Pebax 1657 solution was poured into a glass dish only to damp the dish surface then PVDF substrate was dip one side for 5 seconds. The film dimension was fixed to be 5 cm diameter. Pebax 1657 was coated on the PVDF substrate by 3 times, where every coating the TFC was dried at 60 °C for 15 minutes to let the solvent vaporize. For extra vaporization of the solvent, TFC was further dried at 60 °C for another 24 hours.

2.1 Characterization

The TFC was characterized chemically and physically to detect the presence of each functional group of molecule in the sample. Fourier transform infrared spectroscopy, FTIR Perkin Elmer-Spectrum 100, which allow the samples to absorb all different wavelength characteristic produced from a beam that later will be computerized to obtain the desired data in the form of wave numbers, cm^{-1}. The cross-sectional area of the sample was examined by Scanning electron microscope, SEMJSM-7800F. All samples were freeze and fractured in liquid nitrogen to get the smooth cutting without any part of the membrane blocking the cutting surface for SEM analysis. The sample was then flush with nickel coating to avoid any charge build up by the electron beam which often called space charge effect during surface imaging. The surface topography of the TFC was examined by atomic force microscopy, AFM JPK-NW-Nano-opticsfor any visible peak of roughness due to temperature exposure during film casting.

2.2 Single Gas Permeation Test

Each gas CO_2 and N_2 was tested individually by allowing them to flow at 2 bar toward the membrane cell and the flow rate of the permeate was measured by a bubble flow meter. Equation (1) was used to calculated the gas permeability and it was expressed in Barrer by taking the conversion factor into account [1 Barrer = 1 x 10^{-10} cm^3 (STP) cm/(cm^2scmHg)].

$$P = \frac{1x10^{10}Vl}{At\Delta p} \tag{1}$$

Where P is the permeability, l is the thickness of the membrane in cm, A is the effective membrane area in cm^2, V is the volume in cm^3 displaced in time t(s) and Δp is the trans-membrane pressure expressed in cmHg. The membrane selectivity is the membrane ability to separate the two gases (A and B). It is the ratio of the Permeance A and B - Equation (2). The TFC used have a diameter of 5 cm with 3 times data replication for each sample.

$$\alpha_{AB} = \frac{P_A}{P_B} \quad (2)$$

3. Results and Discussion

3.1 FTIR Characterization

The chemical formula and the spectra of PVDF, Pebax 1657 and PVDF/Pebax 1657 TFC was showed in Figure 2 and 3 respectively. (a) The TFC cast at room temperature, (b) 40°C, (c) 60°C and (d) 80°C exhibit the combination of both PVDF and Pebax 1657 wave numbers. CH_2 deformation of PVDF and Pebax 1657 molecules for all samples was detected as strong bending vibration in range of 1350-1470 cm^{-1}. In[5] the strong stretching vibration of C-F bonding of the dual fluoride found in PVDF was spot around 1000-1400 cm^{-1}. Pebax 1657 was detected through several molecules bonding starting with ether stretching (C-O) and nylon-6 with stretching of N-H at 1000-1300 cm^{-1} and 3278 cm^{-1} respectively[6]. The amide segment of the elastomer was transmitted with the stretching of C=O at 1640 cm^{-17}. Other peaks in the spectrum of the composite membrane are in range of 2869-2939 cm^{-1} can be attributed to the asymmetric and symmetric stretching of the C-H bond[7]. The spectra proved that no additional chemical interfere in the TFC development and no chemical disappear during solvent vaporization and heating procedure.

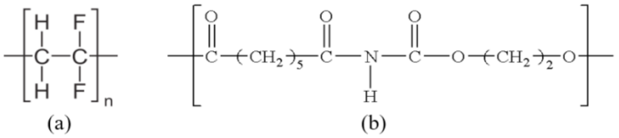

Figure 2. Chemical structure for (a) PVDF and (b) Pebax® 1657

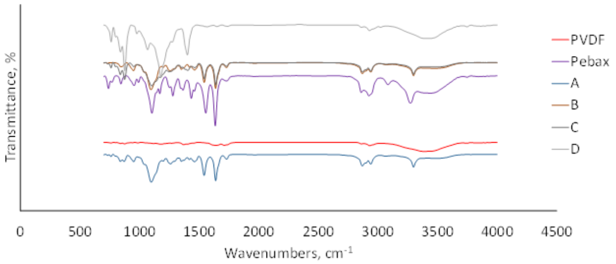

Figure 3. FTIR spectroscopy of the TFC cast at room temperature (a), 40 °C (b), 60 °C (c) and 80 °C (d)

3.2 Surface Morphology

Figure 4 shows the cross-sectional view of the TFC. The membranes exhibit an asymmetric structure with a top side of Pebax 1657 layer, followed with a finger-like macro voids region and a spongy porous bottom. The presence of finger-like structure was believed as an effect from the rapid liquid-liquid demixing during the wet phase inversion in the water bath. The void occurs when the solvent rapidly escaped from the top part of the film and leave the large and long finger-like structure. As we all know, porosity and void might influence the membrane flux[8]. The film was left for 2 hours in the water to let the rest of the solvent slowly come out from the bottom and the spongy porous might be the result from the instant solidify of the top side and the slow pace of solvent demixing[9]. From the cross-sectional view, it is observed that changes in casting temperature have not influenced the pore and void formation of the film.

3.3 Surface Roughness

The used of atomic force microscopy is to view any visible changes of surface roughness of the PVDF/Pebax 1657 TFC as a result of the different substrate casting temperature. Both plane and three-dimensional view of the surface topography was shown in Figure 5 and its respective average roughness parameter, RA and the root mean square, RMS of each sample tabulated in Table 1. Based on the image, the samples which cast at 60°C is the best among all with a rougher surface and a small bump compared to the nanoscale roughness on the other samples. The dark region of the image attribute to the valley and the bright white is the rough peak. The change in temperature might disturb the arrangement of the polymeric chain during dry/wet phase inversion of the film and from the lamellar

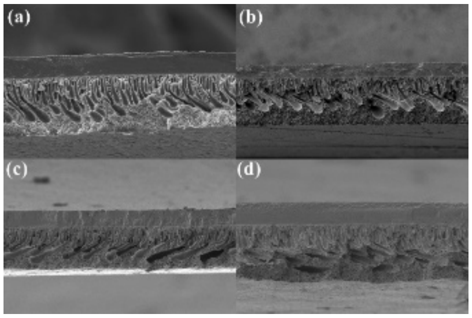

Figure 4. SEM micrograph of TFC cross section, (a) cast at room temperature, (b) 40 °C, (c) 60 °C and (d) 80 °C

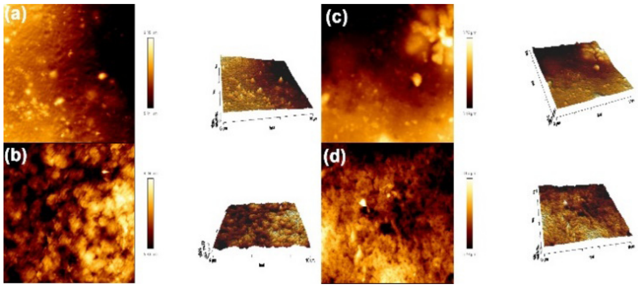

Figure 5. AFM micrograph of TFC which the substrate cast at several temperatures; (a) room temperature, (b) 40 °C, (c) 60 °C, and (d) 80 °C

Table 1. The roughness parameters of the cast film

Samples	RA (nm)	RMS (nm)
A	44.51	52.73
B	47.12	58.04
C	102.6	131.7
D	59.29	78.09

structure which can be clearly seen in figure 4 (a) and (d). This kind of hard phase structure attributes to the crystallinity of the film[10].

3.4 Separation Performance Study

The separation performance of the TFC has been studied via single gas permeance test and the result is tabulated in Table 2. For all samples, CO_2 permeability record a higher figure compared to N_2 as normal gas permeability always follow the kinetic diameter of the gas which $CO_2<N_2$, 3.33 Å and 3.68 Å respectively. Even though gas permeability decreases with increasing of casting temperature but still a significant improvement was observed for the gas selectivity. The data agree with the surface roughness of the samples which the roughness order from smooth to rough is room>40>80>60. The change in casting temperature has disturbed the polymeric chain and result in surface topography of the film.

PVDF/Pebax 1657 is a TFC with a combination of both dense and porous membranes, so the gas transport of the membranes follows a three steps transport behaviour which is the feed side penetrant sorption, penetrant diffusion through the film, and the desorption of the permeate[11]. The rough surface of the TFC provides large adsorption site compared to the smooth one and selectively transport the gas molecules. By having such nanoscale rough surface, the film possibly has a less free volume compared to a rough surface of the one cast at 60°C, so the ability to transport and separate the gas molecules decrease. To answer the objective of the work, the data has been plot on a Robeson curve as in Figure 6. The samples which the PVDF substrate cast at 60°C manage to surpass the trade-off limits with CO_2 permeability and gas selectivity of 749 barrer and 58.54 respectively. As discussed before, the top-notch performance is a result of the surface topography of the film.

Table 2. Gas permeability of each of the samples

Casting Temperature, °C	PCO_2, Barrer	PN_2, Barrer	α CO_2/N_2
Room	1806	132	13.69
40	1821	179	10.17
60	749	13	58.54
80	145	11	13.16

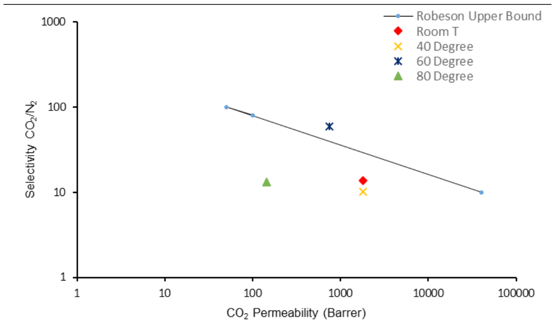

Figure 6. Robeson's plot of the data

4. Conclusion

PVDF/Pebax 1657 TFC was successfully fabricated by dry/wet phase inversion technique. The variations of casting temperature has influence the surface roughness of the film and more or less play a big role towards gas separation. The suitable temperature condition was found to be at 60°C when the gas selectivity able to cross the Robeson trade-off limits. It can be concluded that, casting temperature is one of the factors to be consider for membranes development as the exposure of the film during solvent vaporization could dramatically increase the film roughness and further increase the separation efficiency. The novelty of this work is on the casting techniques itself where many researchers' disregards that exposing the dope solution to certain temperature could affect the polymeric chain and alter the film topography.

5. Acknowledgement

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6. References

1. Nemati M, Hosseini SM. Thin film heterogeneous ion exchange membranes prepared by interfacial polymerization of PAA-co-Iron-Nickel oxide nano-particles on polyvinylchloride based substrate. International Journal of Engineering. 2016 Mar; 29(3):297-305.
2. Robeson LM. The upper bound revisited. Journal of Membrane Science. 2008 Jul; 320(1-2):390-400.
3. Prapainainara P, Theampetch A, Kongkachuichay P, Laosiripojanag N, Holmesh SM, Prapainainar C. Effect of solution casting temperature on properties of nafioncomposite membrane with surface modified mordenite for direct methanol fuel cell. Surface and Coatings Technology. 2015Jun; 271:63-73.
4. Jomekiana A, Behbahania R, Mohammadi T, Kargaric A. Utilization of Pebax 1657 as structure directing agent in fabrication of ultra-porous ZIF-8. Journal of Solid State Chemistry. 2016 Mar; 235:212-16.
5. Wang J, Zheng L, Wu Z, Zhang Y, Zhang X. Fabrication of hydrophobic flat sheet and hollow fiber membranes from PVDF and PVDF-CTFE for membrane distillation. Journal of Membrane Science. 2016 Jan; 497:183-93.
6. Wang S, Liu Y, Huang S, Wu H, Li Y, Tian Z, Jiang Z. Pebax–PEG–MWCNT hybrid membranes with enhanced CO_2 capture properties. Journal of Membrane Science. 2014 Jun; 460:62-70.
7. Esposito E, Clarizia G, Bernardo P, Jansen JC, Sedlakova Z, Izak P, Curcio S, Cindio BD, Tasselli F. Pebax/PAN hollow fiber membranes for CO_2/CH_4 separation. Chemical Engineering and Processing. 2015 Mar; 94:53-61.
8. eow YH. Characterization and performance evaluation of ultrafiltration membrane for humic acid removal. Indian Journal of Science and Technology. 2016 Jun; 9(22):1-8.
9. Meng N, Priestley RCE, Zhang Y, Wang H, Zhang X. The effect of reduction degree of GO nanosheets on microstructure and performance of PVDF/GO hybrid membranes. Journal of Membrane Science. 2016 Mar; 501:169-78.
10. Car A, Stropnik C, Yave W, Peinemann KV. PEG modified poly(amide-b-ethylene oxide) membranes for CO_2 separation. Journal of Membrane Science. 2008 Sept; 307:88-95.
11. Rahman MM, Filiz V, Shishatskiy S, Abetz C, Neumann S, Bolmer S, Khan MM, Abetz V. PEBAX® with PEG functionalized POSS as nano-composite membranes for CO_2 separation. Journal of Membrane Science. 2013 Mar; 437:286-97.