

PRELIMINARY INVESTIGATION ON GAS SEPARATION ABILITY OF POLYSULFONE/PEBAX 1657 COMPOSITE MEMBRANE

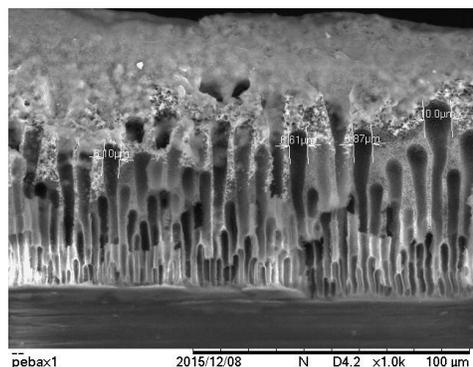
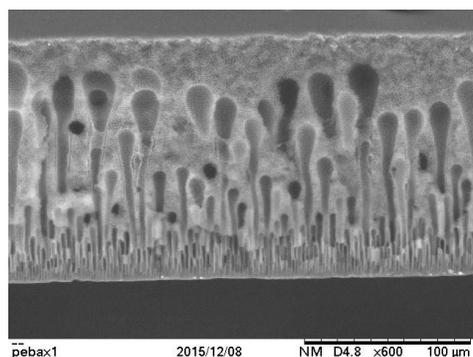
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Article history
Received
10 March 2016
Received in revised form
12 August 2016
Accepted
18 October 2016

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Graphical Abstract



Abstract

Human activities related to coal, petroleum, natural gases and few other energy sources emit carbon dioxide (CO₂) gas to environment and increase global warming. The emission of CO₂ gas from human activities cannot be avoided as they are the main sources of energy. The separation and purification of these gases before they are freely escaped to the atmosphere could be a turning point for a better future. Membranes are one of the methods widely used for gas separation as they are simple mechanism and costly cheap. In this study, Polysulfone (PSf) was introduced as composite membranes with Polyether block amide (Pebax 1657) as a dense selective layer for CO₂/N₂ separation. For the dope preparation, 18% of PSf with 2% Polyethylene glycol (PEG) as an additive was diluted in 80% N-methyl-2-pyrrolidone (NMP) meanwhile, the Pebax 1657 coating solution has been prepared by using 4% Pebax 1657 with 6% lithium chloride (LiCl) as an additive in 70/30 water/ethanol solution. Cross sectional view of the film showed a wide and long cavity with finger-like structure from 6 μm to 10 μm wide with Pebax 1657 selective layer thickness of 29.3 μm. FTIR analysis has proved that all elements present in the film belong to the Pebax 1657, PSf, PEG and LiCl. The permeance test shows a very slight improvement of uncoated and coated samples where uncoated PSf selectivity was found to be 1.17 while the coated sample was 1.23. Even though the permeance result quite low and almost no separation occurs but the slight improvement of uncoated and coated PSf is noticeable and have the potential for future improvement.

Keywords: PEBAX, polysulfone, composite membrane, coating method, CO₂/N₂ separation

Abstrak

Aktiviti manusia yang berkaitan dengan arang batu, petroleum, gas asli dan beberapa sumber tenaga lain membebaskan gas karbon dioksida (CO₂) kepada alam sekitar dan meningkatkan pemanasan global. Pembebasan gas CO₂ daripada aktiviti manusia tidak dapat dielakkan kerana ia adalah sumber utama tenaga. Pemisahan dan penulenan gas-gas ini sebelum mereka bebas ke atmosfera boleh menjadi titik perubahan untuk masa depan yang lebih baik. Membrane adalah salah satu kaedah yang digunakan secara meluas untuk pemisahan gas kerana mereka adalah mekanisme yang mudah dan murah. Dalam kajian ini, Polysulfone (PSf) telah diperkenalkan sebagai membran komposit dengan blok Polyether amide (Pebax 1657) sebagai lapisan terpilih untuk pemisahan CO₂/N₂. Untuk penyediaan larutan dope, 18% PSf dengan 2% Polyethylene glycol (PEG) sebagai bahan tambahan telah dicairkan dalam 80% N-methyl-2-pyrrolidone (NMP) Sementara itu, larutan Pebax 1657 telah disediakan dengan menggunakan 4% Pebax 1657 dengan 6% litium klorida (LiCl) sebagai bahan tambahan dalam 70/30 larutan air/etanol. pandangan keratan rentas filem itu menunjukkan rongga yang luas dan panjang berdiameter 6

mikron hingga 10 mikron lebar dengan ketebalan lapisan Pebax 1657 29.3 mikron. Analisis FTIR telah membuktikan bahawa semua unsur-unsur di dalam filem itu tergolong dalam Pebax 1657, PSf, PEG dan LiCl. Ujian permeance menunjukkan peningkatan yang sangat sedikit. Selektiviti sampel tidak bersalut didapati 1.22 manakala sampel bersalut adalah 1.25. Walaupun hasil permeance agak rendah dan hampir tidak ada pemisahan berlaku tetapi peningkatan yang sedikit diantara PSF tidak bersalut dan bersalut dapat dilihat dan mempunyai potensi untuk penambahbaikan pada masa hadapan.

Kata kunci: PEBOX, polisulfon, membran komposit, kaedah salutan, pemisahan CO₂/ N₂

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1.0 INTRODUCTION

Climate change is a global issue which required global solution as the atmosphere pollution continue to happen and earth temperature keep on rising. Earth temperature expected to rise by 0.5 to 8.6 °F for the next hundred years. Every small change to earth temperature will affect climate. Humans activity incorporated with burning of fossil fuels will soon put our earth in danger as the released of so called greenhouse gases to atmosphere. CO₂ are the major contributor of this greenhouse gas along with methane, nitrous oxide and fluorinated gas. These gases create a layer of protection to earth when sun radiates amount of visible light, ultraviolet and infrared to earth. 30 percent of the radiation will be reflected back to the space while the remaining 70% absorbed by earth and in exchange they reflected amount of IR thermal radiation. This natural event has been disturbed when there is huge amount of GHG accumulated in atmosphere and the radiated heat will be trap and continue to warm more than it supposed to be.

Even though CO₂ is classified as pollutant, this gas also has the good side beneath. CO₂ can be used directly at crude oil reservoir as a gas injection medium. The technique called Enhance Oil Recovery (EOR) was believed can produced 7 % - 23 % or more oil below earth surface [1]. The injected gas can lower down oil viscosity and increase oil flow rate. Currently, most of the CO₂ used in EOR operations is comes from the natural underground 'domes' of CO₂. The limitation of CO₂ natural source has given an idea of Carbon Capture and Storage, CCS. CO₂ gas is captured from the power plant emission and industrial facilities and it is compressed and transported by pipeline to oil fields. CCS was believed can reduced global CO₂ emission by 19 % in 2050 [2]. To further purified the CO₂ gas, several techniques including absorption, adsorption, cryogenic distillation, and membrane separation are proposed.

Membrane separation are used in a broad range of applications and gained important place in chemical technology. The most important property of membrane is their ability to control the rate

permeability of different species. Polymeric membranes are preferable as there are cheap, simple operation, and energy efficient [3]. The first polymeric membranes in gas separation and purification was developed in 1980 by Monsanto where they successfully recover hydrogen from ammonia plant [4]. Later, research in polymeric membranes development continue to gain placed as a significant and important studies for different kind of gas pair. The gas transport takes place following the solution-diffusion mechanism where at first there is feed side penetrant sorption, followed with penetrant diffusion through the membrane and end with desorption of the permeate [5]. In general, the rate at which a particular gas will move through the membrane can be determined by the size of the molecule, the concentration of gas, the pressure difference across the membrane and the affinity of the gas for the membrane material [6].

As approach by Robeson 1991 and 2008, there is a trade-off in polymeric gas membranes where gas selectivity decreases as the membranes performance increase in permeability [7]. Several causes address to this trade-off such as membrane free volume, polymer chain rigidity, segmental mobility, inter-chain distance and chain interaction [8]. In this preliminary study, PSf and PEG was introduced as a base porous film coated with dense selective layer in combination of Pebax 1657 and LiCl. This combination of asymmetric porous-dense composite film could enhance the properties of single porous PSf itself. The well-known plasticization effect of glassy polymer could be improved as there is the combination of glassy-rubbery configuration in this study. The plasticize of glassy polymer by high concentration of penetrant such as CO₂ can affect the membrane matrix and decrease in separation efficiency, including volume-swelling and higher gas permeabilities [9]. The addition of rubbery Pebax 1657 with 60 % polyether and 40 % polyamide content is suitable as they are very flexible, high mechanical strength from the nylon 6 content, also very polar and suitable agent for CO₂ adsorbent [10] [11].

2.0 METHODOLOGY

2.1 Chemicals

The analytical grade of PSf was purchased from Sigma Aldrich. Pebax 1657 which contain 60% Polyether and 40% polyamide was purchased from Arkema France. There are three solvents used in this study, ethanol, water, N-Methyl-2-pyrrolidone (NMP) was supplied by Fisher Scientific. Meanwhile, LiCl and PEG that later used as an additive was supplied also by Fisher Scientific. 99.99 % purified CO₂ and N₂ was used for the single gas permeation test. PSf and Pebax 1657 was dried at 60 °C for 24 hours before the dope preparation to remove humidity.

2.2 PSf Substrate

The dope solution consists of 18 wt.% PSf and 2 wt.% of PEG was prepared by continuous and vigorous stirring at 80 °C for 5h. To remove any air bubbles in the solution, the dope was left at room temperature in a close bottle for 24 h before it can be used for casting purpose. The flat sheet membrane was obtained by casting the solution using automatic casting machine with 0.03 mm knife gap at speed of 100 rpm. The cast film was left in a water bath for 2 h and hang dry for another 24 h.

2.3 Coating Solution

The coating solution which contain 4wt. % Pebax 1657 and 6wt. % of lithium chloride was prepared by dissolving in 90wt. % solvent mixture (30:70 v/v of water/ethanol) for 3 h at 70 °C. The coating solution was then kept rest at room temperature for 24 h to eliminate any air bubbles form during solution preparation.

2.4 The Composite Membrane

The PSf/Pebax 1657 composite film was obtained by utilizing dip coating method where PSf film was dip one side (the top side) in a dish contains 3 ml of Pebax 1657 solution. The composite film was then dry at 60 °C for 24 h to allow the solvent vaporization take place.

2.5 Gas Permeation Experiment

Each gas CO₂ and N₂ was tested individually by allowing them to flow at 1 bar toward the membrane cell and the flowrate of permeate was measured by the bubble flow meter. Equation 1 can be directly used to find the gas permeance in GPU.

$$\frac{P}{l} (GPU) = \frac{1 \times 10^6 V}{At \Delta p} \quad \text{Equation 1}$$

Where $\frac{P}{l}$ is the permeance, l is the thickness of the membrane in cm, A is the effective membrane area in cm², V is the volume in cm³ displaced in time t (s) and Δp is the transmembrane pressure expressed in cm cmHg. The membrane selectivity is the membrane ability to separate 2 gases (A and B). It is the ratio of the Permeance A and B. (Eq.2)

$$\alpha_{AB} = \frac{P_A}{P_B} \quad \text{Equation 2}$$

2.6 Characterization of the Membrane

Fourier transform infrared spectroscopy (FTIR) was used as a chemical characterization to ensure and prove the presence of every chemical added to the composite film by allowing the samples to absorb different kind of wavelength produced from a beam that later will be computerized to obtain the desired data in the form of wavenumbers, cm⁻¹. Every wavenumber was assign specifically to each bonding structured of chemicals. Similarity of the wave produced was compared against the available data from reference. Meanwhile the cross sectional morphology of the was examined by Scanning electron microscope (SEM). To ensure smooth cutting of the film, samples was fractured in a liquid nitrogen and coat with nickel coating to avoid space charge during imaging.

3.0 RESULTS AND DISCUSSION

3.1 Permeance Test

Transmembrane pressure and temperature has been fixed at 1 bar and 30 °C respectively and the permeance of CO₂ and N₂ gases altogether with CO₂/N₂ selectivity were determined. Figure 1 and Figure 2 shows the permeance of CO₂ and N₂ for PSf film with Pebax 1657 coating and without coating respectively. It was observed that the coated samples showed an increment in permeance as much as 15 % for the CO₂ permeance. The enhancement of CO₂ permeance in PSf/Pebax 1657 composite membranes was due to polar nylon in Pebax 1657 structure as they are good CO₂ adsorbent through the dense selective layer [11]. The permeance for N₂ is a bit lower compared to CO₂ as the gas permeance through membrane film influenced by gas condensability and penetrant kinetic diameter. Two parameter control the gas condensability which is critical temperature (T_c) and normal boiling point (T_b). Beside kinetic diameter, gas critical volume also plays a big role in membranes gas diffusion [12]. The critical parameter of this gas pair was tabulated in Table 1. Gas permeance through polymeric membranes was control by gas solubility and penetrant size, as the condensability increase gas permeance will also increase while in term of penetrant size, gas permeance decrease

accordingly with increase of kinetic diameter. Figure 3 illustrated the CO₂/N₂ gas selectivity for this preliminary studies. There is only 4% of improvement of gas selectivity for the composite membranes over PSf film. The small increment was believed due to a very thin selective layer of Pebax 1657. This thin layer has allowed both CO₂ and N₂ diffuse through with high permeance rate.

Table 1 Critical property of CO₂/N₂ gas pair

Size	Condensability			
	Critical volume (Cm ³ /mol)	Kinetic diameter, d _k (Å)	Normal boiling point (K)	Critical temperature (K)
CO ₂	94.07	3.30	194.7	304.12
N ₂	90.10	3.64	63.15	126.1

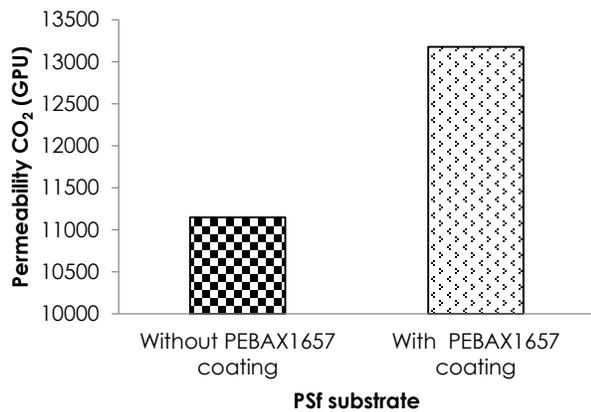


Figure 1 Permeability of CO₂ for PSf substrate with and without Pebax 1657 coating

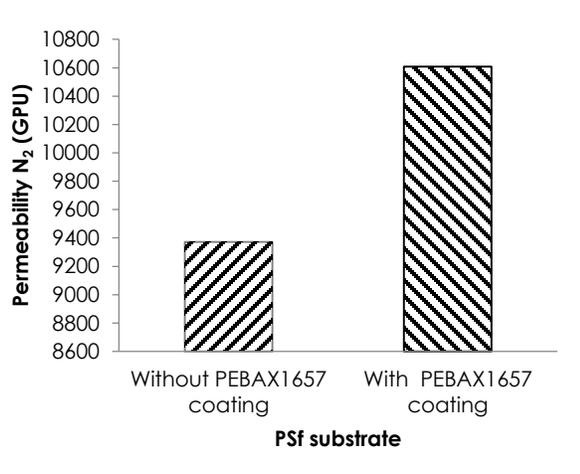


Figure 2 Permeability of N₂ for PSf substrate with and without Pebax 1657 coating

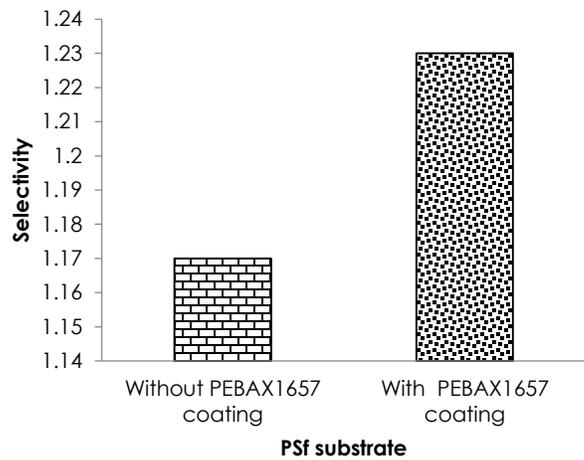


Figure 3 Selectivity for PSf substrate with and without Pebax 1657 coating

3.2 SEM Characterization

Cross sectional view of the composite film showed a large and log cavity with diameter of 6 μm to 10 μm as seen in Figure 4 and Figure 5. This cavity of so called finger-like void might be due to instantaneous liquid-liquid demixing during phase inversion. Fast solidify of the film due to rapid precipitation rate can be address to few condition; i) tendency of solvent-non-solvent interaction and ii) convective flow of solvent to the membrane surface. Having a less tendency of solvent and non-solvent mixing could slow down the precipitation rate of the film and reduced the void formation. There is no different between coated and uncoated samples in term of void and pore formation. Figure 6 shows a composite membrane with Pebax 1657 thickness of 29.3 μm.

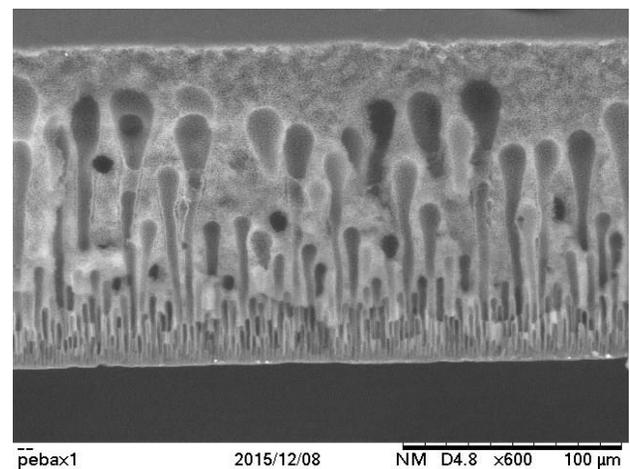


Figure 4 Cross sectional view of PSf substrate without coating

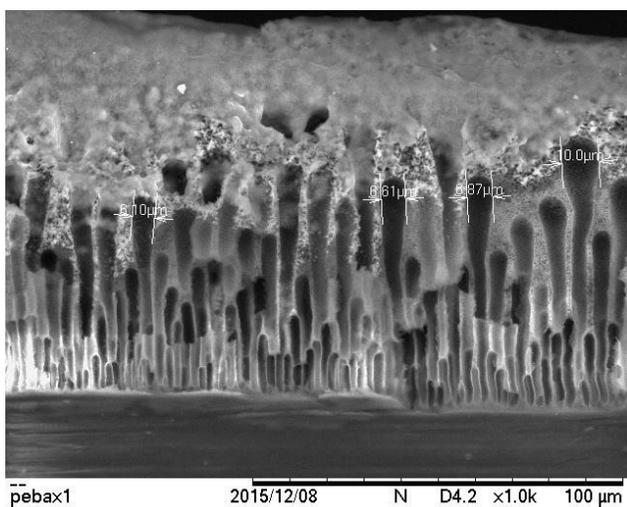


Figure 5 Cross sectional view of composite membrane with Pebax 1657 coating layer

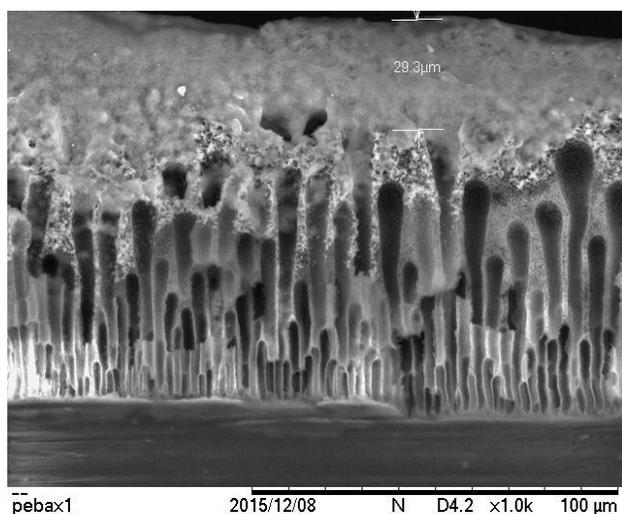


Figure 6 Thickness of composite membrane with Pebax 1657 coating layer

3.3 FTIR Analysis

Figure 7a and 7b shows the spectra wavelength of PSf film and PSf/Pebax 1657 composite membrane respectively. The presence of PSf can be observed from both composite and pure film through several wavelengths. The peak around 1000 – 1100 cm^{-1} is attributed to sulfoxide group while 1200 – 1300 cm^{-1} is belonged to aromatic ether of the PSf. The presence of benzene ring is confirmed by the absorption peak at 1500 cm^{-1} . All peak assign to PSf is available in the composite membrane. Another extra peak in the composite membranes was belong to the Pebax 1657. The peak illustrated wavelength in range of 3500- 3300 cm^{-1} , which attribute to the stretching vibration of N-H from nylon 6 of the Pebax 1657. The peaks around 3500- 3200 cm^{-1} , indicates that the stretching of O-H of alcohol and phenol. From the FTIR graph, there are two peaks in between 3000-2850 cm^{-1} that indicates alkanes group with C-H

stretch. Meanwhile, the wavelength between range 1680-1640 cm^{-1} shows the stretching of C=C in the alkenes class. A conclusion can be made saying that the produced PSf/Pebax 1657 composite membrane does not involve with chemically changing along the process.

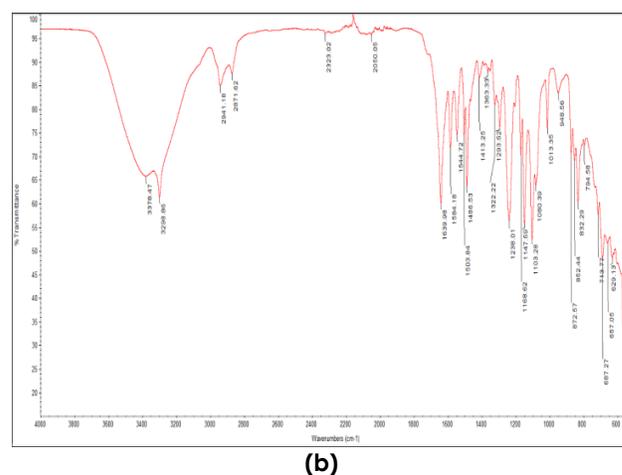
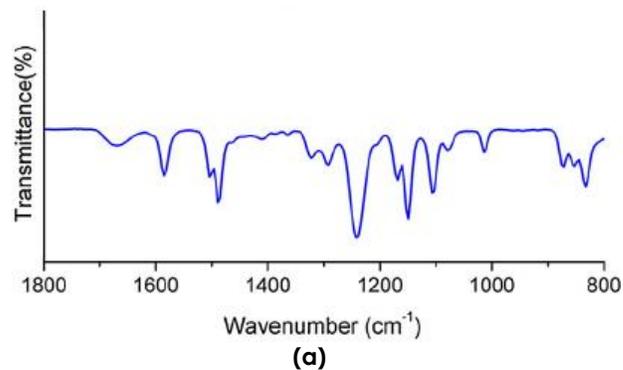


Figure 7 The spectra wavelength of the film; (a) the control data of PSf, (b) PSf/Pebax 1657 composite membranes

4.0 CONCLUSION

In this preliminary study, PSf/ Pebax 1657 composite membranes was successfully prepared and their ability to separate CO_2 from N_2 was studied at 30 °C and 1 bar. The value of permeability CO_2 , N_2 and selectivity for PSf substrate with Pebax 1657 coated always higher than uncoated PSf. Even though the performance is still below than Robeson trade-off curve, yet there is still a huge potential for future improvement in term of coating thickness, void minimizer, and solvent-nonsolvent pair so that a better film could be produced.

Acknowledgement

This research is fully supported by LRGS grant (RDU150901) and UMP Grant (RDU150311).The

authors fully acknowledged Ministry of Higher Education (MOHE) and Universiti Malaysia Pahang for the approved fund which makes this important research viable and effective.

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