Aerosol and Air Quality Research, 17: 2735–2742, 2017

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2016.12.0571

Fabrication and Characterization of Polysulfone Membranes Coated with Polydimethysiloxane for Oxygen Enrichment

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ABSTRACT

This paper presented the application of polymeric membranes for oxygen/nitrogen (O_2/N_2) gas separation. Polysulfone (PSF) hollow fiber membranes were fabricated by phase inversion process using N,N-dimethylacetamide (DMAc) and tetrahydrofuran (THF) as co-solvent and ethanol as additive. The effects of bore fluid flow rate and polydimethysiloxane (PDMS) coating concentration on the separation characteristics of hollow fiber membranes were studied. Prior to gas permeation study, characterizations were performed to study the membrane morphology, its thickness and quality of PDMS coating layer on the membrane surface. It was found that the bore fluid flow rate played an important role for the O_2/N_2 separation as it could alter the membrane structure and dimension. The membrane fabricated with lower bore fluid flowrate exhibited better gas permeance and selectivity, owing to better structural integrity that favored the PDMS coating. The results indicated that the PSF hollow fiber membrane coated with optimum PDMS concentration could show greater O_2/N_2 gas permeability and selectivity relative to the PSF membrane without PDMS coating.

Keywords: Polysulfone; Oxygen; Nitrogen; Gas separation; Polydimethysiloxane; Hollow fiber membrane.

INTRODUCTION

Air pollution is a widely discussed topic in both academic and industry sectors, especially in the developing countries. The notion of air pollution can be expressed as grey smog that clings on the urban skyline, but the air pollution is always much more intimate threat in the indoor. According to the risk assessment study from the Global Burden of Disease Study conducted in 2010, air pollution had caused 6.85 million deaths globally and out of 4.3 million from this number is attributed by the household air pollution. In the effort of mankind reducing outdoor air pollution to prevent permanent destruction of the environment, indoor air pollution is getting its attention as it is a dominant exposure for human.

Human dwelling in the indoor environment everyday for various indoor activities and the adverse health effects associated with indoor air pollution is found to increase because of the toxic content in the construction materials and consumer products. One of the goals to reduce indoor air pollution by maintaining a good indoor air quality (IAQ) is to enhance the oxygen level in the indoor air. The oxygen enriched air is able to provide a better indoor air quality and maintain the freshness of the habitants.

Membrane technology is arising technology in gas separation as it possesses the advantages of low initial capital investment in setting up and smaller foot printcompared to the conventional gas separation processes such as pressure swing absorption and cryogenic distillation (Smith and Klosek, 2001; Shou *et al.*, 2012; Sanders *et al.*, 2013). Several review articles summarized the potential of polymeric membranes for several important industrial applications. These include carbon dioxide removal from natural gas and oxygen enrichment in combustion cycle (Smith and Klosek, 2001; Sanders *et al.*, 2013). However, the performance of gas separation by polymeric membranes is restricted by the trade-off effect between permeability and selectivity (Robeson, 2008). The permeability of a membrane describes gas permeation through the polymeric membrane surface per unit area and pressure and it is governed by both the diffusivity andsolubility of the gas molecules as depicted by the solution-diffusion model (Kamaruddin and Koros, 1997). Selectivity meanwhile is an important parameter in gas separation where it describes the ability of the materials in separating two different gases. A superior polymeric

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membrane in gas separation is desirable to exhibit both high permeability and selectivity for it to be commercially feasible.

To fabricate polymeric membrane for gas separation process, there are several commonly used techniques such as interfacial polymerization, dry-jet wet phase inversion and electrospinning. Dry-jet wet phase inversion is the most commonly method attributed to ease of operation and highly compatible for all type of solvent soluble polymer. Fabrication of dense layer membrane is one of the factors to increase the gas permeance. With the advancement of the membrane technology, this can be achieved by optimizing spinning conditions of hollow fiber membrane making process (Khayet *et al.*, 2009). It has been previously reported that the spinning conditions with respect to the air gap distance, type of coagulants, force convection flow rate and bore fluid flow rate play a vital role in producing a dense layer membrane for gas separation (Khayet and Matsuura, 2011). These studies concluded that the key to produce a superior membrane in gas separation are (1) to obtain an optimum air gap distance and convection flow rate as these two parameters are affecting the rate of phase inversion, and (2) to control the chemistry of the coagulant so as a better surface roughness and uniformity is achieved. Nevertheless, a literature search found that only few studies have demonstrated the effect of bore fluid flow rate on the membrane structure.

Polysulfone (PSF) is a glassy polymer introduced by Union Carbide to replace polycarbonate attributed to its superior thermal and mechanical strength (Chong *et al.*, 2016). The properties of PSF gained the attention from Monsanto where it later became the first polymeric material used in membrane fabrication for gas separation (Sanders *et al.*, 2013). Compared to the other advanced polymeric materials that are used for membrane gas separation in the recent years, PSF still remains mainstay in commercial membranes until present. This is mainly due to its relatively low manufacturing cost and largely available in the market.

Coating materials such as aerogel (CX) and polydimethysiloxane (PDMS) have been found to be able to modify membrane surface and enhance its gas permeability and selectivity (Wahab *et al.*, 2012; Kiadehi *et al.*, 2015). Moaddeb and Koros (1997) and Magueijo (2013) reported that a layer of rubbery coating material on the membrane surface is able to facilitate better permeability and selectivity in binary gas separation.

In this work, we attempted to fabricate hollow fiber membranes with different characteristics by varying the bore fluid flow rate during spinning process and investigate its effect on the gas separation performance. The effect of PDMS coating material on the membrane surface was also studied, aiming to further enhance the gas separation performance. Several membrane characterization tests were performed to determine the hollow fiber membrane properties with respect to morphology, cross sectional structure and wall thickness. The performance of the hollow fiber membranes was evaluated via pure gas permeation study using oxygen and nitrogen.

METHODS

Materials

The polymeric material used in this study was commercial polysulfone in pellet form (PSF, UDEL-P3500) obtained from Amoco Chemicals, Illinois U.S.A. N,N-dimethylacetamide (DMAc, > 99.5%) and ethanol (EtOH, > 99%) obtained from Merck, New Jersey, U.S.A., were used as solvent and weak co-solvent, respectively during dope solution preparation. Tetrahydrofuran (THF, > 99.5%) from QReC, Rawang, Malaysia was used as additive as it is able to produce a denser membrane by delaying liquid-liquid demixing during phase inversion process. Polydimethylsiloxane (PDMS) and hexane purchased from Sigma Aldrich, Missouri, U.S.A. were used to prepare coating solution for thin layer formation on the outer surface of hollow fiber membranes.

Preparation of Spinning Solution and Hollow Fiber Membranes

The PSF hollow fiber membranes in this study were fabricated using dope solution composed of 30 wt% PSF, 30 wt% DMAc, 30 wt% THF and 10 wt% EtOH. The membranes were designated as PSF-1, PSF-2 and PSF-3, depending on the bore fluid flow rate (0.3, 0.7 and 1.0 mL min^{-1}) set during spinning process. Prior to use, the PSF pellets were first dried in a vacuum oven at 70°C for 24 h in order to remove the moisture content. A predetermined amount of PSF pellets were then slowly dissolved in the solvents composed of DMAc, THF and EtOH under vigorous stirring. The mixing process was continued for another 24 h in order to form a homogeneous dope solution. At last, the dope solution was sonicated in an ultrasonic bath to completely remove microbubbles that might trap in the dope solution.

The hollow fiber membranes used in this study were fabricated by dry-jet wet phase inversion method using spinning machine as shown in Fig. 1. The dope solution was first transferred into the spinning reservoir before being delivered to a spinneret using gear pump. The dope solution was then extruded from the annular space of the spinneret (insertion in Fig. 1) while the bore fluid flowed through the center of the spinneret to initiate the solvent exchange process. The dope extrusion rate was varied in the range of 0.3–1.0 mL min^{-1} in order to produce membranes with different morphology. The as-spun hollow fiber was then guided through the coagulation bath that made up of pure water before it was being collected by a windup drum. It was followed by immersion of the hollow fiber membranes in a water container for 1–2 days to remove the solvent residual from the membranes. At last, the membranes were dried in a vacuum oven at 70°C for 24 h before being used for membrane module preparation (insertion in Fig. 1). The detailed spinning conditionsare tabulated in Table 1.

Preparation of PDMS Solution for Membrane Coating

PDMS solutions with two different PDMS concentrations (3 wt% and 10 wt%) were prepared according to the procedure described by Zulhairun *et al.* (2015). The approach is shown schematically in Fig. 2. The PDMS base was first

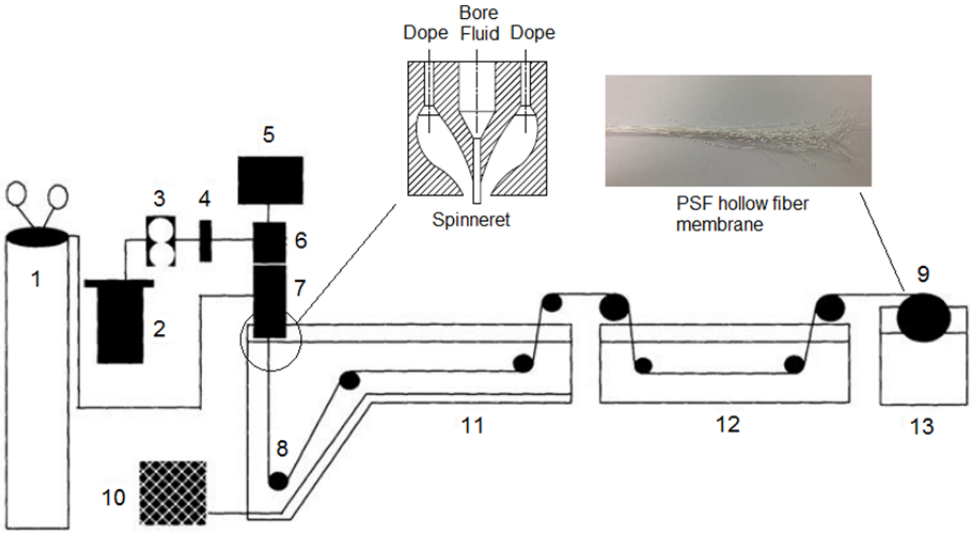


Fig. 1. Schematic diagram of the dry-jet wet phase inversion apparatus setup for PSF hollow fiber membrane fabrication: (1) gas cylinder; (2) dope reservoir; (3) gear pump; (4) filter (optional); (5) syringe pump; (6) spinneret; (7) force convective tube (optional); (8) roller; (9) wind-up drum; (10) refrigeration/heating unit; (11) coagulation bath; (12) washing/treatment bath and (13) wind-up bath.

Table 1. Spinning conditions of hollow fiber membrane fabrication.

Parameter	Value
Spinneret OD/ID (mm mm^{-1})	0.6/0.3
Bore liquid	Distilled water
Bore liquid temperature (°C)	25
Bore liquid flow rate (mL min^{-1})	0.3 or 0.7 or 1.0
External coagulant	Tap water
External coagulant temperature (°C)	25
Air gap distance (cm)	30
Room relative humidity (%)	55 ± 5

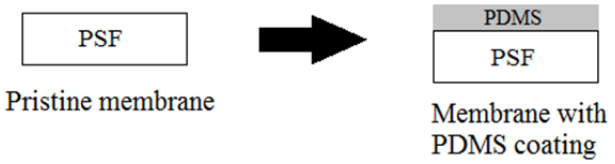


Fig. 2. Illustration of PDMS coating protocol.

mixed with the predetermined hexane solution so as to obtain the desired PDMS concentration. The solution was stirred by an overhead mechanical stirrer for 2 h to achieve homogeneous condition.

The coating process was performed by dip-coating method in which the dried PSF hollow fiber was immersed in a 100 mL conical flask containing either 3 wt% or 10 wt% PDMS for 10 min. The PDMS-coated membranes were then dried in room temperature for 24 h for curing purpose. The same procedure was repeated for 5 times in order to acquire a perfect PDMS coating layer.

Membrane Characterization

The hollow fiber membrane surface morphology and cross section structure were characterized by scanning electron microscope (SEM, Hitachi S3400N). Prior to analysis,the membrane sample was immersed in liquid nitrogen and cryogenically fractured to obtain a prefect-cut structure. It was followed by gold coating on the membrane sample using sputter coater machine (SC7620, Emitech). Energy dispersive X-ray spectrometer (EDX) with an accelerated voltage of 20 kV equipped with SEM was used to elementally analyze the sample to investigate the presence of PDMS on the membrane surface.

Gas Permeation Study

The gas permeation study (Fig. 3) for the hollow fiber membrane was carried outusing pure O_2 and N_2 gas (purity > 99.99%). Five units of hollow fiber membranes with the length of 23 cm were potted as single module using epoxy resin. One end of the membrane module was then connected to the soap-bubble flow meter to measure the volumetric flowrate while the other end of the module was completely sealed. Pure single gas was fed to the shell side of the membrane and permeate was diffused from its lumen to the soap-bubble flow meter. The permeance of the membrane was measured at room temperature. The procedure was repeated five times in order to yield the average value. Membrane permeance (P_A/l) can be calculated as the ratio of membrane permeability, P_A to the membrane thickness, l and represented in unit of gas permeation unit (GPU) (1 GPU = 10^{-6} cm^3 (STP) /cm^2 cm Hg) as expressed in Eq. (1).

$$\frac{P_A}{l} = \frac{Q}{A\Delta P}\frac{273.15\times10^6}{T} \quad (1)$$

where P_A/l is the gas permeance of membrane in GPU, Q is the volumetric flowrate of gas transport across the membrane (cm^3 s^{-1}, STP), A is the effective membrane

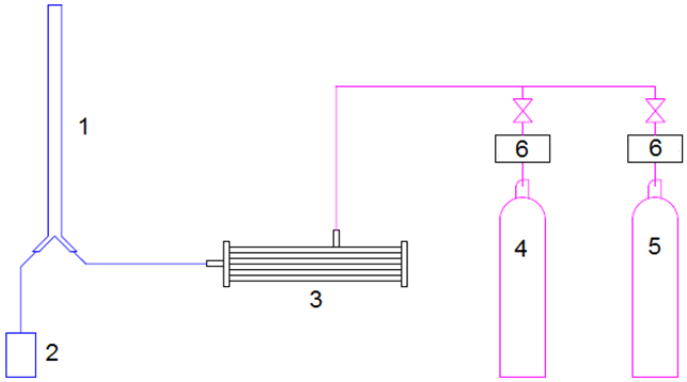


Fig. 3. Schematic diagram for gas permeation study: (1) soap-bubble flow meter; (2) soap container; (3) membrane module; (4) oxygen gas cylinder; (5) nitrogen gas cylinder; (6) gas pressure regulator.

area (cm^2), ΔP is the transmembrane pressure (cmHg) and T is the temperature during the gas permeation test is carried.

In addition to the permeability and permeance, the selectivity of the membrane, $\alpha_{A/B}$ plays a vital role as it represents the permeation ability of binary gas separation (e.g., gas A and gas B) in the membrane. The O_2/N_2 selectivity can be calculated based on the ratio of the permeability of respective gases in binary separation as expressed in Eq. (2) (Robeson, 1991),

$$\alpha_{O_2/N_2} = \frac{P_{O_2}}{P_{N_2}} \tag{2}$$

where P_{O2} and P_{N2} are the membrane permeability of gas O_2 and N_2, respectively.

RESULTS AND DISCUSSION

Morphology of Hollow Fiber Membranes

Fig. 4 shows the SEM images of PSF hollow fiber membrane made of different bore fluid flow rate. All the self-fabricated membranes exhibit a very similar membrane structure where teardrop-like void is developed on the outer shell side and is supported by spongy structure. It is noteworthy to mention that, the thin selective layer for the PSF hollow membranes is appeared on the outer shell surface. The formation of such asymmetric structure is attributed to the strong interaction between the solvents and water that leads to the rapid solvent/non-solvent exchange (Chong *et al.*, 2014). The formation of sponge structure is due to the existence of air gap distance prior to immersion in coagulation bath. The hollow fiber membrane spun at a larger air gap distance would lead to a packed orientation and denser molecule packing density attributed to elongation stress that induced by gravitational force (Khayet *et al.*, 2009). On the other hand, the work conducted by Farah *et al.* (2015) and Wang *et al.* (2000)found that at lower air gap distance, it tended to produce membrane with larger voids and is unfavourable to the permeance of gas separation.

Effect of Bore Fluid Flow Rate

Bore fluid flow rate is crucial during spinning process as it affects the dimension and structure of the resultant hollow fiber membranes (Wu *et al.*, 2007). Table 2 summarizes the characteristics of the PSF hollow fiber membranes fabricated at different bore fluid flow rate. Obviously, the diameter of the membrane is found to increase with the increase of the bore fluid flow rate. It is also found that the membrane wall thickness is in the order of PSF-1 > PSF-2 > PSF-3 with respect to the bore fluid flow rate. The increment of the hollow fiber membrane diameter and the decrease of the wall thickness are in good agreement with the literature findings where increasing bore fluid speed tended to have higher competitive force between the bore fluid liquid and dope solution in phase inversion process (Bonyadi *et al.*, 2007). In this work, the formation of thin hollow fiber membrane is attributed to the rapid solidification of polymer arise from the high bore fluid flow rate although the inner and outer diameters of the spinneret remained constant.

Fig. 5 presents the gas permeation results of the hollow fiber membranes. As can be seen, PSF-1 shows better permeance performance compared to PSF-2 and PSF-3 in O_2 gas separation. It records the highest O_2/N_2 selectivity (4.28 ± 0.11) compared to PSF-2 (4.07 ± 0.10) and PSF-3 (3.92 ± 0.09). The results indicate that both gas permeance and selectivity are affected by the bore fluid flow rate. The results can be explained by the larger membrane thickness and improved packing density of the membrane structure as the slower elongation induced by the lower bore fluid flow rate tends to yield more interstitial chain space in the membrane to improve permeance and selectivity (Sanders *et al.*, 2013; Zulhairun *et al.*, 2014). Therefore, by lowering the bore fluid flow rate, one could produce a hollow fiber membrane with a better packing density structure and achieve greater permeance and selectivity.

Effect of PDMS Coating versus Pristine Hollow Fiber Membrane

In this study, PSF-1 membrane is selectedfor further investigation to study the effect of PDMS coating on its performance with respect to permeance and selectivity. The PSF-1 membranes coated with 3wt% PDMS (PSF-3PDMS) and 10wt% PDMS (PSF-10PDMS) solutions were used to evaluate the gas separation performance. The

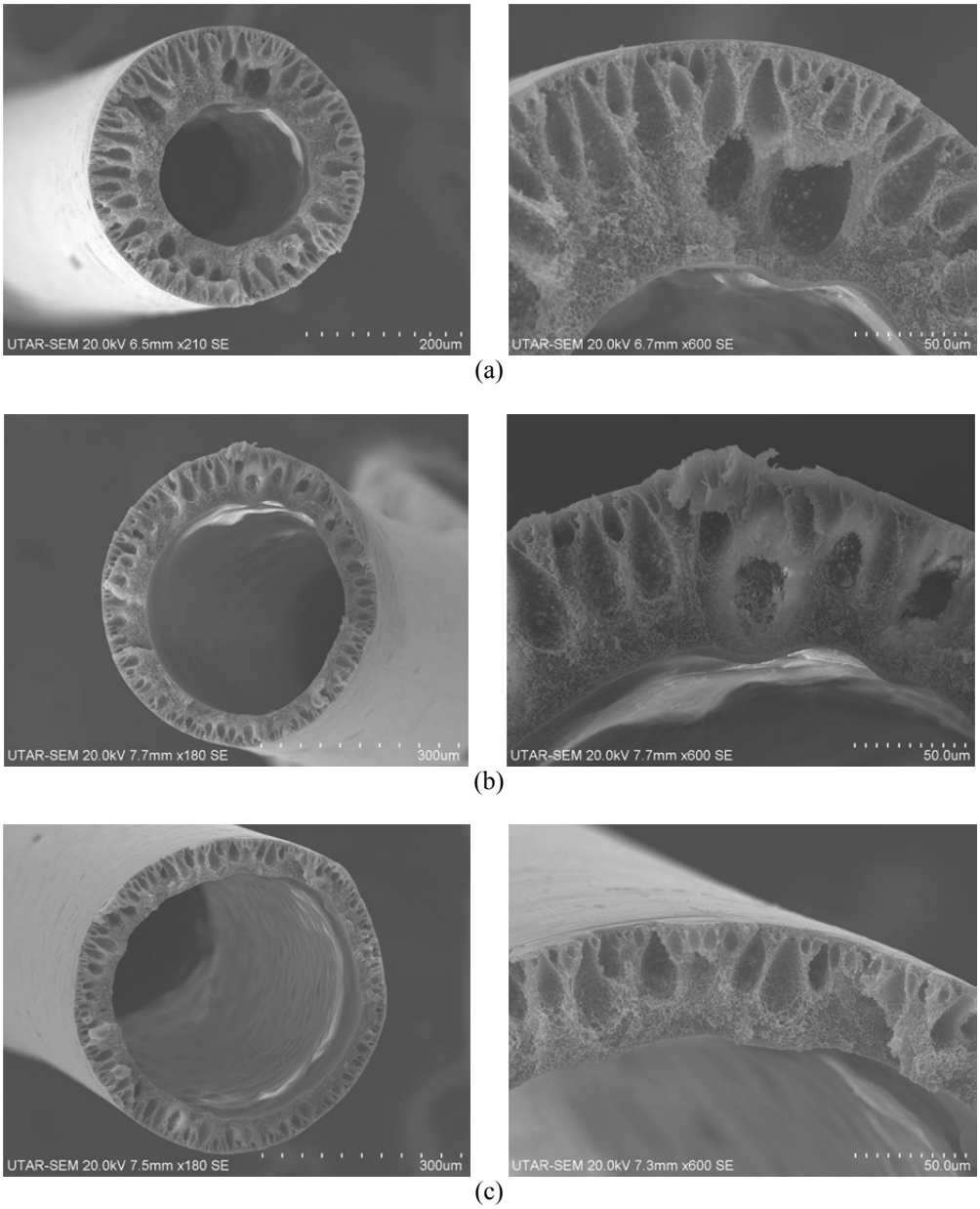


Fig. 4. Membrane cross section morphology for (a) PSF-1, (b) PSF-2 and (c) PSF-3.

Table 2. Characteristics of as spun hollow fiber membranes.

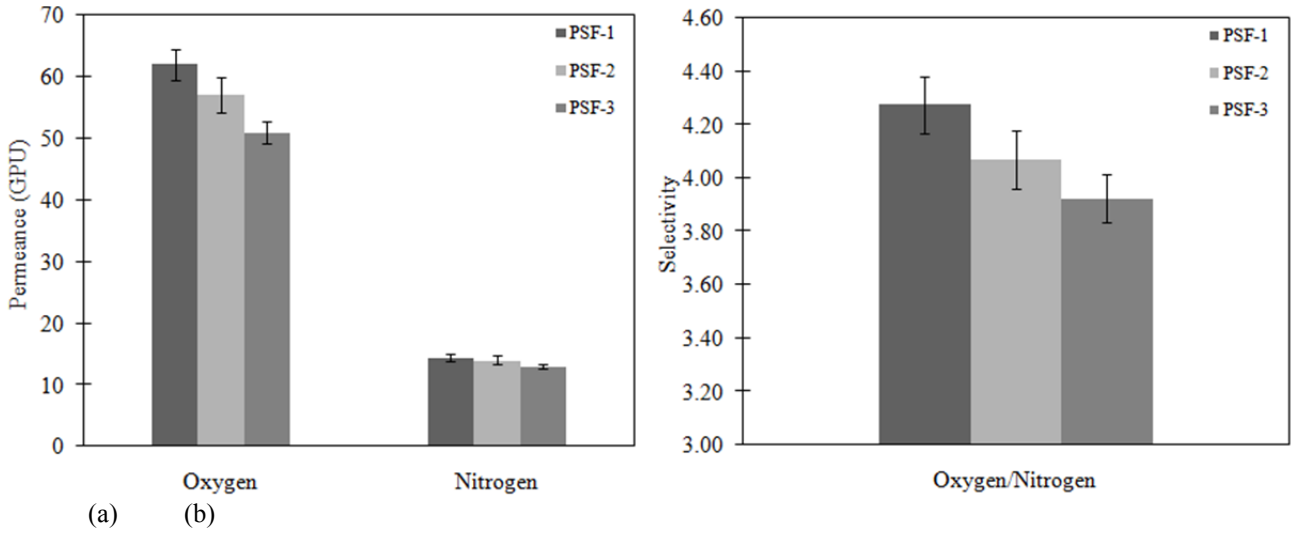
Membrane	PSF-1	PSF-2	PSF-3
Internal diameter (μm)	210 ± 10	310 ± 12	370 ± 10
Wall thickness (μm)	90 ± 5	60 ± 7	50 ± 4

membrane morphology and characteristics for the PSF hollow fiber membrane are not able to clearly demonstrate the coating of the PDMS solution, and hence EDX analysis is performed. The EDX results as shown in Table 3 confirm the successful coating of the PDMS as silicon element is detected on the surface of PSF-3PDMS and PSF-10PDMS. The silicon element meanwhile is not detected in the pristine PSF membrane (PSF-1).

The permeance and selectivity of the O_2/N_2 gas for the PDMS-coated membranes are presented in Figs. 6(a) and 6(b), respectively. The results show that both permeance and selectivity are increased when the surface of PSF membrane is coated with PDMS. The coating layer is believed not only to cover the membrane surface defects but also to improve diffusion of gases as PDMS has higher affinity towards both O_2 and N_2 (Rao *et al.*, 2007; Rowe *et al.*, 2009). Nevertheless, higher concentration of PDMS coating, i.e., PSF-10PDMS experience lower permeance and selectivity attribute to the formation of thicker layer of PDMS on the membrane surface which increases the mass

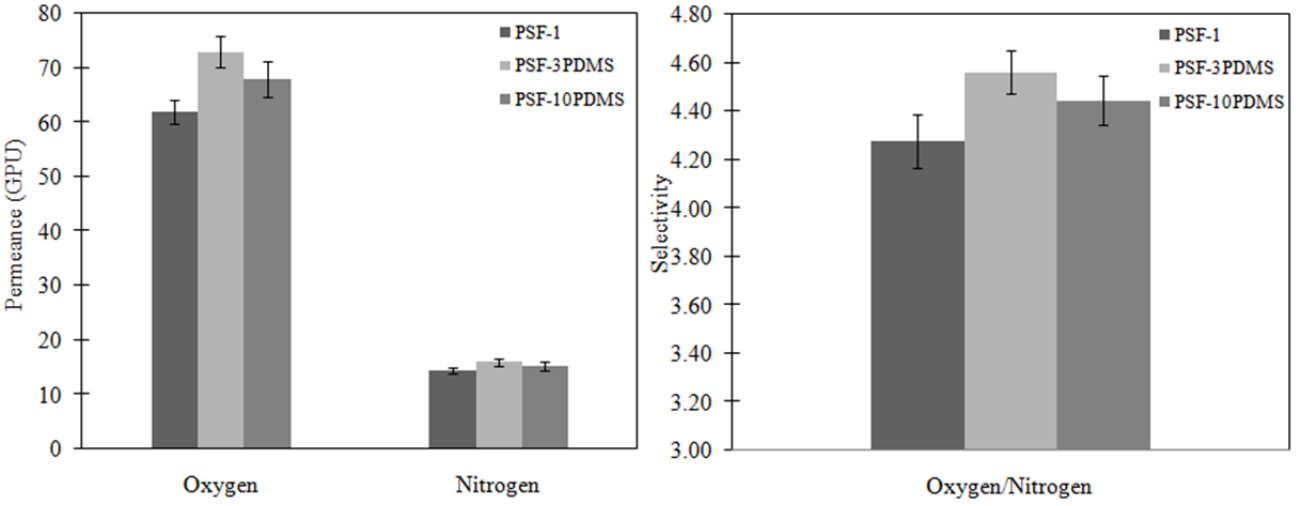
Table 3. EDX Analysis of as spun hollow fiber membranes.

Trace Element	PSF-1 (wt%)	PSF-3PDMS (wt%)	PSF-10PDMS (wt%)
Carbon (C)	86.54	83.47	80.32
Oxygen (O)	13.46	13.81	12.61
Silicon (Si)	Not detected	2.72	7.07



(a) (b)

Fig. 5. Effect of bore fluid flow rate on (a) gas permeance and (b) selectivity.



(a) (b)

Fig. 6. Effect of PDMS coating on (a) gas permeance and (b) selectivity.

transfer resistance. It is noteworthy to mention that, the optimum ratio of the concentration of PDMS coating is 3 wt% in this study as PSF-3PDMS recorded highest yield for both permeance and selectivity compared the other membranes (Fig. 6).

Comparison of Previous Studies on O_2/N_2 Separation with PDMS-Coated Hollow Fiber Membrane

There are many works reported the use of PSF membranes in gas separation mainly due to the good thermal and mechanical properties of the polymer, commercial available and ease in membrane synthesis. To the best of our knowledge, there is very little literature reported the effect of coating material on the hollow fiber membrane for O_2/N_2 separation. Table 4 summarizes the data obtained from several recent studies on the PSF membranes with coating layer for O_2/N_2 separation. It is noteworthy to mention that the membranes produced from our work have greater O_2/N_2 gas permeance relative to the literature studies but lower in terms of the selectivity. This can be explained by the structure of the hollow fiber membranes that possess a mixture of teardrop like voids and spongy layer, allowing more gases to diffuse through the membrane. It is our interest in the near future to further investigate the parametersof

Table 4. A comparison of PSF hollow fiber membranes with coating for O_2/N_2 gas separation.

Membrane	Permeance (Barrer)		O_2/N_2 Selectivity	Ref.
	O_2	N_2		
PSF + 0.01 wt% CNF[a]	0.3	0.2	1.50	Kiadehi *et al.*, 2015
PSF + 0.1 wt% CNF	1.2	0.6	2.00	Kiadehi *et al.*, 2015
PSF + 1 wt% CNF	2.1	1.1	1.91	Kiadehi *et al.*, 2015
PSF + 5 wt% CX[b]	13.4	2.5	5.36	Magueijo *et al.*, 2013
PSF + 10 wt% CX	12.4	2.6	4.77	Magueijo *et al.*, 2013
PSF + 5 wt% CX[c]	11.5	1.6	7.19	Magueijo *et al.*, 2013
PSF + 0.1 wt% FS[d]	9.5	1.5	6.34	Wahab *et al.*, 2012
PSF + 3 wt% FS	8.8	1.7	5.18	Wahab *et al.*, 2012
PSF + 10 wt% FS	12.7	6.3	2.01	Wahab *et al.*, 2012
PSF-1	15.5	3.8	4.28	This work
PSF-3PDMS	18.3	4.0	4.56	This work
PSF-10PDMS	17.2	3.8	4.44	This work

[a] CNF is the abbreviation for carbon nano filler.
[b] CX is the abbreviation for aerogel.
[c] μCX is the abbreviation for micro aerogel.
[d] FS is the abbreviation for fumed silica.

membrane fabrication in order to produce a hollow fiber membrane with improved dense layer structure properties that may lead to a better permeability and selectivity.

CONCLUSIONS

In this study, PSF hollow fiber membranes with different properties were successfully fabricated by varying the bore fluid flow rates during spinning process. The membranes were evaluated with respect to the permeance and selectivity of O_2/N_2 gas separation. The morphology study revealed that the membrane fabricated at the lowest bore fluid flow rate, i.e., 0.3 mL min^{-1} possessed highest thickness and greater spongy structure compared to the membranes made of higher bore fluid rate. This has resulted the membrane to have better gas separation performance. Further investigation showed the PDMS coating on the PSF membrane surface could further improve the permeance and selectivity in O_2/N_2 gas separation. Overall, it was found that the PDMS-coated PSF hollow fiber membrane have good potential to be applied in O_2/N_2 gas separation applications for IAQ enhancement.

ACKNOWLEDGMENTS

The authors would like to thank Mayair Manufacturing (M) Sdn. Bhd. for providing financial support in this work under the Studentship Research Grant (Vote No: 4464/000) and Universiti Teknologi Malaysia for the research funding provided under Research University Grant (Vot no: Q.J130000.2546.15H41)

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Received for review, December 26, 2016
Revised, April 26, 2017
Accepted, April 26, 2017