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To cite this article: Pusfita Sari *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **546** 042042

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Simple Method to Enhance O₂/N₂ Separation on P84 co-polyimide Hollow Fiber Membrane

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Abstract. In this study, a simple coating technique to enhance the selectivity performance of P84 co-polyimide hollow fiber polymer membrane was investigated. The hollow fiber membrane was coated with polydimethylsiloxane (PDMS) to prevent gas flow through the defect surface. The prepared membranes were characterized using X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and pure gas permeation measurement. The pure gas of O₂ and N₂ were used to determine the permeation properties of the hollow fiber membrane. The single gas measurement showed that the perm-selectivity of O₂/N₂ of the hollow fiber membrane increased up to 181% after the coating treatment. It is concluded that the simple coating technique has significant effect in enhancing the selectivity performance of the hollow fiber membrane.

1. Introduction

Nowadays, gas separations in industry has moved to focus on oxygen enrichment from air. This separation used for medical or metallurgical purposes. To achieve oxygen enrichment, cryogenic distillation, pressure swing adsorption, absorption and membrane are the accessible technologies. The later offers interesting features such as environmentally friendly, ease operational system, low capital due to energy efficiency, and has much potential for improving make membrane got a lot of attention in the recent years [1-4]. In order to produce high permeability and selectivity, the membrane should have good chemical, thermal and mechanical stability and can be produced continuously without any defects [4,5].

Asymmetric polymer membranes are known as the most used membrane in gas separation industry. One of polymeric materials such as polyimide (PI) shown has high of selectivity and permeability with acceptable value [6]. Polymeric membranes are able to attain decent permeability and selectivity at low temperature and pressure, thus making these membranes preferred as gas separation materials. However, these types of membranes still have some limitations such performance of trade-off and their performance will decrease over time when used in extremely environments [7]. Besides, most of the transport gas through an asymmetric polymer membrane determined by the characteristics of dense



selective layer of membrane. The dense-selective layer is formed on the membrane structure that is porous integrally through the phase inversion process. Although it produces a very thin layer (less than 100 nm) on the membrane, the formation of defects such as pin holes are almost unavoidable. A membrane with a defective layer will show poor gas selectivity because the gas will move through pin holes in non-selectively [8].

Nearly four decades ago, Monsanto patented the sealing technique on the defect layer membrane by a simple coating method. Therefore, the separation on membrane will depend on the intrinsic structure of the membrane itself. Since then, sealing technique that utilized dilute silicon rubber, such as polydimethylsiloxane (PDMS), in alkene have been applied to coat asymmetric membrane surfaces in industry [8]. Ying et al [9] prepared hollow fiber MMM from Polysulfone/zeolite- β /Matrimid for O₂/N₂ separation that coated with 2 wt% PDMS in *iso*-octane with drying time 48 h. Surface coating in membrane resulting improvement permeability and selectivity. They found out that the permeability and selectivity of O₂ gas on uncoated membrane was 1.84 GPU and 1.01 respectively, while the O₂ permeability and selectivity of PDMS coated membrane was 0.0529 GPU and 5.2 respectively. Moreover, Magueijo et al [10] prepared asymmetric MMM from polysulfone that 3 wt% PDMS coating in *n*-hexane for O₂/N₂ separation. They found out that surface coating in membrane resulting in significantly enhanced selectivity, from 1.00 into 8.35 for uncoated to coated membrane, respectively with small reduction in permeability from 135 into 84.9 GPU. These results shown that surface coating is an attempt to reduce any defects on the membrane layer [11]. Basically, the technique is to coat the membrane surface with highly permeable silicon polymers to fill the compatible membrane surface voids and increase selectivity for gas separation because the gas molecule will pass through the polymer, not the pin holes [9,11]. The hydrophobic silicon could attach perfectly on the membrane surface due to the same properties, thus make this method as an efficient way to reduce surface defect.

In this study, polymeric material used is polyimide as precursor. Polyimide has good thermal and chemical stability. Polyimide can be resisted at a temperature higher than 300°C and decomposes before reaching its melting point. Polyimide is a good precursor for carbon material because it does not pass through the melting phase transition and its shape is fixed [13]. Among other polyimide, commercially available polyimide such as P84 co-polyimide, Matrimid and Kapton are the most used polyimide for gas separation. Among them, P84 offer interesting feature such as high thermal resistance, good gas separation and applicable to almost every membrane application [14-17]. Furthermore, P84 co-polyimide exhibits properties such as has high glass transition temperature (T_g) 315 °C, high solubility to many organic solvents including N-Methyl-2-Pyrrolidone (NMP) and good resistance to various pH conditions [18]. For these reasons, P84 co-polyimide was utilized as polymer precursor.

Therefore, in this study, a coating simple method on P84 co-polyimide hollow fiber membrane was explored to enhance gas separation. The findings of this study are expected will contribute in a better understanding of surface coating for gas separation properties.

2. Experimental

2.1. Materials

P84 co-polyimide (BTDA-TDI/MDI) was acquired from HP Polymer GmbH, Austria. The solvent, N-Methyl-2-Pyrrolidone (NMP), was procured from Merck (Germany). Polydimethylsiloxane (PDMS, Sylgard® 184) was purchased from Dow Corning, used as coating material. The PDMS solvent, *n*-hexane was purchased from Sigma–Aldrich, Germany.

2.2. Methods

2.2.1. Fabrication of hollow fiber polymer membrane. Prior to dope solution formation, P84 co-polyimide powder was dried at 80 °C for 24 h in an oven to remove moisture. The dope solution contains of 20wt% of P84 co-polyimide and 80 wt% of NMP [19]. Preparation of polymeric solution was initiated by adding P84 co-polyimide slowly into the solvent and stirred at 700 rpm at 80 °C for 24 h. Then,

sonication was conducted on the dope solution for 1 h to remove excess bubble during stirring process. The hollow fiber membrane was fabricated using dry-wet spinning set-up system. The parameter used for membrane fabrication was as follow, the dope solution containing P84 co-polyimide/NMP (20:80 w/w) and bore fluid containing NMP/H₂O (70:30 w/v) were pumped simultaneously using gear pump with the rate of 2.4 mL/min and 0.7 mL/min, respectively. The inner diameter (i.d.) and the outer diameter (o.d.) were 400 μ m and 600 μ m, respectively. After passing the spinneret, the membrane was passed through 5 cm air gap prior to experience complete phase inversion in coagulant bath containing tap water. The fibers were then collected in collecting reservoir until future treatment. The post treatment of membranes was conducted by immersion in water for 24 h at room temperature and followed by immersion in ethanol for 2 h for solvent-exchange and dried at room temperature at least 48 h for further use.

2.2.2. Preparation of PDMS coating solution. The coating solution was prepared by dissolving PDMS in *n*-hexane (3:97 w/w). Prior to coating, the membrane was modulated into a lab scale testing module by potting into a stainless-steel holder (SS Swagelok 1/4 in. Tube OD x 1/4 in. Male NPT) and then sealed using epoxy resin. Each module contained 5 fibers with the length of 15 cm. The coating was conducted by dipping the membrane into chemical flask containing PDMS solution. The potted fibers were dip coated for 10 min and dried at room temperature for at least 24 h until further handlings [8].

2.3. Membrane Characterization

The membrane morphological surface and cross-sectional were observed by scanning electron microscopy (SEM), Hitachi TM 3000. The microstructure properties of membranes were examined by X-ray diffractometer (XRD) with the diffraction angle of 2θ , between 5° - 50° and Ni filtered Cu $K\alpha$ radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$. The interplanar distance (d-spacing) of the polymer membranes was calculated from the highest peak using the Bragg's Law. Then the functional groups alteration after each treatment were evaluated using Fourier transform infrared spectroscopy (FTIR).

2.4. Gas Permeation Test

The gas used for permeation measurement were N₂ and O₂ with UHP grade (99.9999% purity) on that order, which was supplied by Mega Mount Industrial Gases Sdn. Bhd. (Malaysia). The following gas permeation equipment is illustrated in Fig. 1. The gas was connected into permeation apparatus and the permeate side was connected into bubble meter. The measurement was conducted at 25 °C and a feed pressure of 2 bar. The permeance, P/l (GPU) and selectivity, α of the membranes were calculated using equations below:

Permeance, P:

$$(P/l)_i = \frac{Q_i}{\Delta p \cdot A} = \frac{Q}{n\pi D l \Delta P} \quad (1)$$

Selectivity, α :

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B} \quad (2)$$

Where P/l is the permeance of membrane (GPU), Q_i the gas is rate of volumetric flow of at standard temperature and pressure (cm³ (STP/s), A is the area of membrane surface (cm²), n is the fiber quantity in module, p is the difference pressure between the feed the permeation side of the membrane (cmHg), D is the membrane's outer diameter (cm), and l is the membrane's effective length (cm). The selectivity is defined as the permeation ratio of fast gas permeation to slow gas permeation.

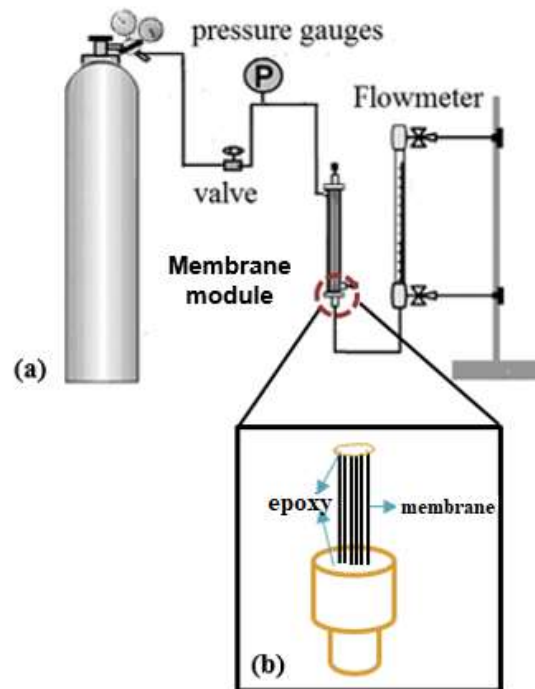


Figure 1. Scheme of equipment set-up (a) gas permeation on hollow fiber membrane and (b) potting preparation of membrane fibers on holders.

3. Results and discussion

3.1 Morphological structure analysis

The morphological of both cross-section and surface of each membrane were illustrated in Figure 1. As can be seen in Figure 2, the morphology of the cross-section between uncoated and coated membrane were the same. The cross-section consists of dense layer on the top and macrovoid on the middle to bottom. This macrovoid was formed due to Tap water is a strong and very mild coagulant compared to the mixed internal NMP/water coagulant (70/30 %wt). As result, the P84 co-polyimide phase inversion takes place much faster on the outer surface than on the inner surface after exiting spinneret. Instant mixing of the outer layer forms a solid outer surface structure and a cross-section structure filled with macrovoids such as fingers, while the mixture which delayed in the inner layer produces a highly porous inner surface structure [3]. The only changes observed were the dense layer got thickening after the coating process, which was not significant from 0.83 into 0.85 μm . While the rest like macrovoid structure, dimension and even the minor change in the dense layer thickness still can be neglected or remain the same. This indicate that PDMS coating did not alter the intrinsic properties of the membrane. In the other hand, the surface experience significant change of both membranes. The uncoated membrane surface was rough, and a lot of pin holes were observed. The observed rough surface was probably produced during the spinning process and mishandling during the spinning process. Rough surfaces on membrane can affect membrane performance [8, 20]. Whereas the coated membrane showing a smoother surface with less to none pin hole. Moreover, the PMDS coating did not showing a clear boundary between PDMS and P84 co-polyimide surface, which mean have good compatibility with the membrane. With such structure, it is predicted that the selectivity will greatly improve on the coated membrane. Overall, the SEM observation showed that PDMS was able to fix the defect on the membrane surface without altering the intrinsic properties of the membrane.

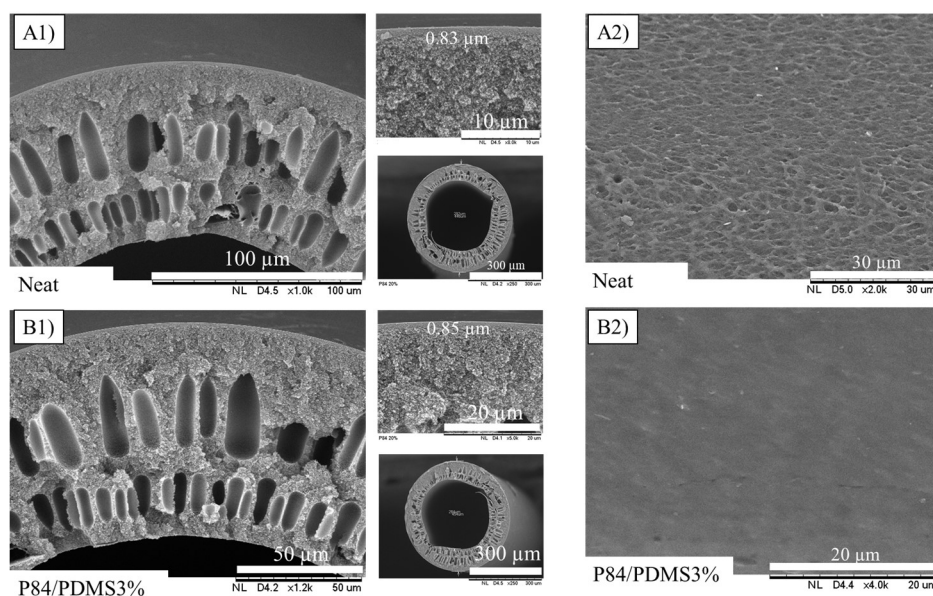


Figure 2. Cross-section (1) and surface morphology (2) of (A) neat and (B) PDMS coated P84 co-polyimide hollow fiber membrane.

3.2 Fourier transform infrared spectroscopy (FTIR)

Figure 3 shows the FTIR spectra of the prepared membranes. Based on the results, there was no significant changes in functional groups for all the polymeric membranes. Both membranes showing similar peak, which were at 725 cm^{-1} assigning to C-H (alkenes), 1100 cm^{-1} and 1360 cm^{-1} exhibited to OC-N-CO (imide II). The peaks at 1510 cm^{-1} , 1615 cm^{-1} , 1720 cm^{-1} and 1780 cm^{-1} show O=C-N (amide II), C=C (alkenes) and asymmetric OC-N-CO (imide I), respectively [21]. The Si-O peak which were appeared in the range of $950\text{-}1000\text{ cm}^{-1}$ was not clearly observed due to overlapped with the CH₃ and CO in the beam. Moreover, there was no new peaks appeared which indicate no new functional group formed after coating process. This indicates that the interaction between PDMS and P84 co-polyimide membrane were physical and did not alter the chemical composition on the membrane.

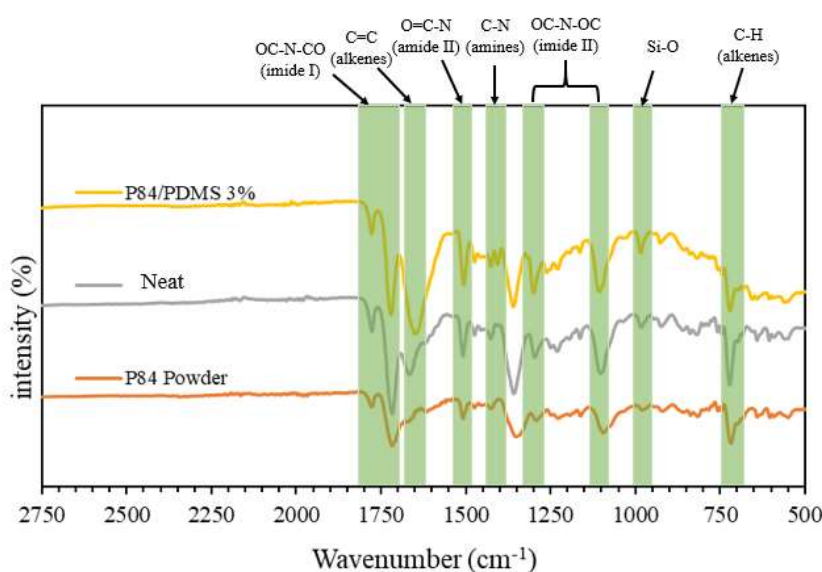


Figure 3. FTIR spectra of the prepared membrane.

3.3 Wide-angle X-ray diffraction pattern

The diffractogram pattern of the P84 co-polyimide and PDMS coated P84 co-polyimide membrane were shown in Figure 4. As can be seen in the Figure 3, the diffractogram on both membranes showing the same pattern. The d-spacing values were determined at the maximum broad peaks using Bragg Law and only reflect the average space between the centers of the chain segments in the polymer matrix [22]. The reflection at $2\theta=17.50$ (d-spacing: 5.01 nm) can be observed for the neat membrane (P84 co-polyimide), while the PDMS coated P84 co-polyimide membrane reflection at $2\theta=17.50$ (d-spacing: 4.98). This mean that PDMS coating did not affect the matrix of the polymer which agrees with the SEM and FTIR result. A slight decrease in d-spacing value might affect the permeability of the membrane as this was related to the free volume. However, in order to achieve good selectivity, the membrane requires low d-spacing that result in low distance of the atomic planes and subsequently obtain a superior gas separation selectivity [21].

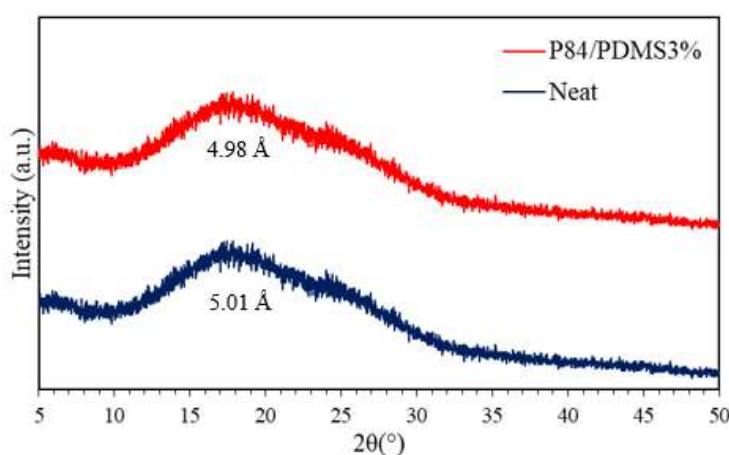


Figure 4. XRD pattern of P84 co-polyimide and PDMS coated P84 co-polyimide.

3.4 Gas permeation results

The gas permeation properties of the prepared hollow fiber P84 co-polyimide and PDMS coated P84 co-polyimide membranes were measured using the gas permeation test apparatus at room temperature. The gas permeation data were listed in Table 1. The result showed that neat membrane possesses high permeability and low selectivity. The high permeability was due to surface defects where the gas can move non-selectively through defects or pin holes on the membrane surface. Since the neat membrane suffered from surface defects, an effort to fix this issue was conducted by PDMS coating. Figure 5 shows how the membrane were coated with PDMS solution via dip-coating method. Performance wise, the permeation of O_2 and N_2 were affected by coating as it got lower compared to the uncoated membrane. As the surface were less rough and defect, the gas transport though the membrane was mainly controlled by solution diffusion of gas into membrane. As a result, the O_2/N_2 selectivity of the coated P84 co-polyimide membrane was significantly enhanced from 4.11 to 7.46. This means that the permeation value on the coated membrane was the real intrinsic properties of the P84 co-polyimide membrane and showing that the PDMS layer efficiently sealed the pin holes that are not selective in the active layer of the membrane [8, 26]. The estimated selective dense layer of the P84 co-polyimide membrane was around 0.83 μm and silicone coated P84 co-polyimide membrane was around 0.85 μm . It means that thin layer of silicone coat can improved selectivity with sealing any defects. Moreover, Table 1 also shown results from previous work and found same trend in various polymer with any modifications for selectivity of O_2/N_2 . However, O_2/N_2 selectivity in this work shown good result compared to others, indicates that P48 co-polyimide has good properties as membrane precursor.



Figure 5. PDMS 3% wt (in *n*-hexane) coated P84 co-polyimide membrane.

Table 1. Gas permeation properties of PDMS coated P84 co-polyimide and previous work.

Sample	Permeability (GPU)		Selectivity	Ref
	O ₂	N ₂	O ₂ /N ₂	
PAN/PDMS3% (in <i>n</i> -hexane)	77.8	28.4	2.74	[3]
PSF/zeoliteβ/Matrimid/PDMS2% (in <i>iso</i> -octane)	0.0529	0.0102	5.20	[9]
PSF-carbon xerogel/PDMS3% (in <i>n</i> -hexane)	15.32	2.18	7.03	[10]
PSF-MCM41/PDMS30% (in <i>n</i> -hexane)	5.02	0.71	7.10	[12]
PES-modified zeolite/PDMS3% (in <i>n</i> -hexane)	0.574	0.08	7.26	[26]
Neat	8.57	2.09	4.11	This work
P84/PDMS3%	0.182	0.02	7.46	This work

unit in GPU ($1 \text{ GPU} = 10^{-6} \frac{\text{cm}^3 (\text{STP})}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}$)

PAN = Polyacrylonitrile

PSF = Polysulfon

PES = Polyethersulfone

4. Conclusion

The gas separation properties of the hollow fiber P84 co-polyimide membranes were significantly improved by simple PDMS coating. This was due to decrease the formation of defects in surface membrane, which resulted in improving the membrane performance. PDMS coating has efficiently sealed the non-selective pinholes manifested on the membrane active skin layer without altering the membrane intrinsic and chemical properties. In addition, PDMS layer has provided an appropriate medium to accommodate adsorptive submicron filler on the surface of hollow fiber membrane. The O₂/N₂ selectivity of the silicone coated P84 co-polyimide membrane was noticeably enhanced from 4.11 to 7.46. The overall results demonstrated that coating layer was simple method to the direct improvement of gas separation properties of the membrane.

Acknowledgments

The authors gratefully acknowledge the financial support from Institut Teknologi Sepuluh Nopember under Fresh Graduate Scholarship for Magister Program (Number: 039762/IT2/HK.00.01/2017) and Ministry of Research, Technology and Higher Education of the Republic of Indonesia about Research Funding Recipients at Legal Entity State Universities (PTNBH) for Magister Thesis, contract no: (6/E/KPT/2019). The authors also would like to acknowledge The Ministries of Research, Technology, and Higher Education Republic of Indonesia for providing financial support under PMDSU scholarship for doctoral degree for Triyanda Gunawan and PMDSU research fund, contract no: (028/SP2H/PTNBH/DRPM/2018).

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