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Fabrication of PES/PDMS/ZIF-L Composite Membrane for CO_2, N_2 and CH_4 Permeation

Meor Muhammad Hafiz Shah Buddin[1,2] and Abdul Latif Ahmad[1*]

[1]School of Chemical Engineering, Universiti Sains Malaysia Engineering Campus, 14300 Nibong Tebal, Pulau Pinang, Malaysia
[2]School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

[*]Corresponding author: chlatif@usm.my

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ABSTRACT: *This manuscript reports the fabrication of polyethersulfone (PES)/polydimethylsiloxane (PDMS)/zeolitic imidazolate framework (ZIF-L) composite membrane for gas separation. ZIF-L is a new type of nanosheet metal-organic frameworks that can selectively separate CO_2. Hypothetically, its presence in the selective layer will simultaneously improve CO_2 permeance and selectivity. The effect of four parameters (PDMS concentration, withdrawal speed, holding time and ZIF-L:PDMS ratio) involved during the fabrication process on the separation performance were thoroughly looked at. Except for ZIF-L:PDMS ratio, it was found that, all parameters have a significant influence on both, the thickness of selective layer and amount of ZIF-L present. ZIF-L:PDMS ratio has substantial impact on the ZIF-L adhered on the support. The ideal fabrication condition was 3 wt% PDMS concentration, 5 mm/s withdrawal speed, 120s holding time and 1:1 ZIF-L:PDMS ratio. At these conditions, the composite membrane recorded 4.25 GPU, 15.71 GPU and 8.93 GPU of CO_2 permeance, CO_2/N_2 and CO_2/CH_4 selectivity, respectively.*

Keywords: polymeric membrane, metal-organic frameworks, composite membrane, gas separation

1. INTRODUCTION

Recently, IEA reported that the emission of CO_2 in 2021 has rebounded to 33 gigatons where the amount is close to the pre-pandemic years.[1] Interestingly, emissions from natural gas combustion reached its all-time high and contributed

to 22% of global CO_2 emissions. Such a situation calls for an urgent need for alternative methods to reduce CO_2 release into the atmosphere. Membrane technology is a well-known way to separate and capture CO_2 from many effluents such as flue and syngas. Additionally, polymeric membrane is attractive as it is easy to process, robust and highly stable in harsh operating conditions. Nevertheless, this technology is associated with permeability and selectivity trade-offs.[2] In a mixed matrix membrane, the trade-off occurs due to interfacial defect and incompatibility between polymer and inorganic phase, among others.[3] Meanwhile, the formation of a composite membrane causes additional resistance for the gas to permeate. As a result, the permeability of CO_2 reduces although selectivity increases. Altering the selective layer in a composite membrane is an approach to deal with this issue.

This study proposes the incorporation of a selective layer that contains metal-organic frameworks (zeolitic imidazolate framework [ZIF-L]) on an asymmetric support (polyethersulfone [PES]). Such a configuration could resolve the issue of low CO_2 permeance in the composite membrane due to the presence of ZIF-L which has CO_2-philic structure. This is because, ZIF-L has a small pore size that can selectively sieve CO_2 with a kinetic diameter of 3.4Å.[4] To date, there are several reported works on the fabrication of composite membrane using metal-organic frameworks. For instance, Zulhairun et al. formed a composite of PSf/PDMS/$Cu_3(BTC)_2$ while Zakariya et al. incorporated NH_2-MIL-125(Ti).[5,6] None of the studies has explored the utilisation of 2D metal-organic frameworks. 2D materials has high aspect ratio and hypothetically covers a larger surface area by using much lower amount than the typical 3D shaped materials. In this regard, the presence of the 2D material will enhance the selectivity of the system by providing a highly tortuous path for a gas molecule to travel. However, it is vital to obtain the best condition to form the composite membrane. This study looked at these parameters to form the selective layer on PES membrane, PDMS concentration, withdrawal speed, holding time and ZIF-L:PDMS mass ratio. Hypothetically, PDMS concentration and withdrawal speed heavily influence the thickness of the selective layer, as the Landau-Levich theory suggests. It is also speculated that dipping time and ZIF-L shall affect the amount of ZIF-L available on the separation layer. Besides, holding time could possibly cause intrusion of the coating layer into the support.[7] These parameters must be ideal to avoid the trade-off between CO_2 permeance and its selectivity as additional resistance is to be introduced on the membrane. Theoretically, their influence on the coating thickness and the amount of ZIF-L adhered on the membrane's surface will be paid attention too as these factors will directly influence the resistance for the gas to permeate.

2. EXPERIMENTAL

2.1 Chemicals

The chemicals used in this work are PES (Ultrason E6020P from BASF), n-heptane for analysis (Merck), two components Sylgard 184 (Dow Corning), methylimidazole (99% purity, Sigma Aldrich), zinc nitrate hexahydrate (99% purity, Sigma Aldrich), triethylamine for synthesis (Merck) and 1-methyl-2-pyrrolidone (99.5% purity, Merck).

2.2 ZIF-L synthesis

The ZIF-L was synthesised by adopting the method outlined by Khan et al., where triethylamine was used as an additive to control the nucleation that took place as a result of mixing of methylimidazole and zinc nitrate hexahydrate. The product of the reaction was centrifuged, washed with deionised water and dried at 65°C before its use.[8]

2.3 Composite membrane fabrication

Firstly, the support asymmetric membrane was fabricated using 29 wt% PES dissolved in 1-methyl-2-pyrrolidone. The hollow fiber membrane was fabricated by adopting the conditions reported by Ahmad et al., with some modifications (20 cm air gap and 2.4 mL/min dope flowrate).[9] The membrane was fabricated using the dry-wet phase inversion method and it was immersed in distilled water for 3 days. Before it was used, the membrane was air-dried at room temperature. The PES membrane used as the support has dense skin with an average thickness of 8 μm and no noticeable pores on the surface.

In every experiment, a 10 cm of PES hollow fiber membrane was potted using slow setting epoxy. At the same time, the coating solution was prepared by dissolving two-component PDMS at 1:10 ratio by mass in n-heptane.[10] After an hour, ZIF-L was added to the solution at varying ratios and stirring was continued for another 45 min. To avoid sedimentation of ZIF-L, the solution was sonicated for 15 min at room temperature. The composite membrane was then prepared by dipping the membrane in the PDMS/ZIF-L solution for a specific duration. At the end of the process, the membrane was dried at room temperature for at least 24 h to ensure no solvent remains. All manipulated variables during the composite membrane fabrication and their range are as listed in Table 1.

Table 1: Manipulated variables in this study and their range.

Variables	Range
PDMS concentration in (wt%)	1, 3, 5, 7 and 10
Withdrawal speed in (mm/s)	1, 3, 5 and 7
Holding time in (s)	60, 120, 180, 240 and 300
ZIF-L:PDMS ratio	0.5:1, 1:1, 1.5:1 and 2:1

2.4 Permeation test

All membranes were subjected to 5 bar of N_2, CO_2 and CH_4 as the feed. Such pressure value was chosen to showcase that the composite membrane does not experience the molecular chain collapse at high pressure.[11] Experiments were conducted at room temperature. The permeation rig was equipped with a pressure transmitter and a soap bubble flowmeter. The permeance of each gas was calculated by the following equation:

$$\frac{P_i}{l} = \frac{Q_{STP}}{A\Delta p} \tag{1}$$

Where $\frac{P_i}{l}$ is the permeance of the gas in GPU (1 GPU = 1×10^{-6} cm^3 [STP]/[cm^2·s·cmHg]). Q_{STP} is the corrected volumetric flow rate to standard temperature and pressure (273 K, 1 atm), Δp is the trans-membrane pressure difference (cmHg) while A is the effective membrane surface area (cm^2). Meanwhile, the ideal selectivity was calculated by dividing the permeance of CO_2 by N_2 or CH_4 to calculate the selectivity of $S_{CO2/N2}$ and $S_{CO2/CH4}$, respectively.

3. RESULTS AND DISCUSSION

3.1 Effect of PDMS concentration

The performance of the PES/PDMS/ZIF-L composite membrane fabricated at varying PDMS concentrations can be found in Figure 1. Based on the graph, increasing PDMS concentration results in a decreasing trend of CO_2 permeance. This is mainly because of the additional resistance for gas to permeate as PDMS/ZIF-L layer is introduced on the PES. Figure 2 provides the morphology of the membrane at varying PDMS concentrations. It is apparent that the PDMS/ZIF-L layer gets thicker at high PDMS concentration. Also note that a very minimal amount of ZIF-L was adhered at minimal PDMS concentration. As a result, the selectivity of the composite membrane is close to the uncoated membrane at 1 wt%. Such observation contributes to the high CO_2 permeance as well.

A compelling increment of CO_2/N_2 selectivity from 1 wt% to 3 wt% was observed as more ZIF-L were attached to the membrane's outer skin, as shown by the morphology image. ZIF-L is known to have a high affinity towards CO_2 and its role on the performance of PES/PDMS/ZIF-L membrane can be validated.[4] The selectivity peaked at 3 wt% PDMS and a significant decline was noted at higher concentrations. Apparently, this is because the permeance of N_2 did not show much difference at high PDMS concentration and the thicker selective layer impacted the permeation of CO_2 at a greater extent. Interestingly, the effect of PDMS concentration is less significant on CO_2/CH_4 selectivity and a slight increment can be observed at the low range of PDMS concentration, as similarly reported by Madaeni et al.[12] In this case, 3 wt% PDMS was selected as the ideal concentration to develop the composite membrane. At this condition, the CO_2 permeance, CO_2/N_2 and CO_2/CH_4 selectivity is 4.54 GPU, 17.02 GPU and 2.77 GPU, respectively. The composite membrane resulted in high CO_2/N_2 selectivity, surpassing the intrinsic selectivity of PDMS while the CO_2 permeance is higher than the inherent PES value.

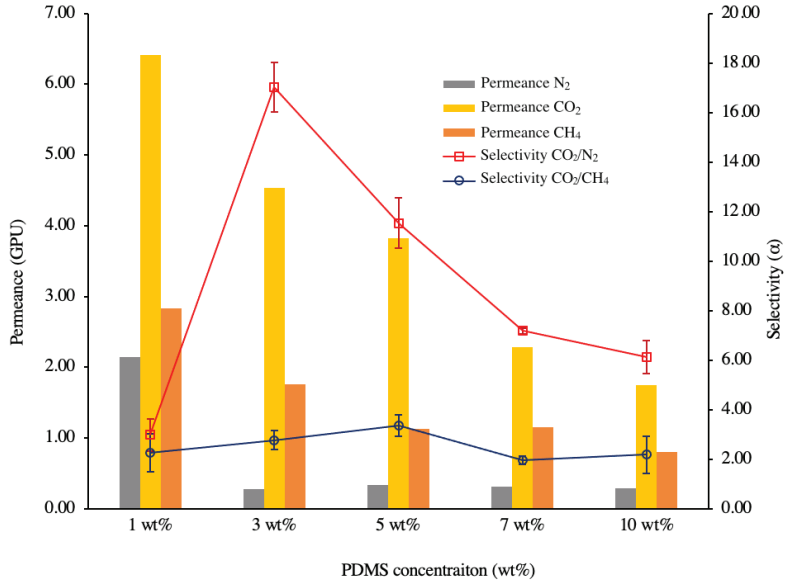

Figure 1: Effect of PDMS concentration on PES/PDMS/ZIF-L membrane separation performance. Experimental conditions: 180 s holding time, 5 mm/s withdrawal speed and 1:1 ZIF-L:PDMS ratio.

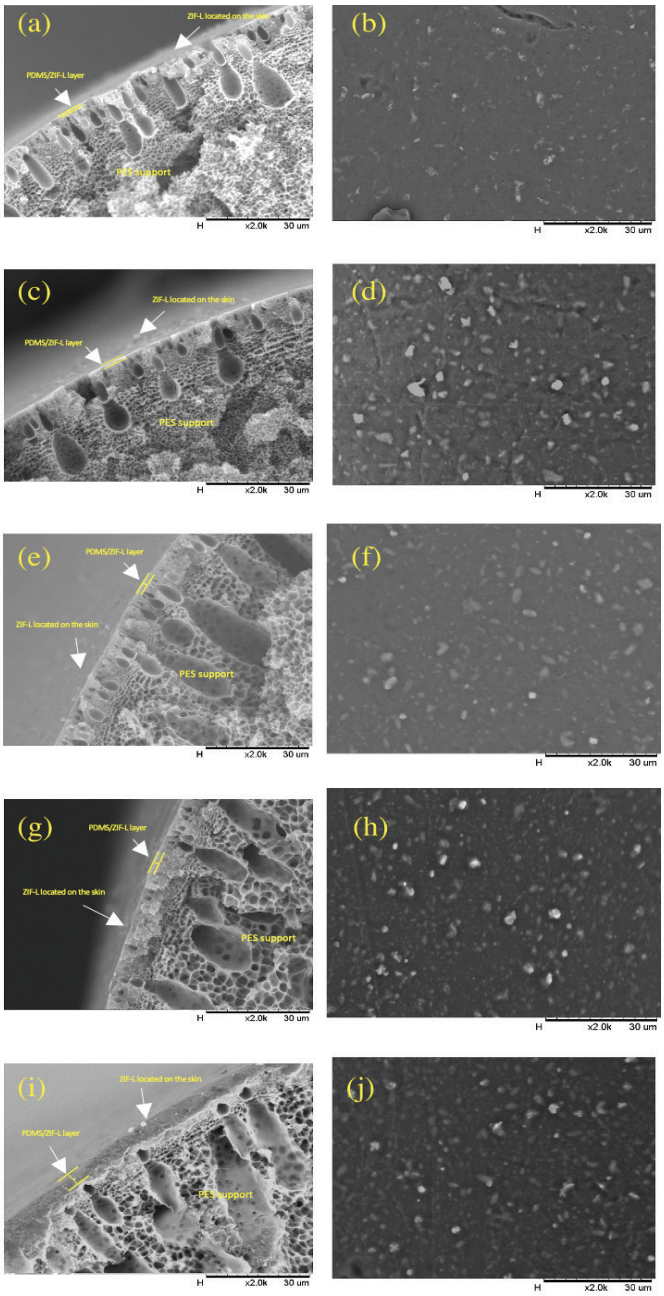

Figure 2: Cross-sectional and surface morphology of PES/PDMS/ZIF-L membrane fabricated at (a,b) 1 wt%, (c,d) 3 wt%, (e,f) 5 wt%, (g,h) 7 wt% and (i,j) 10 wt% PDMS.

3.2 Effect of withdrawal speed

The influence of withdrawal speed on the performance of the composite membrane is elucidated in Figure 3. It is evident that the CO_2 permeance decreases as a function of the withdrawal speed whereas, it oppositely impacted the selectivity. Based on the morphologies provided in Figure 4, the withdrawal speed influences the amount of ZIF-L adhered to the membrane's skin and the coating thickness. According to the report by Chen et al.,[13] the thickness of the coating film is a function of withdrawal speed, besides the concentration of the coating solution. Based on the Landau-Levich theory, the withdrawal speed applied in this work will result in a linear increase in the coating thickness. Lasseuguette et al.,[14] reported similarly and highlighted the importance of withdrawal speed on the gas permeability as well.

The separation is considered to take place via the following mechanisms; solution-diffusion, size exclusion and sorbent-adsorbate interaction. The synergy between these mechanisms was reflected by the results obtained. With denser ZIF-L on the membrane's skin and thicker coating, the permeance was reduced, accompanied by improved selectivity. It can be seen from Figure 3 that the maximum CO_2/N_2 selectivity was obtained at 5 mm/s before showing no significant improvement at higher speed. CO_2/CH_4 selectivity showed a similar trend. 7 mm/s was not selected as the best condition due to large errors in the data. In this regard, the best withdrawal speed was chosen as 5 mm/s.

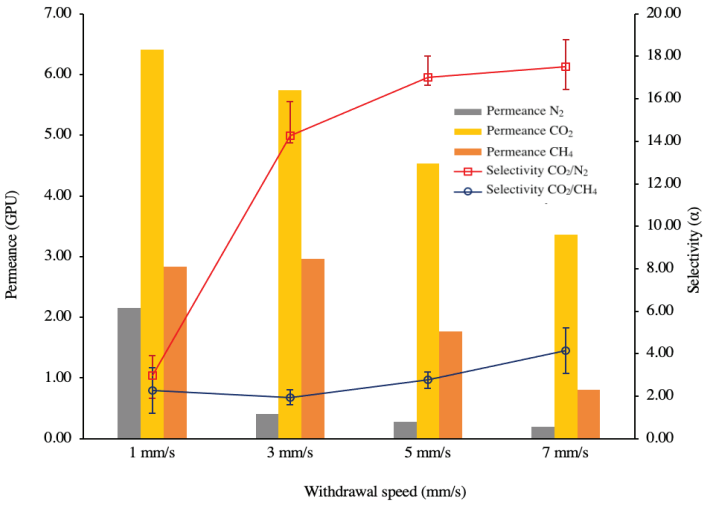

Figure 3: Effect of withdrawal speed on PES/PDMS/ZIF-L membrane separation performance. Experimental conditions: 3 wt% PDMS, 180 s holding time and 1:1 ZIF-L:PDMS ratio.

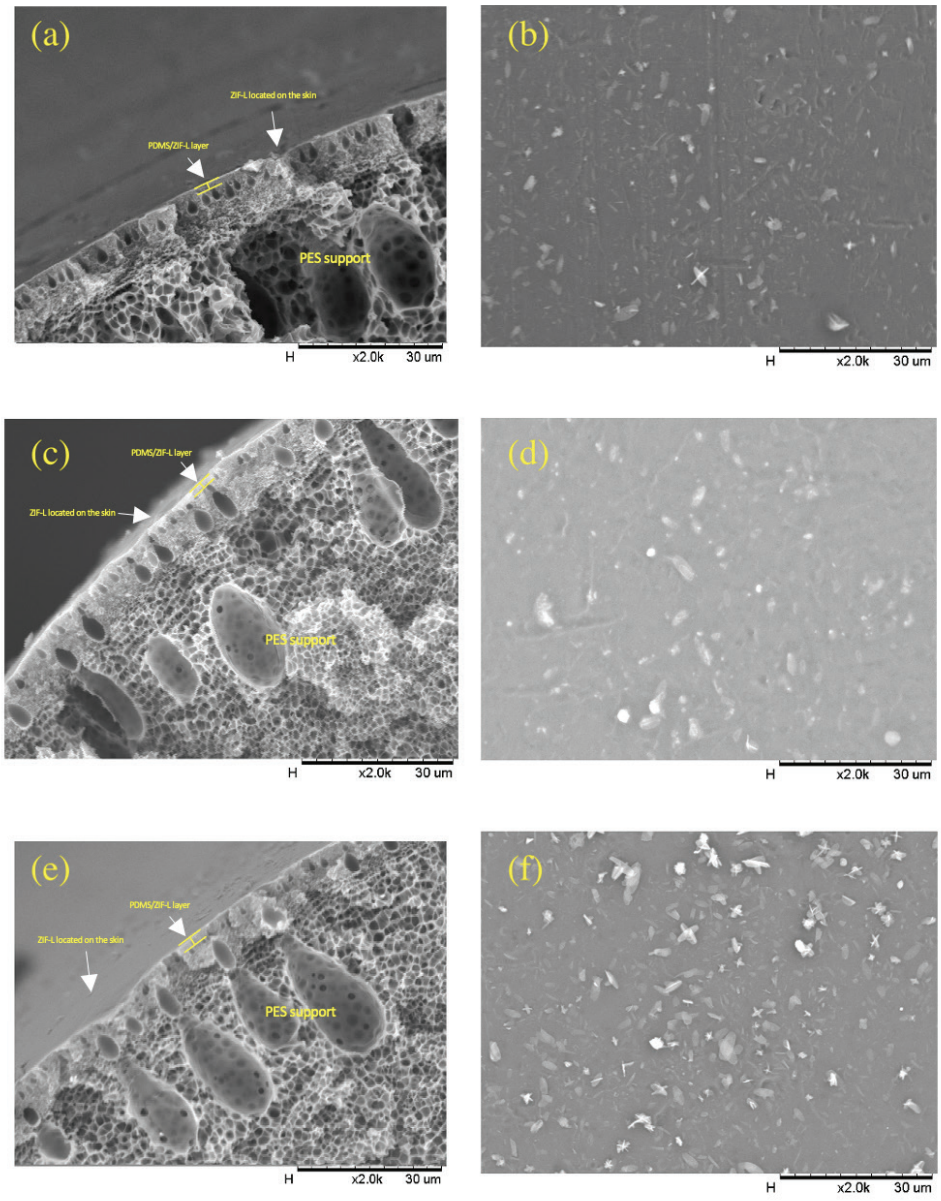

Figure 4: Cross-sectional and surface morphology of PES/PDMS/ZIF-L membrane fabricated at (a,b) 1 mm/s, (c,d) 3 mm/s and (e,f) 7 mm/s of withdrawal speed.

3.3 Effect of holding time

Figure 5 illustrates the PES/PDMS/ZIF-L membrane performance at varying holding times while Figure 6 provides their morphologies. The composite membrane requires an optimum time to achieve peak performance based on the data available. In general, prolonged duration of holding time resulted in an improvement of CO_2 permeance and its selectivity. However, such a trend is valid until 180 s before the membrane experience a significant performance downturn. Firstly, the improvement was achieved due to the thicker selective layer and molecular sieving effect at the presence of ZIF-L. PDMS is known to have good intrinsic selectivity of CO_2 while ZIF-L has a pore structure that is similar to the kinetic diameter of CO_2. The synergistic effect of these two factors enhanced the membrane's performance.

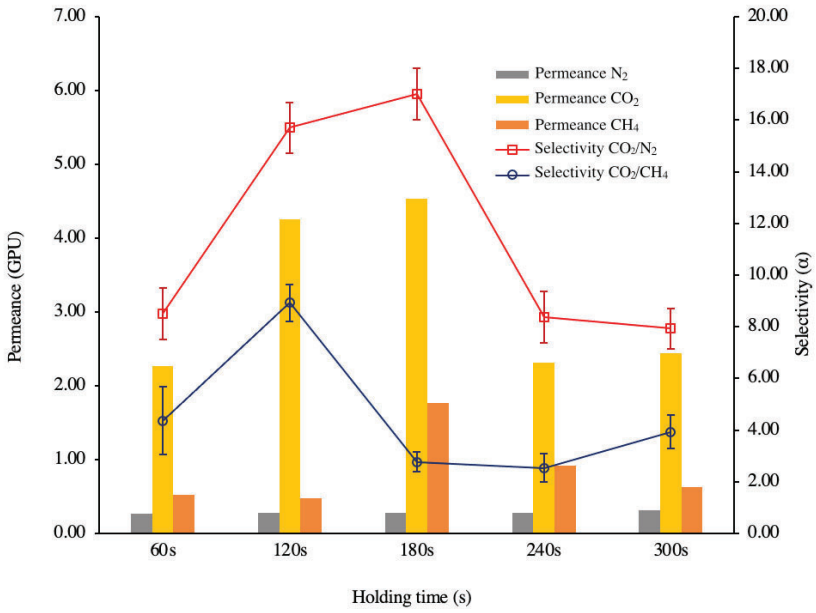

Figure 5: Effect of holding time on PES/PDMS/ZIF-L membrane separation performance. Experimental conditions: 3 wt% PDMS, 5 mm/s withdrawal speed and 1:1 ZIF-L:PDMS ratio.

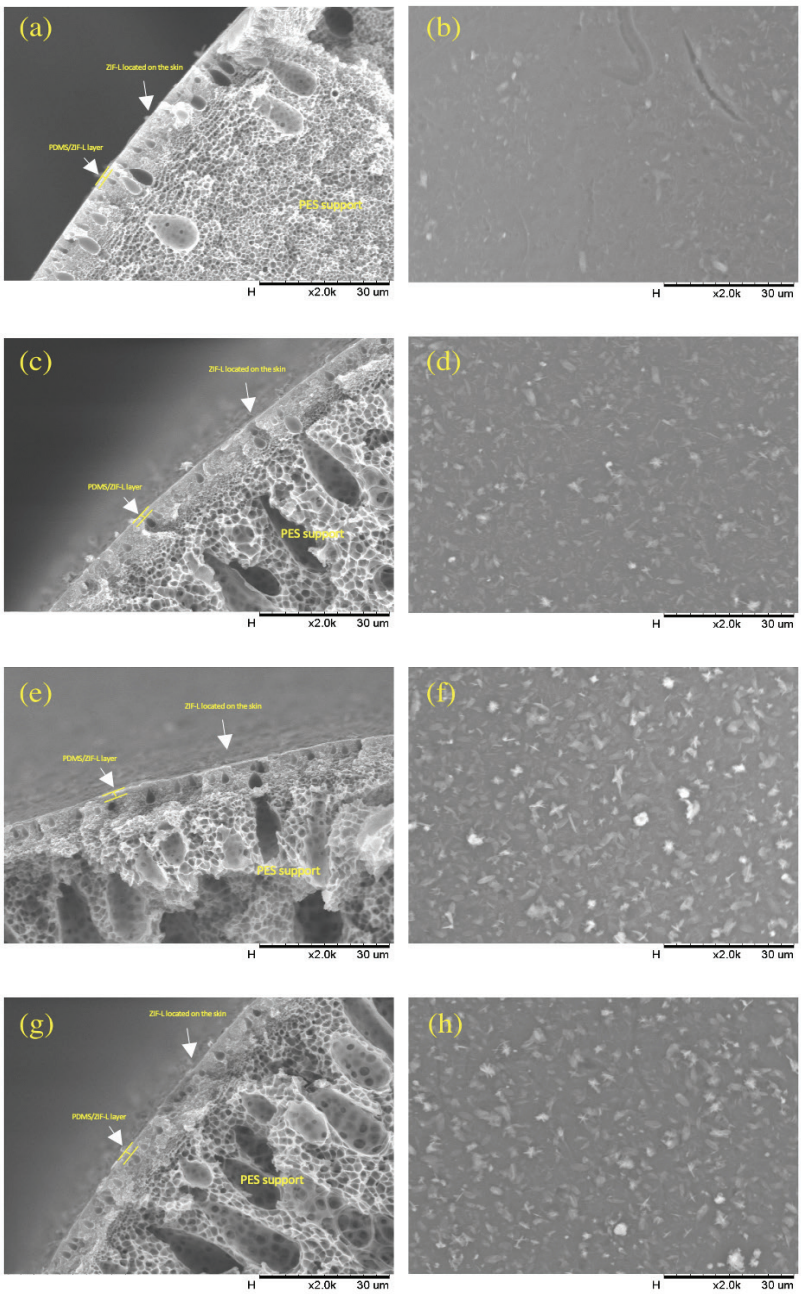

Figure 6: Cross-sectional and surface morphology of PES/PDMS/ZIF-L membrane fabricated at (a,b) 60 s, (c,d) 120 s, (e,f) 240 s and (g,h) 300 s of holding time.

At unnecessarily long duration, the selective layer gets too thick as also reported by Hassan et al.[15] Apparently, the long period of coating resulted in highly populated ZIF-L on the surface, too. As a result, a highly tortuous path was created, and all gases suffered from the low permeance. The selectivity was likely reduced in response to increased free volume in the selective layer at high amount of ZIF-L. Observe that the agglomeration of ZIF-L (forming petal-like) is obvious on the membranes prepared at > 240 s. Accordingly, 120 s was selected as the appropriate duration to prepare PES/PDMS/ZIF-L composite membrane. At this condition, the CO_2 permeance, CO_2/N_2 selectivity and CO_2/CH_4 selectivity are 4.25 GPU, 15.71 GPU and 8.93 GPU, respectively.

3.4 Effect of ZIF-L:PDMS ratio

Effect of ZIF-L:PDMS ratio (by mass) was evaluated by varying the value from 0.5:1 to 2:1 and the data of the membrane's performance can be found in Figure 7. According to the figure, CO_2/N_2 selectivity and CO_2/CH_4 selectivity peaked at 1:1. Apparently, the ZIF-L:PDMS ratio has less profound effect on the CO_2 permeance, especially at ratio higher than 1:1. The results are in line with Madaeni et al., who worked on the fabrication of PES coated with TiO_2.[16] A higher mass of ZIF-L incorporated in the coating solution has introduced more ZIF-L on the membrane's skin. Such a claim can be validated by Figure 8 where the morphology of the membrane can be found. However, high ratio causes agglomeration of the nanosheet as similarly reported by Zakariya et al.[6] This factor also causes interfacial defects, on top of the high free volume of the PDMS matrix. Consequently, the selectivity was reduced. Nevertheless, the crucial role of ZIF-L on the membrane's performance is undeniable. Based on the data, using a low ZIF-L:PDMS ratio has resulted in very poor CO_2/CH_4 selectivity, where it only improved at 1:1 ratio. The influence of coating thickness was ruled out since all membranes were fabricated at identical conditions except the ratio of ZIF-L:PDMS. It is inferred that this parameter only affects the amount of ZIF-L adhered on the surface of the membrane.

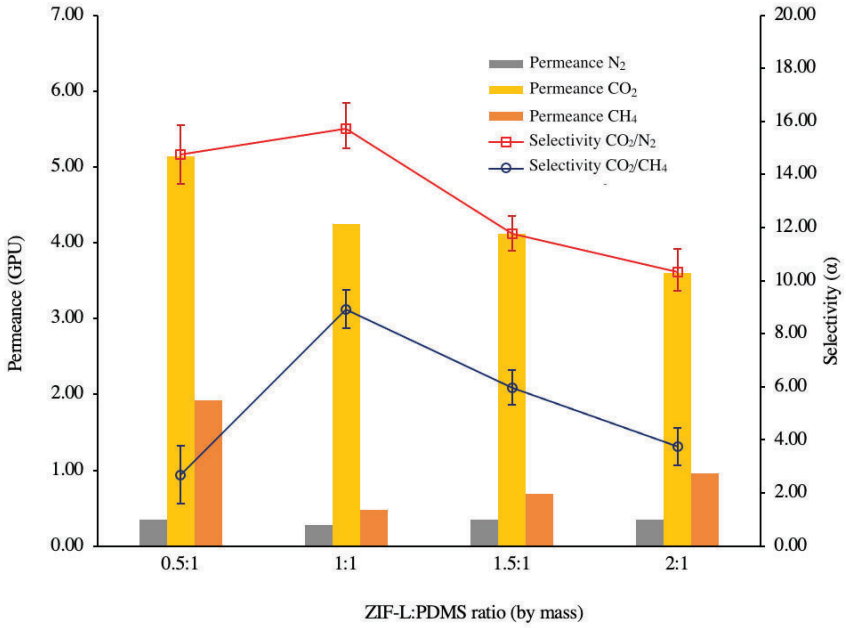

Figure 7: Effect of ZIF-L:PDMS ratio on PES/PDMS/ZIF-L membrane separation performance. Experimental conditions: 3 wt% PDMS, 5 mm/s withdrawal speed and 120 s holding time.

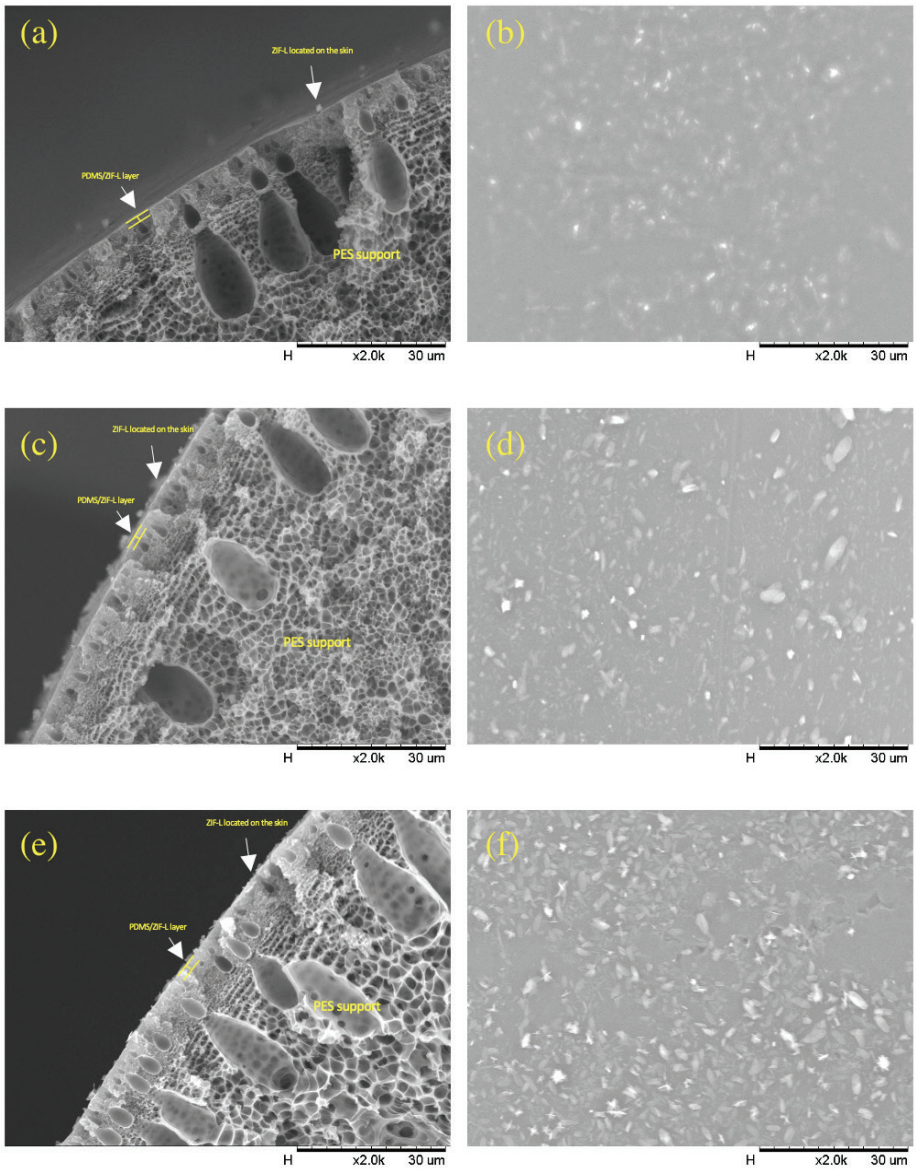

Figure 8: Cross-sectional and surface morphology of PES/PDMS/ZIF-L membrane fabricated at (a,b) 0.5:1, (c,d) 1.5:1 and (e,f) 2:1 of ZID-L:PDMS ratio.

4. CONCLUSIONS

Four parameters involved in the fabrication of PES/PDMS/ZIF-L composite membranes have been analysed. Their effects on the performance of the membrane to separate CO_2 are clear. This study reveals that PDMS concentration, withdrawal speed and holding time significantly influence the selective layer thickness and the amount of ZIF-L present. Meanwhile, ZIF-L:PDMS ratio affects only the latter. Nevertheless, the gas separation was improved by enhancing the solubility and diffusivity of CO_2 by the presence of PDMS layer while ZIF-L molecularly sieved the gases.

5. ACKNOWLEDGEMENTS

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