MULTILAYER COMPOSITE POLYSULFONE HOLLOW FIBER MEMBRANE MODIFIED BY GRAPHENE OXIDE FOR GAS SEPARATION

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DEDICATION

This study is wholeheartedly dedicated to my beloved father (Roslan bin Che Din), late mother (Zuriyah Binti Jaafar) and step mother (Rosziana Binti Jusoh) as well as my better half, Mohamad Ainuddin Bin Wahidin, who have been source of inspiration and strength. I appreciate your moral, spiritual, emotional, financial and supports through thick and thin during my PhD journey. Thanks for all the prayers, advices and guidance. Also, to my brothers, sisters, relatives, mentors and friends who shared their words of advice and encouragement to finish my study. Lastly, this thesis is dedicated to the Almighty God, thank you for the guidance, strength, power of mind and protection.

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ABSTRACT

One of the most critical issues encountered by polymeric membranes for gas separation process is the trade-off effect between gas permeability and selectivity. The aim of this work is to develop a simple yet effective coating technique to modify the surface properties of commonly used polysulfone (PSF) hollow fiber membranes to address the trade-off challenge on CO_2/CH_4 and O_2/N_2 separation issue. More specifically, the first objective of this work is to study the effects of different types of PSF hollow fiber support on the gas separation performance of surface-coated membranes by varying significant imperative parameters, i.e., air gap (1–4 cm), dope extrusion rate (1–2 mL/min), bore fluid rate (0.33–0.67 mL/min) and polymer concentration (15–35 wt.%). Results showed that the support membrane spun at highest air gap of 4 cm and lowest dope extrusion rate at 1 mL/min were ideal for the coated membrane preparation owing to its good structural integrity that could produce a membrane with optimum balance composition for gas permeance and selectivity. The findings also revealed that the support membrane made of 25 wt.% PSF was the best for single layer coating and the membrane coated with polyether block amide (Pebax) performed better in terms of selectivity than the membrane coated with polydimethylsiloxane (PDMS) because Pebax solution tended to form denser layer as a result of its higher solution viscosity. However, the Pebax solution is prone to penetrate into the pores of support membrane, and thus lowering its permeability. Due to this, the second objective of this work is to investigate the efficiency of multilayer coating technique by forming Pebax (1–9 wt%) as selective outer layer and PDMS (3 wt%) as gutter layer on the PSF membrane surface. Results indicated that the optimized multilayer coated membrane at 3 wt% Pebax could achieve CO_2/CH_4 and O_2/N_2 selectivity of 35.19 and 6.56, respectively. As a comparison, the membrane coated with 1 wt% Pebax only showed 29.47 and 6.07, respectively. To further enhance the performance of multilayer coated membrane, the third objective of this work is to evaluate the impacts of graphene oxide (GO) loading from 0–1.0 wt% on the Pebax selective layer on the membrane performance. Experimental findings revealed that incorporating 0.8 wt% GO into the composites could further improve membrane performance, achieving selectivity as high as 52.57 and 8.05 for CO_2/CH_4 and O_2/N_2, respectively. This is due to formation of improved tortuous structure that created higher resistance to larger gas molecules (CH_4 and N_2) compared to smaller gas molecules (CO_2 and O_2). In conclusion, it can be said that the newly developed multilayer coating technique that combines polymeric materials and nanofillers could overcome the drawbacks of typical PSF membranes, producing a multilayer composite hollow fiber membrane with improved surface properties for gas separation.

ABSTRAK

Salah satu isu yang kritikal yang dihadapi oleh membran polimer untuk proses pemisahan gas adalah tidak keseimbangan di antara kebolehtelapan dan pemilihan gas. Tujuan kerja ini adalah untuk menghasilkan teknik salutan yang mudah lagi berkesan untuk mengubahsuai ciri permukaan membran gentian berongga polisulfon (PSF) untuk mengatasi ketidak keseimbangan pemisahan gas CO_2/CH_4 dan O_2/N_2. Untuk lebih terperinci, objektif pertama kerja ini adalah untuk mengkaji kesan kepelbagaian membran gentian berongga PSF yang dijadikan sebagai sokongan bagi proses salutan dengan mempelbagaikan beberapa parameter penting seperti sela udara (1–4 cm), kadar penyemperitan dop (1–2 mL/min), kadar cecair penggerek (0.33–0.67 mL/min) dan kepekatan polimer (15–35 wt%). Hasil eksperimen menunjukkan bahawa membran sokongan yang dipintal pada sela udara yang tinggi pada 4 cm dan kadar penyemperitan dop yang rendah pada 1 mL/min didapati sesuai untuk proses salutan kerana memiliki kekuatan stuktur yang bagus yang mempunyai keseimbangan komposisi yang optima bagi kebolehtelapan dan pemilihan gas yang baik. Hasil kajian juga menunjukkan membran sokongan yang dihasilkan dari 25 wt% PSF adalah paling bagus untuk digunakan bagi proses satu lapisan salutan dan membran yang disaluti dengan polieter blok amida (Pebax) menunjukkan prestasi yang lebih baik dari segi pemilihan gas berbanding membran yang disaluti oleh poli-dimetil-siloksana (PDMS) kerana cairan Pebax berkecenderungan untuk menghasilkan lapisan yang lebih padat. Namun begitu, larutan Pebax yang kerap memasuki liang membran sokongan menjadikan kebolehtelapan gas menurun. Dalam pandangan ini, objektif kedua kerja ini adalah untuk mengkaji kecekapan teknik salutan lapisan pelbagai dengan menggunakan Pebax (1–9 wt%) sebagai lapisan pemilih luaran dan PDMS (3 wt%) sebagai lapisan tengah ke atas permukaan membran PSF. Keputusan analisis menunjukkan membran salutan pelbagai pada 3 wt% Pebax dapat mencapai pemilihan gas CO_2/CH_4 dan O_2/N_2 secara optimum masing-masing 35.19 dan 6.56. Sebagai bandingan, salutan membran 1 wt% Pebax masing-masing hanya menunjukkan 29.47 dan 6.07. Bagi menaikkan lagi prestasi membran salutan pelbagai, objektif ketiga kerja ini adalah untuk menilai impak muatan grafena oksida (GO) pada 0.0–1.0 wt% dalam lapisan pemilih Pebax ke atas prestasi membran. Penemuan kajian mendedahkan bahawa gabungan 0.8 wt% GO ke dalam membran dapat menaikkan lagi prestasi membran, mencapai pemilihan gas masing-masing yang setinggi 52.57 dan 8.05 bagi CO_2/CH_4 dan O_2/N_2,. Ini oleh kerana pembentukan struktur liang berliku yang memberikan rintangan tinggi kepada molekul gas yang lebih besar (CH_4 dan N_2) berbanding molekul gas yang lebih kecil (CO_2 dan O_2). Kesimpulannya, penghasilan teknik salutan lapisan pelbagai baru dengan cairan salutan dan pengisian-nano yang sesuai dapat mengatasi kelemahan teknik salutan konvensional bagi pengubahsuaian permukaan membran, menghasilkan membrane gentian berongga dengan ciri permukaan yang ditambah baik untuk pemisahan gas.

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LIST OF ABBREVIATIONS

AA	-	Acrylic Acid
AFM	-	Atomic Force Microscope
Ar	-	Argon
ATR	-	Attenuated Total Reflection
BFR	-	Bore Fluid Rate
CA	-	Cellulose Acetate
CD	-	Cyclodextrin
CH_4	-	Methane
CMS	-	Carbon Molecular Sieve
CO_2	-	Carbon Dioxide
$Cu_3(BTC)_2$	-	Copper Benzene-1,3,5-Tricarboxylate
DER	-	Dope Extrusion Rate
DMAc	-	Dimethylacetamide
EDX	-	Energy Dispersive X-ray
F_2	-	Fluorine Gas
FESEM	-	Field Emission Scanning Electron Microscope
FFV	-	Free Fraction Volume
FTIR	-	Fourier Transform Infrared
GO	-	Graphene Oxide
GPU	-	Gas Permeation Unit
H_2O_2	-	Hydrogen Peroxide
H_2SO_4	-	Sulphuric Acid
HCl	-	Hydrochloric Acid
HF	-	Hydrogen Fluoride
ID	-	Inner Diameter
ILs	-	Ionic Liquids
$KMnO_4$	-	Potassium Permanganate
MBHBA	-	N-(3-tert-butyl-2-hydroxy-5 methylbenzyl) acrylamide
MMMs	-	Mixed Matrix Membranes
MOF	-	Metal Organic Framework

N_2	-	Nitrogen
$NaNO_3$	-	Sodium Nitrate
NFs	-	Nanofillers
NMP	-	N-Methyl-2-pyrrolidone
NPs	-	Nanoparticles
O_2	-	Oxygen
OD	-	Outer Diameter
PA	-	Polyamide
PAN	-	Polyacrylonitrile
PANI	-	Polyaniline
PDMS	-	Polydimethylsiloxane
PE	-	Polyether
Pebax	-	Polyether Block Amide
PEG	-	Polyethylene Glycol
PEG	-	Polyethylene Glycol
PEI	-	Polyether Imide
PEO	-	Polyethylene oxide
PES	-	Polyether Sulfone
PI	-	Polyimide
PIMs	-	Polymers of Intrinsic Microporosity
PMMA	-	Polymethylmetacrylate
PNMs	-	Polymer Nanocomposites Membrane
PPO	-	Poly(phenylene oxide)
PS	-	Polystyrene
PSA	-	Pressure Swing Adsorption
PSF	-	Polysulfone
PTMSP	-	Poly-1-trimethylsilyl-1-propynel
PU	-	Polyurethane
PVA	-	Polyvinyl Alcohol
PVC	-	Polyvinyl Chloride
PVDF	-	Polyvinylidene Fluoride
PVP	-	Polyvinylpyrrolidone
RO	-	Reverse Osmosis

RTIL	-	Room Temperature Ionic Liquid
SEM	-	Scanning Electron Microscope
SHPAA	-	Sterically Hindered Polyallyamine
STPD	-	Segmenting, Targeting, Positioning and Differentiation
TEM	-	Transmission Electron Microscope
TEOS	-	Tetraethyl Orthosilicate
THF	-	Tetrahydrofuran
UV	-	Ultraviolet
XPS	-	X-ray Photoelectron Spectroscope
XRD	-	X-ray Diffraction
ZnO	-	Zinc Oxide

LIST OF SYMBOLS

A	-	Effective membrane area (cm^3)
i	-	Fast penetrating gas species
j	-	Slow penetrating gas species
L	-	Length of hollow fiber membrane (cm)
l	-	Membrane thickness (cm)
n	-	Numbers of membrane fiber
P	-	Pressure (cmHg)
Q	-	Gas or liquid volumetric flow rate (cm^3/s)
r	-	Radius of hollow fiber membrane (cm)
T	-	Absolute temperature (K)
T_g	-	Glass transition temperature (^oC)
W	-	Weight (g)
α	-	Selectivity or aspect ratio
Δ	-	Difference
β	-	Beta
ε	-	Porosity of membrane
λ	-	Wavelength (nm)
μ	-	Micro
π	-	Pi
ρ	-	Density

CHAPTER 1

INTRODUCTION

1.1 Research Background

Gas separation is an important unit operation employed widely in different sectors. Its industrial applications include carbon dioxide (CO_2) capture, CO_2/methane (CH_4) separation and hydrogen enrichment. Gas separation is also used in medical field to produce oxygen (O_2)-enriched gas from the ambient air. In recent years, membrane-based gas separation processes have been the subject of considerable research and have attracted the interest of industry, which is always looking for a new technology that is less invasive in terms of environment impact and efficient from an economic point of view (Ahmed *et al*., 2020). In the last 40 years, the use of membranes in separation process has grown very rapid due to its inherent advantages in comparison to the traditional methods such as cryogenic distillation and adsorbent (Javaid, 2005; Baker, 2012; Kargari *et al*., 2020).

Polymeric membrane offers energy efficient with low capital cost, flexible process, ease of scale up and high efficient of raw material. Various polymers have been used as based material, mixing and coating altogether to achieve desired need of gas separation including polyether sulfone (PES), polyvinylidene fluoride (PVDF), polyvinyl chloride (PVC) and polysulfone (PSF). These polymers are known for their toughness and stability at relatively high temperatures. However, polymeric membranes are limited by the trade-off between selectivity and permeability and very few have been found to exceed the Robeson upper bound for gas separation (Robeson, 2008; Bryan *et al*., 2014).

To improve polymeric membrane performance, a considerable research effort has been put in to modify membrane surface properties through blending with secondary polymers such as polyvinylpyrrolidone (PVP), polyaniline (PANI) and polyethylene glycol (PEG) (Kajekar *et al*., 2015; Ovcharova *et al*., 2017), incorporation with inorganic nanoparticles such as zeolite and silica (Wahab *et al*., 2012; Zulhairun *et al*., 2017), UV-assisted graft polymerization (Xueli *et al*., 2013), plasma-to-induced graft polymerization (Chittrakarn *et al*., 2016), surface coating using polymeric materials (Liu *et al*., 2004a; Liu *et al*., 2004b; Suleman *et al*., 2016), etc.

Of these modification methods, surface coating is considered the easiest one to be carried out. This method uses secondary polymer (usually different from the support membrane) to improve membrane gas separation performance without affecting the structural integrity. The coating layer aims to seal not only the pinholes (defects) on the surface of skin layer, but also help improving gas pair selectivity (Ismail *et al*., 1999; Ng *et al*., 2004). Polydimethylsiloxane (PDMS) and polyether block amide (Pebax) materials are two polymers that have been used widely as in the coating solution as their ability in handling gas separation process. Although single-layer coated membranes were reported to perform better than the uncoated membrane, studies had shown that using two different materials to form dual-layer coated membrane could outperform single-layer coated membrane as it combines the positive features of two different materials (Chen *et al*., 2014; Wang *et al*., 2014a).

To fabricate multilayer membrane, gutter layer is first established on the membrane surface to provide a smooth and defect-free surface before a selective layer coating solution is used. Gutter layer is also important to reduce the possible penetration of the selective layer coating solution into the porous support layer (Dai *et al*., 2016a). PDMS is suitable used for gutter layer as it is highly permeable, smooth and had potential to prevent the diluted polymer solution from penetrating into the porous structure which tends to block the pores. Compared to poly-1-trimethylsilyl-1-propynel (PTMSP), PDMS with a unique flexible siloxane backbone is favourable as a gutter layer as it experiences slower performance loss than PTMSP (Chen *et al*., 2014).

With respect to selective layer, the unique structure of Pebax that consists of both crystal polyamide (glassy polymer) and amorphous polyether (rubbery polymer) is able to provide a balancing increase in both permeability and selectivity (Wang *et al*., 2014a; Wang *et al*., 2014b; Ren *et al*., 2012; Ahmadpour *et al*., 2014). However, it must be pointed out that the membrane made of pure Pebax has technical challenges as it suffers from low mechanical strength that prevents it from being used. Therefore, Pebax can only be considered as coating material to modify membrane properties.

The properties of selective layer are reported to be further improved upon incorporation of inorganic nanomaterials. Zulhairun *et al*. (2015), for instance, introduced metal organic framework (MOF) - $Cu_3(BTC)_2$ into polydimethysiloxane (PDMS) coating solution and reported that the hybrid coating layer improved the CO_2 permeance of PDMS-coated membrane (without $Cu_3(BTC)_2$ incorporation) by 28.6%, leading to increase in CO_2/CH_4 and CO_2/N_2 selectivities from 28.06 to 30.46 and from 31.34 to 33.40, respectively. The improved membrane performance was explained by the fact that $Cu_3(BTC)_2$ showed higher affinity towards CO_2 due to the coordinatively unsaturated copper sites in its crystal network. This provided exceptionally high adsorptive capability for polar molecules, resulting in the increase of gas permeance and selectivities.

In addition, Liang *et al*. (2018) reported that when beta-cyclodextrin (β-CD)/polymers of intrinsic microporosity (PIMs) coating solution was applied on the PDMS-coated membrane surface, the resultant multilayer coated membrane was able to increase the N_2, O_2 and CO_2 permeance of the membrane (without β-CD incorporation) by 53.4%, 63.9% and 66.8%, respectively. In addition, the presence of β-CD in the PIMs layer was reported to enhance the selectivity of O_2/N_2 and CO_2/N_2 of membrane by 9.4% and 8.8%, respectively. The authors elucidated that the incorporation of three dimensional β-CD into the main polymer chains of PIM had created more micro-pore volumes or free fraction volume (FFV) which increased CO_2 sorption capacity.

In view of this, the aim of this work is to develop a multilayer coating technique that is suitable to fabricate hollow fiber membrane with nanofillers incorporated into its selective layer for enhanced gas separation. Graphene Oxide (GO) nanosheet was selected in this work as it has been previously demonstrated to improve the gas separation performance of mixed matrix membrane (MMM) (Dai *et al*., 2016b; Jamil *et al*., 2019).

1.2 Problem Statement

Membrane-based gas separation is becoming increasingly popular due to its inherent advantages over the traditional methods such as cryogenics distillation and adsorbent bed processes. Although the commercial PSF is widely used in producing membrane for industrial gas separation, it still suffers from trade-off relationship between permeability and perm-selectivity (Robeson, 2008). Thus, such polymeric membrane needs to be modified in order to increase its affinity against gas permeance.

A conventional anisotropic polymeric membrane with dense skin layer can offer a reasonably good gas pair selectivity, but the properties of dense layer (e.g., thickness, density, porosity, etc.) are difficult to be precisely controlled via phase inversion technique. Hence, surface coating using a secondary polymer has been employed to solve this issue. This approach can develop a thinner dense layer made of different polymers on the surface of microporous PSF substrate, but the performance of the thin layer is still governed by the characteristics of the PSF substrate. In view of this, an optimization on both the PSF substrate properties and coating conditions is required in order to achieve desired outcomes.

Among the surface coating techniques that are used for the membrane surface modification, dip-coating method using PDMS solution is widely performed owing to its simplicity and low manufacturing cost. However, it must be pointed out that PDMS is mainly used to seal the defects on the membrane surface and does not really improve gas pair selectivity. Compared to PDMS, Pebax is a much better candidate as a selective layer to improve both membrane permeance and selectivity due to its unique structure that consists of both crystal polyamide (glassy polymer) and amorphous polyether (rubbery polymer). The presence of both glassy and rubber polymers tends to increase the membrane permeability and selectivity simultaneously.

Although the membranes coated with single polymer are always performing better compared to the uncoated membrane, these coated membranes are still not able to exceed the Robeson upper bound theory. Thus, two steps coating process using two different materials are found to be effective as it combines the positive features of each material used. Furthermore, single coating using Pebax always has tendency to penetrate into porous support layer and reduce the efficiency of the composite membrane. Thus, PDMS as gutter layer is needed to avoid the phenomenon. Previously, Wang *et al*. (2014a) applied multilayer coating on polyacrylonitrile (PAN) flat sheet membrane and reported that the membrane permeance and selectivity were higher compared to single layer coating. Furthermore, by applying two-step coating approach, one can ensure the defects on substrate hollow fiber membrane to be completely sealed before a highly selective layer is coated on the membrane surface.

Currently, the typical polymeric membranes are suffered from permeability-selectivity trade-off effect and one strategy that can be adopted to address the issue is by introducing inorganic nanofillers into the membrane matrix. Inorganic membranes though are reported to exhibit much better selectivities than those of polymeric membranes, its high manufacturing cost remains a main concern to many. Besides, inorganic membrane exhibits significantly lower packing density (m^2/m^3) compared to the polymeric membrane, particularly in hollow fiber configuration. Thus, in order to take the unique advantages of inorganic materials, the incorporation of inorganic nanofiller into polymeric membrane matrix is one of the current main research focuses for the membrane development (Qin and Chung, 2004; Zulhairun *et al*., 2014a; Zulhairun *et al*., 2014b; Kiadehi *et al*., 2015).

One of the popular nanofillers reported in the literature and suitable for membrane gas separation process is GO nanosheet. GO nanosheet is selected in this work as it was previously demonstrated to have positive roles in improving the gas separation performance of MMM (Dai *et al.*, 2016b; Jamil *et al*., 2019). However, this high-performance 2D nanomaterial is quite expensive. Thus, a new approach is required in order to minimize the usage of GO during membrane fabrication. Instead of adding large amount of GO directly into dope solution to form MMM, only a very small amount of GO is required for the coating solution that is used to form a thin layer on top of the membrane surface. This approach is workable as GO generally exhibits good compatibility with the coating solution. On the other hand, the presence of GO on the membrane surface is expected to show enhanced performance as the membrane gas pair selectivity is mainly governed by the skin layer rather than the entire membrane structure.

1.3 Research Objectives

The aim of this research is to develop a new multilayer coating technique that is practical for the surface modification of hollow fiber membrane for enhanced gas separation of CO_2/CH_4 and O_2/N_2. More specifically, the objectives of this work are:

1. To investigate the effects of dry-jet wet spinning conditions and polysulfone (PSF) concentration in the dope solution on the properties of hollow fiber membranes that are suitable to be used as support for surface coating process.
2. To determine the impacts of different coating solutions and coating approaches on the surface properties of hollow fiber membranes for CO_2/CH_4 and O_2/N_2 separation.
3. To evaluate the impacts of graphene oxide (GO) loading in the coating layer of hollow fiber membrane for gas separation and its prolonged stability performance.

1.4 Scope of Study

The following scopes of study are identified in order to achieve the three main objectives as stated in previous sub-section:

Objective 1:

(a) Preparing dope solution composed of 30 wt% polysulfone (PSF), 30 wt% dimethylacetamide (DMAc) (as non-volatile solvent), 30 wt% tetrahydrofuran (THF) (as volatile solvent) and 10 wt% ethanol.

(b) Investigating the effects of spinning parameter of dry-wet spinning technique using prepared dope solution by varying air gap (1 cm or 4 cm), bore fluid rate (0.33 mL/min or 0.67 mL/min) and dope extrusion rate (1 mL/min or 2 mL/min).

(c) Preparing two different coating solutions by dissolving 3 wt% PDMS in 97 wt% n-hexane and 3 wt% Pebax in the 97 wt% ethanol/water mixture (70/30 in weight ratio).

(d) Coating PSF support with different polymeric materials (10 min for PDMS and 3 s for Pebax) using dip-coating method.

(e) Investigating the effects of polymer concentration (15, 20, 25 and 35 wt%) on the properties of PSF substrates.

(f) Evaluating the effect of coating materials on fabricated composite membrane performance in terms of permeance and selectivity of four gases (CO_2, CH_4, O_2 and N_2) through gas permeation test at 5 bar and at room temperature.

(g) Characterizing the produced membrane properties with respect to porosity, surface and cross-section structure (using scanning electron microscope (SEM)) and elemental composition (using energy dispersive X-ray (EDX) spectroscope).

Objective 2:

(a) Fabricating the PSF hollow fiber support membrane (via dry-wet spinning technique using the best parameters obtained from objective 1.

(b) Preparing two different coating solutions, (i) 3 wt% PDMS dissolved in 97 wt% n-hexane and (ii) 3 wt% Pebax dissolved in 70/30 (v/v) ethanol/water.

(c) Forming multilayer coating layer on the outer surface of PSF membrane using PDMS solution as the gutter layer followed by Pebax solution as the selective layer.

(d) Optimizing the properties of Pebax selective layer by varying its concentration in the range of 1–9 wt%.

(e) Evaluating the effect of coating materials on fabricated composite membrane performance in terms of permeance and selectivity of four gases (CO_2, CH_4, O_2 and N_2) at 5 bar and at room temperature.

(f) Characterizing the produced membranes using field emission scanning electron microscope (FESEM) and EDX and infrared spectroscopy (FTIR/ATR).

Objective 3:

(a) Synthesizing GO using the modified Hummers' method.

(b) Characterizing GO using transmission electron microscope (TEM) and X-ray diffraction (XRD).

(c) Preparing hybrid Pebax coating solution by adding different amount of GO nanoparticles (0.1–1.0 wt%) into the optimized Pebax solution (3 wt% obtained from Objective 2).

(d) Applying multilayer coating method on the best performing PSF substrate using PDMS as the gutter layer and hybrid GO/Pebax as the selective layer.

(e) Evaluating the effect of coating materials on fabricated composite membrane performance for gas separation at 5 bar.

(f) Investigating the plasticization behaviour of optimized multilayer coated membrane at different feed pressure (1 to 9 bar) at constant temperature (T: 25ºC).

(g) Investigating prolonged performance stability of optimized multilayer coated membrane for up to 3000 min at 5 bar.

(h) Characterizing the multilayer coated membranes using FESEM, FTIR, X-ray photoelectron spectroscope (XPS) and atomic force microscope (AFM).

1.5 Significance of Study

Anisotropic polymeric membrane which consists of a thin skin layer (formed over a porous structure) has always been identified as a promising candidate to tackle the trade-off effect between selectivity and permeability in the pressure-driven membrane process. The significance of this study is the development of anisotropic polymeric membrane with thinner and highly selective skin layer using a simple and yet practical coating technique to enhance the existing performance of PSF hollow fiber membranes for possible adoption in industry. This research that employed two different polymeric coating solutions on the surface of fine-tuned hollow fiber support membrane is able to minimize not only the defects on the membrane surface (through gutter layer coating) but also to improve gas pair selectivity (through selective layer coating). Furthermore, incorporation of 2D nanofillers in the membrane selective layer could further enhance the membrane performance against CO_2/CH_4 and O_2/N_2 separation. The 2D GO nanosheet as reported in the literature has shown excellent properties in the membrane gas separation application when it was used for mixed matrix membrane fabrication. However, this work offers additional benefits as it could significantly reduce the quantity of GO used for membrane modification. The coating approach used in this work only disperses small GO amount into coating solution to develop hybrid selective layer on the hollow fiber membrane. Such multilayer coating approach is practical and feasible as the resultant multilayer coated hollow fiber composite membrane was reported to exhibit very stable enhanced gas separation performance during prolonged testing period. However, this study only focused on membrane performance towards gas permeation test without taking into account the possible impacts of operating temperature (especially high temperature) on the membrane surface chemistry and mechanical properties. Such parameter is worthy of further investigation in the future.

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LIST OF PUBLICATIONS

1. **Roslan, R. A.**, Lau, W. J., Sakthivel, D. B., Khademi, S., Zulhairun, A. K., Goh, P. S., Ismail, A. F., Cong, K. C., Lai, S. O. (2018). Separation of CO_2/CH_4 and O_2/N_2 by polysulfone hollow fiber membranes: effects of membrane support properties and surface coating materials. *Journal of Polymer Engineering*, *38*, 871–880. **(Q3, IF: 1.126)**
2. **Roslan, R. A.**, Lau, W. J., Zulhairun, A. K., Goh, P. S., Ismail, A. F. (2020) Improving CO_2/CH_4 and O_2/N_2 separation by using surface-modified polysulfone hollow fiber membranes. *Journal of Polymer Research*, *27*, 119. **(Q2, IF: 2.426)**
3. **Roslan, R. A.**, Lau, W. J., Lai, G. S., Zulhairun, A. K., Yeong, Y. F., Ismail, A. F., Matsuura, T. (2020) Impacts of Multilayer Hybrid Coating on the PSF Hollow Fiber Membrane for Enhanced Gas Separation. *Membranes,* 10, 335. **(Q2, IF: 3.094)**