MISCIBLE BLEND OF POLYETHERSULFONE/ POLYIMIDE MEMBRANE CROSSLINKED WITH DIAMINE FOR HYDROGEN/ CARBON DIOXIDE SEPARATION

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FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
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ABSTRACT

Hydrogen (H_2)/carbon dioxide (CO_2) separation application is crucial to fully utilize H_2 gas as the next generation fuel source. Polyimide membranes have been intensively developed for H_2 purification. However, polyimide has a low CO_2 plasticization resistance and the separation performance of current neat polyimide membranes are insufficient to achieve industrial demands. Therefore, modification approach is required to overcome the limitation. Gas separation efficiency of mixed crosslinking agent on polyimide (PI) membrane is studied in this research by blending 1,3-diaminopropane (PDA) and 1,4-diaminobutane (BuDA) at different concentrations. It was found that the H_2/CO_2 selectivity increased significantly and H_2 permeability decreased dramatically with higher concentration of PDA in crosslinking solution. Therefore, PDA is used as the crosslinking agent. Polyethersulfone (PES) and polyimide (P84) blend with three different ratios (25/75, 50/50 and 75/25 wt. %) are synthesized to form asymmetric membranes. Pure H_2 and CO_2 gas permeation tests were conducted on the polymer blends to find the best ratio for H_2 purification. PES/P84 (75/25 wt. %) exhibits the highest H_2 permeability value of 187.3 Barrer compared to all polymer blends tested. Next, chemical modification was carried out on the polymer blend ratio with superior H_2/CO_2 separation performance by immersing in PDA:methanol solution at different reaction times. After 15 minutes modification, the polymer membrane achieved an improvement on H_2/CO_2 selectivity by 96.9 % due to the increase in chain packing density and reduction in free volume caused by diamino crosslinking confirmed by XRD analysis. Hence, this study contributed significantly in improving H_2 selectivity performance of the membranes.

Keywords: Crosslinking, gas separation, hydrogen separation, membrane

ABSTRAK

Aplikasi pemisahan hidrogen (H_2) / karbon dioksida (CO_2) sangat penting untuk memanfaatkan gas H_2 sepenuhnya sebagai sumber bahan bakar generasi seterusnya. Membran polyimide (PI) dikembangkan secara intensif untuk penulenan H_2. Walau bagaimanapun, PI mempunyai rintangan keplastikan CO_2 yang rendah dan prestasi pemisahan membran PI semasa tidak mencukupi untuk mencapai permintaan industri. Oleh itu, pendekatan pengubahsuaian diperlukan untuk mengatasi batasan tersebut. Keberkesanan pemisahan gas bagi campuran agen pautan silang pada membran PI dikaji dalam penyelidikan ini dengan mencampurkan PDA dan BuDA dengan kepekatan yang berbeza. Didapati bahawa selektiviti H_2/CO_2 meningkat dengan ketara dan kebolehtelapan H_2 menurun secara mendadak dengan kepekatan PDA yang lebih tinggi dalam larutan penyilangan. Oleh itu, PDA digunakan sebagai agen pautan silang. Campuran polyethersulfone (PES) dan polyimide (P84) dengan tiga nisbah berbeza (25/75, 50/50 dan 75/25 % berat) disintesis untuk membentuk membran asimetri. Penyerapan gas H_2 dan CO_2 tulen kemudian dilakukan pada campuran polimer untuk mencari nisbah terbaik untuk penulenan H_2. PES/P84 (75/25 % berat) menunjukkan kebolehtelapan H_2 tertinggi berbanding campuran polimer yang lain iaitu 187.3 Barrer. Seterusnya, pengubahsuaian kimia dilakukan pada nisbah campuran polimer dengan prestasi pemisahan H_2/CO_2 yang terbaik dengan merendamnya dalam larutan PDA:metanol dalam masa tindak balas berbeza. Setelah 15 minit pengubahsuaian, membran polimer mencapai peningkatan pada selektiviti H_2/CO_2 sebanyak 96.9 % disebabkan oleh peningkatan kepadatan pembungkusan rantai serta pengurangan isipadu bebas yang berpunca dari pautan silang diamino yang terbukti dari analisis XRD. Oleh itu, kajian ini memberi sumbangan yang penting dalam menambah baik membran selektif H_2.

Kata kunci: Pautan silang, pemisahan gas, pemisahan hidrogen, membran

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LIST OF SYMBOLS AND ABBREVIATIONS

6FDA	:	Fluorinated hexafluoroisopropylidene-diphtalic anhydride
BOD	:	Biochemical oxygen demand
BuDA	:	1,4-diaminobutane
CO	:	Carbon monoxide
CO_2	:	Carbon dioxide
Co-PI	:	Co-polyimide
COD	:	Chemical oxygen demand
EDA	:	Ethylene diamine
FESEM	:	Field Emission Scanning Electron Microscope
FTIR	:	Fourier-Transform Infrared Spectroscopy
H_2	:	Hydrogen
H_2S	:	Hydrogen sulfide
IL	:	Ionic liquids
IPPO	:	Ionic liquid modified PPO
N_2	:	Nitrogen
NH_3	:	Ammonia
NMP	:	N-methyl-2-pyrrolidone
O_2	:	Oxygen
PBI	:	Polybenzimidazole
PDA	:	1,3-diaminopropane
PE	:	Polyether block
PEO	:	Poly(ethylene oxide)
PES	:	Polyethersulfone
PI	:	Polyimide
POME	:	Palm oil mill effluent

PPO	:	Poly(2,6-diphenyl-1,4-phenylene oxide)
PSA	:	Pressure swing adsorption
PSf	:	Polysulfone
PTMSP	:	Poly(1-trimethylsilyl-1-propyne)
PVTMS	:	Poly(vinyl trimethylsilane)
PyIPPO	:	Pyridinium-based IPPO
SEM	:	Scanning Electron Microscope
T_g	:	Glass transition temperature
THF	:	Tetrahydrofuran
XRD	:	X-ray diffraction

CHAPTER 1: INTRODUCTION

1.1 Introduction

Palm oil plays a significant role in Malaysia’s overall economy as it contributes to employment creation as well as the generation of income from exports. With the production of approximately 19.1 million tons of crude palm oil in 2020 (Board, 2021), the resulting amount of palm oil mill effluent (POME) is enormous as well. One ton of palm oil generates approximately 5.5 - 7.5 tons of POME (Norfadilah et al., 2016). POME is a thick brownish liquid with high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), which makes it inappropriate for direct discharge into the environment (Poh & Chong, 2009). These biomass residues however have shown great potential in the production of hydrogen (H_2) in an economical way, which is a promising alternative to fossil fuels as the reserves have been decreasing with the increasing demand of worldwide energy (Norfadilah et al., 2016). On top of that, the combustion of fossil fuels brings a negative impact to the environment due to carbon dioxide (CO_2) emission, which is the main cause of global warming (Norfadilah et al., 2016). Therefore, there have been researches to explore new sustainable energy sources as alternatives (Apak et al., 2017; Jia et al., 2018; Norfadilah et al., 2016).

H_2 is known as a clean fuel because of zero carbon emissions since its utilization via combustion or via fuel cells produces intense heat with only pure water as a byproduct (Norfadilah et al., 2016; Yang et al., 2020). Moreover, H_2 yields 2.75 times greater energy than hydrocarbon fuels (Kapdan & Kargi, 2006). Apart from being the source of energy, H_2 is extensively used as a feedstock for the production of chemicals, hydrogenation of fats and oils in the food industry, production of electronic devices, processing steel, and also desulfurization and re-formulation of gasoline in refineries (Kapdan & Kargi, 2006). The annual production of H_2 worldwide is approximately 60 million metric tons while the global H_2 market is worth \$122 billion in 2018 and is forecasted to rise to \$155 billion in 2022 (Bezdek, 2019; Cardoso et al., 2018).

Presently, the most common method for H_2 production is steam methane reforming to produce carbon monoxide (CO), followed by the water-gas shift reaction (Equation 1.1) whereby CO_2 is released as a byproduct (Lin et al., 2014). Alternatively, biohydrogen (Bio-H_2) can be obtained from biogas produced from biomass residues such as POME through dark fermentation (Chong et al., 2009). Dark fermentation is the fermentative conversion of substrates to bio-H_2 by anaerobic bacteria (Łukajtis et al., 2018). The resultant biogas mixture from POME fermentation mainly comprises 39 % H_2 and 49 % CO_2 with the presence of remaining gases such as oxygen (O_2) and nitrogen (N_2) due to the gas sampling during gas chromatography analysis (Mohamad et al., 2016).

$$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{CO_2}\ \text{(byproduct)} \qquad \text{(Equation 1.1)}$$

Hence, H_2 purification has gained importance in order to achieve the purity requirements for various applications. H_2 utilized for fuel cell technology needs to be at least 99.99 % pure, meanwhile only ~70 - 80 % pure hydrogen is required to be used as raw material for hydro-cracking (Shao, Low, et al., 2009). There are several methods employed to enrich H_2 including pressure swing adsorption (PSA), cryogenic distillation, and membrane separation (Shao, Low, et al., 2009). PSA has been extensively used in industries where high pressure adsorption is used to produce H_2 with up to 99.99 % purity (Shao, Low, et al., 2009). Moreover, another approach that is also used to purify H_2 is cryogenic distillation, where gas separation occurs when the mixture of gases are frozen and the difference in their boiling points are utilized for separation (Shao, Low, et al., 2009). This approach however only achieves a moderate purity of H_2 ($\leq$ 95 %) (Shao, Low, et al., 2009). Additionally, both methods require a large amount of energy consumption (Shao, Low, et al., 2009).

As a result, membrane technology is poised with great potential for H_2 separation compared to other technologies. Membrane separation exhibits greater energy efficiency, ease of operation, smaller equipment size, as well as portability (Rezakazemi et al., 2014; Shao, Low, et al., 2009). Moreover, this approach is eco-friendly and considered cost-effective due to smaller operation units (Shao, Low, et al., 2009).

As shown in Figure 1.1, a membrane is generally a selective barrier that enables certain constituents to permeate and retains the others (Li et al., 2015). Gas separation membrane specifically focuses on gas molecule permeability and selectivity as crucial parameters for separation performance evaluation (Li et al., 2015). Greater selectivity will result in greater efficiency and therefore reduces the driving force needed for a separation to occur and leads to low operation cost. Meanwhile, higher permeability will lessen the membrane area required which therefore will lower the capital cost of the system.

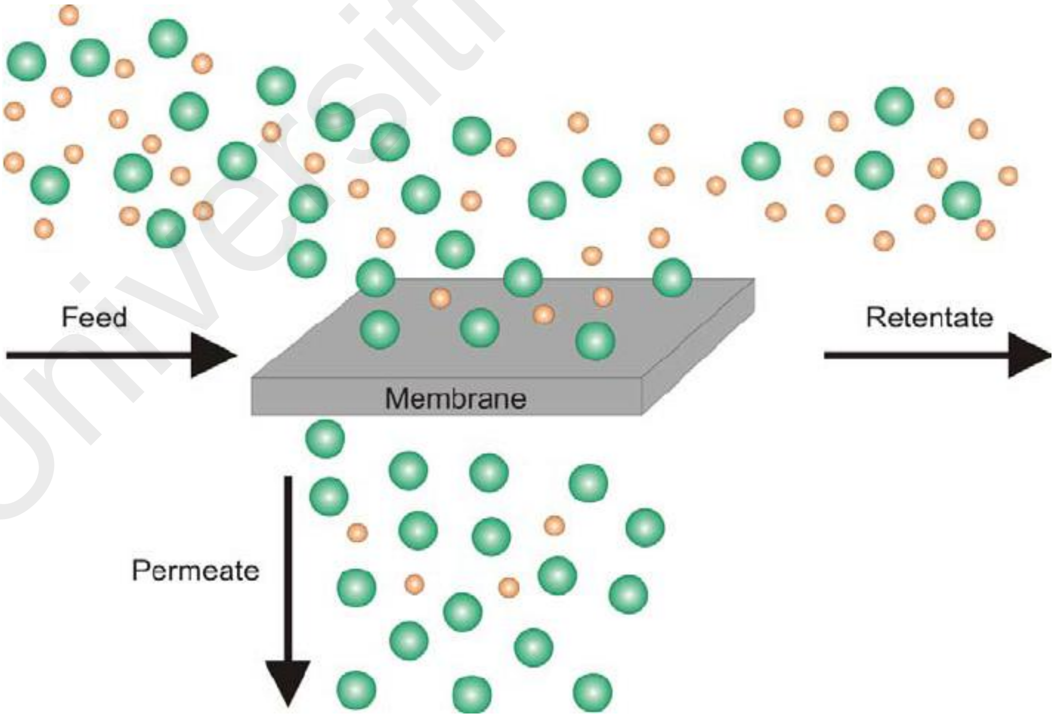


Figure 1.1: Schematic diagram of how membrane works (Hunger et al., 2012)

The common gas-transport mechanism in membrane separation are Poiseuille flow, Knudsen diffusion, molecular sieving, capillary condensation, surface diffusion, and solution diffusion (Shao, Low, et al., 2009). The schematic diagram in Figure 1.2 represents the fundamental characteristics of each mechanism. Gas transport for non-porous polymeric membrane usually takes place via solution-diffusion mechanism where it happens in three steps as shown in Figure 1.3, (i) sorption of the preferential permeate at the upstream, (ii) activated diffusion through the membrane, and (iii) desorption at the downstream side (Shao, Low, et al., 2009).

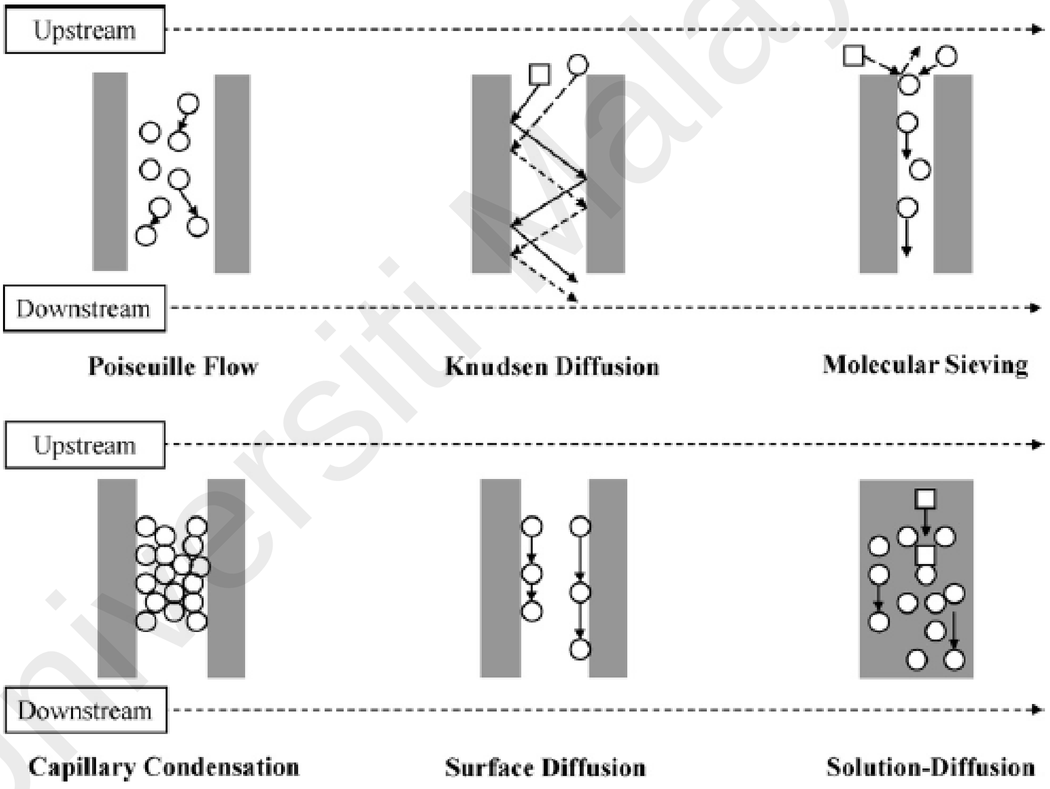


Figure 1.2: Gas-transport mechanisms in membrane separation (Shao et al., 2009)

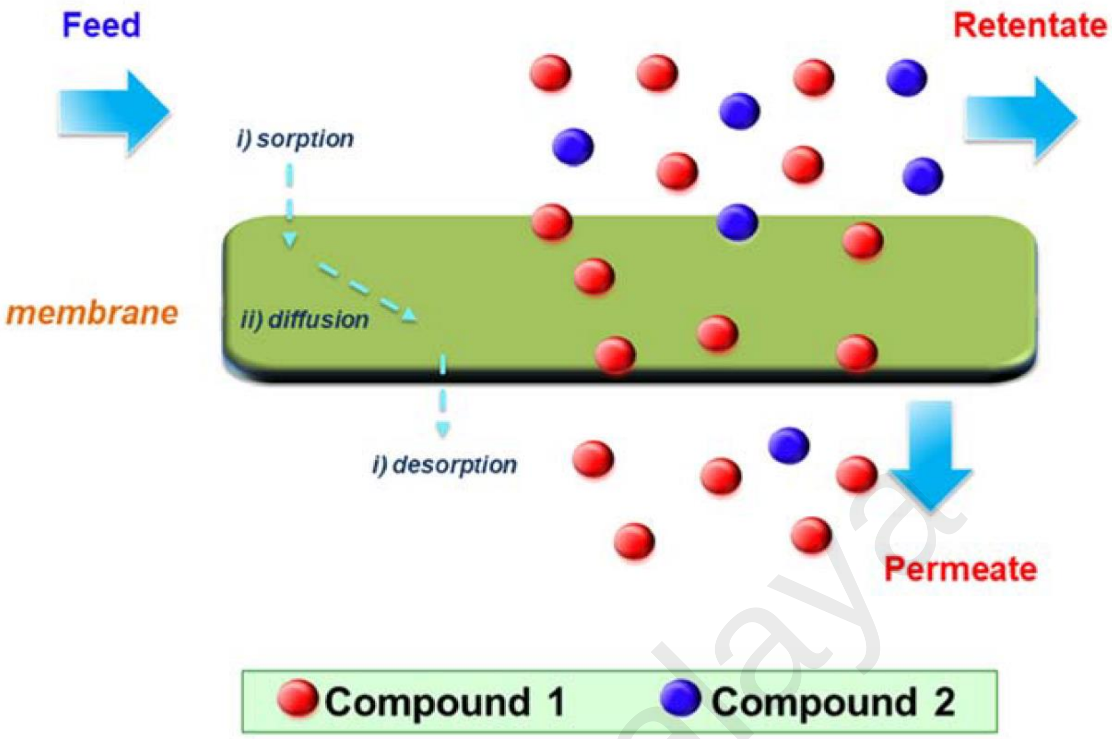


Figure 1.3: Detailed overview of mass transfer by solution-diffusion (Conidi et al., 2020)

Membranes can be categorized into biological and synthetic membranes depending on their nature. There are two types of synthetic membranes which are organic (polymer) and inorganic (ceramic or metallic) (Nikolaidis & Poullikkas, 2017). The characteristics of both types of membranes are listed in Table 1.1. Inorganic membranes exhibit long term durability as well as superior stability in extreme operating conditions. However, they are difficult to manufacture and costly. Meanwhile, polymeric membranes are cost-effective, easy to fabricate and able to operate at relatively mild operating temperatures and pressures (G. Q. Lu et al., 2007).

Table 1.1: Advantages and disadvantages of inorganic and polymeric membranes

Membrane	Advantages	Disadvantages
Inorganic	• Long term durability • High thermal stability (> 200 ^{o}C) • Chemical stability in wide pH • High structural integrity	• Not flexible, brittle • Expensive • Some have low hydrothermal stability
Polymeric	• Cheap • Mass production (larger scale) • Ease of processability • Ability to operate in long term at relatively mild operating temperatures and pressures	• Structurally weak, not stable, temp. limited • Prone to denature and be contaminated (short life)

Source: (G. Q. Lu et al., 2007; Shao, Low, et al., 2009)

Currently, polymeric membranes are predominantly used as commercial membranes despite the fact that some inorganic membranes possess superior performances (Li et al., 2015). Polymeric membranes for H_2/CO_2 separation can either be selective for H_2 or CO_2 (Shao, Low, et al., 2009). H_2-selective polymeric membranes are mainly manufactured using glassy polymers such as polyimide (PI) and polybenzimidazole (PBI) and the gas molecules are distinguished depending on size distinction (Shao, Low, et al., 2009). Currently, most gas separation membranes reported for H_2/CO_2 separation are selective for H_2 which is speculated because the kinetic diameter of H_2 molecule is smaller resulting in a higher diffusion coefficient, achieving its preferential permeation through membranes (Li et al., 2015).

However, the proximity in kinetic diameters of H_2 (2.89 Å) and CO_2 (3.30 Å) makes it difficult for polymers to discern H_2 and CO_2 molecules, with CO_2 having a higher solubility in polymers compared to H_2 which thereby leads to poor H_2/CO_2 selectivity (Chung et al., 2006; Shao, Low, et al., 2009). Membrane modification via cross-linking has shown to improve the separation performance, nevertheless the enhancement is limited for H_2/CO_2 separation (Chung et al., 2006). Hence, this study aims to develop the polymeric membrane by applying the blending and cross-link modification to obtain superior H_2/CO_2 separation efficiency.

1.2 Problem Statements

Membrane modification has been widely studied as a means to overcome the trade-off limit between permeability and selectivity for gas separation polymeric membranes (W.-J. Lau et al., 2016; Robeson, 2008). Crosslinking method is one of the most promising methods of membrane modification specifically via diamine. There are several types of diamine employed as crosslinking agents for H_2/CO_2 separation membranes. However, there are not enough studies on the influence of different types of diamines as crosslinking agents for H_2/CO_2 separation membrane. Therefore, the study on this matter is important to enhance the separation efficiency via crosslinking.

Aside from crosslinking, blending modification is an attractive approach to achieve an improvement on the permeation performance as well as the physicochemical properties of the membrane (Hamid et al., 2019). Based on literature review, no extensive study has been reported on the blend of P84 and PES for H_2/CO_2 separation membrane application. Hence, the blend composition merits consideration to achieve compatibility of both polymers for superior separation performance.

Diamino crosslinking is an attractive approach towards the enhancement of H_2/CO_2 separation. However, several modification parameters are needed to measure expected improvements. Therefore, it is essential to study the influence of diamine surface modification parameters towards membrane properties in terms of chemical, physical and separation properties.

1.3 Research Objectives

i. To study the effect of the ratio of 1,3-diaminopropane and 1,4-diaminobutane as crosslinking agents in enhancing H_2/CO_2 separation performance of pure P84 membrane.
ii. To investigate the effect of polymer blend composition/ratio of PES/P84 blend membrane towards its characteristics and H_2/CO_2 separation performance.
iii. To evaluate the influence of crosslinking reaction time towards newly developed blend membrane characteristics and separation properties.

1.4 Thesis Outline

This thesis is divided into five chapters as described below:

i. Chapter 1 describes the background of this study, problem statements and the objectives of the study.
ii. Chapter 2 covers a relevant review on the membranes employed for H_2 purification application and the different modification approaches available to overcome the membrane performance limitations.
iii. Chapter 3 presents the experimental method as well as materials and equipment used in this study.
iv. Chapter 4 presents the experimental outcomes and detailed discussions.

v. Chapter 5 concludes the findings and contributions of the study. Recommendations for future work are included in this chapter.

CHAPTER 2: LITERATURE REVIEW

2.1 Membrane for Hydrogen Separation

H_2 is an auspicious alternative source of energy because of zero carbon emission and high energy efficiency. However, H_2 is not a primary fuel and it is produced from the conversion of fossil fuels and biomass. A purification process is necessary to separate H_2 from the other gases since the composition of the final product consists of a mixture of H_2 and CO_2 as well as other contaminants such as CO, hydrogen sulfide (H_2S), N_2, and ammonia (NH_3) (Cardoso et al., 2018; Conde et al., 2017). Nowadays, membranes for H_2 separation are favoured because of cost-effectiveness, ease of operation, low energy consumption, and environmentally benign features (Cardoso et al., 2018). Compared to inorganic membranes, polymeric membranes are more favorable due to their low cost and ease of fabrication (Li et al., 2015). Presently, commercial membranes are using polymeric membranes instead of inorganic membranes (Li et al., 2015). Table 2.1 tabulates the H_2/CO_2 separation performance of several conventional polymers.

Currently, PI and its derivatives are representative materials for H_2/CO_2 separation (Li et al., 2015). PI, however, is severely affected by highly soluble penetrants, such as CO_2, which above a given partial pressure can result in the plasticization of the polymer matrix (Kapantaidakis et al., 1996). This limitation can be overcome by blending with Polyethersulfone (PES) which has satisfactory gas permeabilities and acceptable permselectivities, as well as high plasticization resistance (Kapantaidakis et al., 1996).

Table 2.1: H_2/CO_2 separation performance of several conventional polymers

Polymers	T (^{0}C)	P (atm)	Permeability (Barrer)		H_2/CO_2 selectivity
			H_2	CO_2	
Ethyl cellulose	30	-	87	26.5	3.28
Polyetherimide	30	-	7.8	1.32	5.91
Polyphenyleneoxide	30	-	113	75.8	1.49
Polysulfone (PSf)	30	-	14	5.6	2.50
Polymethylpentene	30	-	125	84.6	1.48
Polyimide (Matrimid)	30	-	28.1	10.7	2.63
Polyimide (6FDA-durene)	-	3.5	786	612	1.28
Polyethersulfone (PES)	35	3.5	8.96	3.38	2.65
Polystyrene	39	1.36	23.8	10.4	2.3
Poly(vinylidene floride) (Kynar)	30	1.36	2.4	1.2	2.0
Poly(methyl methacrylate)	30	1.36	2.4	0.6	4.0
Polybenzimidazole (PBI)	35	3.5	0.6	0.16	3.75

Source: (Hosseini et al., 2008; Shao et al., 2008; Shao, Low, et al., 2009)

2.2 Polyimide Membrane (PI)

Polyimides (PI) are denoted by the presence of the imide group (Figure 2.1) in the polymer backbone (Vanherck et al., 2013). They are widely applied in matrices of advanced composites, from aerospace to microelectronics (Vanherck et al., 2013). PIs are known to exhibit superb heat resistance, good mechanical strength, and superior resistance to chemical solvents (Vanherck et al., 2013).

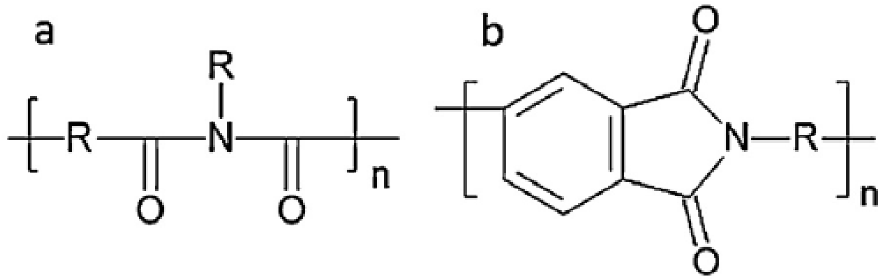
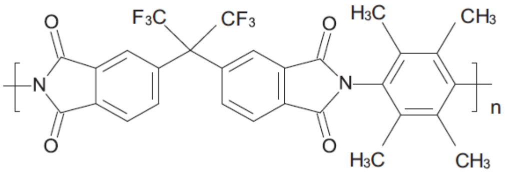
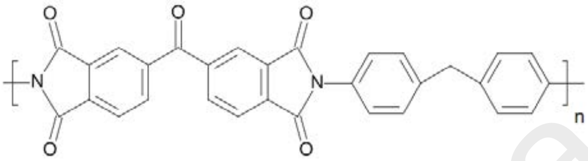
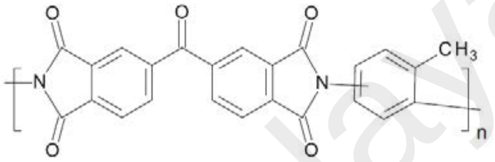
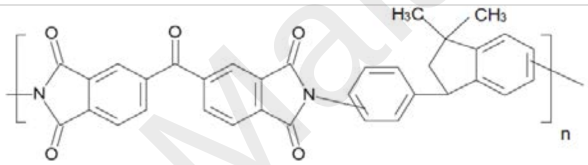
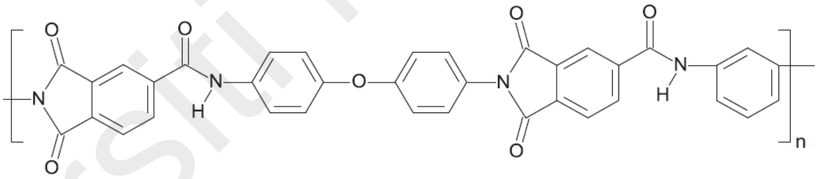
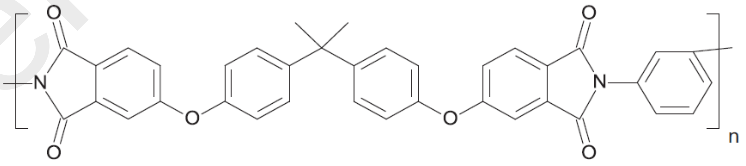
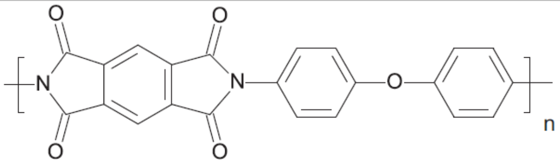


Figure 2.1: General structure of (a) a linear PI and (b) a heterocyclic aromatic PI

The structure of the PI backbone determines their heat resistance and chemical resistance (Vanherck et al., 2013). The combination of the imide structure with an aromatic structure provides rigidity resulting in a very high glass transition polymer (T_g) (Vanherck et al., 2013). Apart from that, the partial conjugation of the imide structures promotes good oxidative stability (Vanherck et al., 2013). The combination of PI's outstanding properties, as well as their high permselectivity, make them a perfect material for membrane applications (Vanherck et al., 2013). PIs nowadays constitute the largest group of organic polymers utilized for gas separation membranes and have been developing very rapidly in recent years resulting in the screening of the different PI types (Table 2.2) (Vanherck et al., 2013). The fluorinated hexafluoroisopropylidene-diphtalic anhydride (6FDA) is one of the most commonly used monomers in gas separation (Vanherck et al., 2013). The CF_3 groups within 6FDA increase the chain stiffness due to steric hindrance and thereby minimize the chain packing (Vanherck et al., 2013).

Table 2.2: Common PIs used for membrane applications and their structures

Polyimide	**Chemical structure**
6FDA-durene	
Lenzing P84® (HP Polymer Inc., Austria, now Evonik)	 
Matrimid® (Huntsman, Switzerland)	
Torlon® (Solvay Advanced Polymer)	
Ultem® Polyetherimide (Plastics International)	
Kapton® (DuPont Electronics)	

Source: (Vanherck et al., 2013)

In comparison with other commercial membranes based on PSf and cellulose acetate, PI-based membranes generally demonstrate superior H_2 separation performances as well as more favorable stability under harsh conditions (Li et al., 2015). However, the intrinsic H_2/CO_2 selectivity of most PIs generally does not exceed 10, which is below the requirement for hydrogen purification (Li et al., 2015). Consequently, some modification techniques have been explored to enhance H_2/CO_2 selectivity while maintaining comparatively high gas permeability (Li et al., 2015). Several studies on PI-based membrane for H_2/CO_2 separation are listed in Table 2.3.

Among the PI-based membranes, P84 membrane has gained recognition in various applications including ultrafiltration, nanofiltration as well as gas separation (Qiao et al., 2005). It exhibits the most outstanding performance on H_2/CO_2 selectivity as presented in Table 2.3. On top of that, Barsema et al. (2003) confirmed that P84 demonstrates superior anti-plasticization properties against CO_2 compared to other PI-based membranes.

Table 2.3: Recent studies on Polyimide-based membrane for H_2/CO_2 separation

Membrane	H_2/CO_2 selectivity	Reference
6FDA- durene	1.0	Chung et al. (2006)
Matrimid	3.88	Hosseini et al. (2008)
P84	4.78	Choi et al. (2010)
P84	5.72	Chatzidaki et al. (2007)
6FDA-durene	1.03	Shao, Lau, et al. (2009)

2.3 Polyethersulfone membrane (PES)

Polyethersulfones (PES) are amorphous, thermoplastic engineering polymers and are characterized by diphenylene sulfone repeat units (-Ar-SO_2-Ar'-) which are known to possess high chemical and thermal stability (Sanders et al., 2013). The repeating phenylene rings in the structure form backbone rigidity, a steric hindrance to rotation within the molecule, and an electronic attraction of resonating electron systems between adjacent molecules (Sanders et al., 2013). These features contribute to a high degree of molecular immobility, resulting in high rigidity high T_g, high strength, good creep resistance, dimensional stability, and high heat deflection temperature (Sanders et al., 2013).

PES possess superb properties to be utilized as the membrane for gas separation such as superior mechanical properties, wide operating temperature range, good chemical resistance, good stability, high critical pressure of plasticization and ease of membrane fabrication as well as low cost (Han et al., 2010; Sanders et al., 2013).

PES are regarded among the most common glassy polymers applied for gas separation due to the fact that glassy polymers can form rigid structures besides having more molecular size-selective characteristics which result in better gas separation performance compared to rubbery polymers (Suhaimi et al., 2014). However, conventional polymeric membranes such as PES usually suffer from a performance trade-off between the permeability and selectivity where the membranes are either more permeable or selective and vice versa, and this trade-off is referred as upper bound to membrane performance (Olajire, 2010; Robeson, 2008). It has become the goal of many researchers to overcome this upper bound to achieve a superior membrane with high permeability and selectivity (Olajire, 2010).

Two approaches can be made to improve the gas permeability which is by changing the composition of polymers to increase the solubility of H_2 in the membrane (Olajire, 2010). The other approach is by altering the polymer packing within the membrane to increase the diffusion of H_2 (Olajire, 2010). Table 2.4 displays several related studies on PES for membrane separation with various gas pairs.

Table 2.4: Related studies on PES for gas separation membranes

Membrane	Gas permeability	Gas selectivity	Reference
PES	H_2 : 7.25 Barrer CO_2 : 3.09 Barrer	H_2/CO_2: 2.3	Farrokhnia et al. (2015)
PES	H_2 : 513.96 GPU CO_2 : 191 GPU	H_2/CO_2: 2.69	Kamal et al. (2014)
PES	CO_2 : 10.98 GPU CH_4 : 0.21 GPU	CO_2/CH_4: 51.26	A. Ismail, Rahim, et al. (2011)
PES	O_2 : 2.13 GPU N_2 : 0.8 GPU	O_2/N_2: 2.56	A. Ismail, Rahim, et al. (2011)
PES	CO_2 : 654 GPU N_2 : 4.25 GPU	CO_2/N_2: 154	Wu et al. (2016)
PES	O_2 : 9.71 GPU N_2 : 1.28 GPU	O_2/N_2: 7.95	A. Ismail, Norida, et al. (2011)

2.4 Membrane modification

Overcoming the limitations of the permeability-selectivity trade-off on the Robeson upper bound (Figure 2.2(a)) has been the interest of many membrane research. The trade-off illustrates that membranes with high permeability usually have low gas pair selectivity and vice versa (W.-J. Lau et al., 2016). Figure 2.2(b) depicts the effect of operating pressure on the gas separation performance of membranes where there is a tendency for highly condensable gas to dissolve in the membrane at high operating pressure causing the polymer chain packing to be excessively disrupted, simply known as pressure-induced plasticization (W.-J. Lau et al., 2016). For H_2/CO_2 separation, the proximity of kinetic diameter of H_2 (2.89 Å) and CO_2 (3.30 Å) makes it difficult for most polymers to discern H_2 and CO_2 molecules and therefore results in poor selectivity (Chung et al., 2006). As a result, significant works have focused on membrane modification via various approaches to overcome these issues (Figure 2.3).

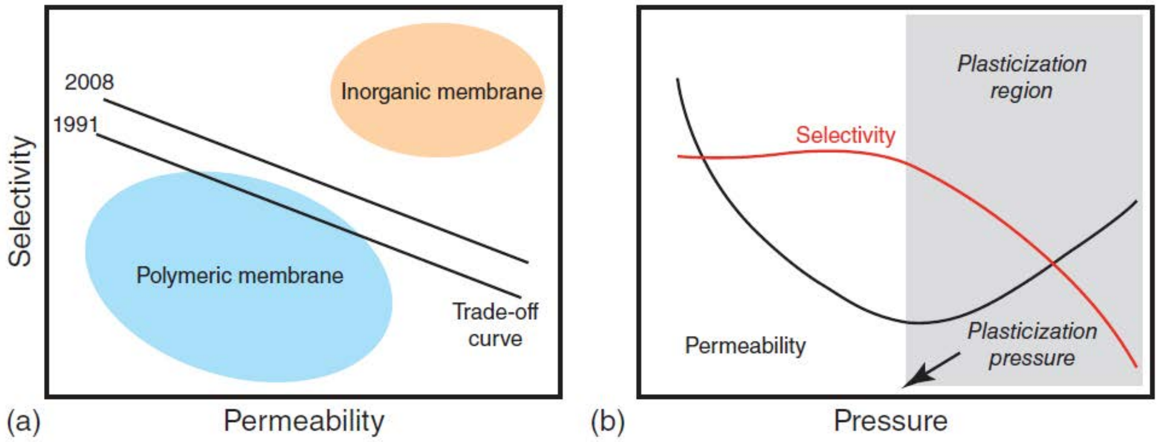


Figure 2.2: (a) Permeability-selectivity trade-off on Robeson upper bound and (b) the pressure-induced plasticization phenomena (W.-J. Lau et al., 2016)

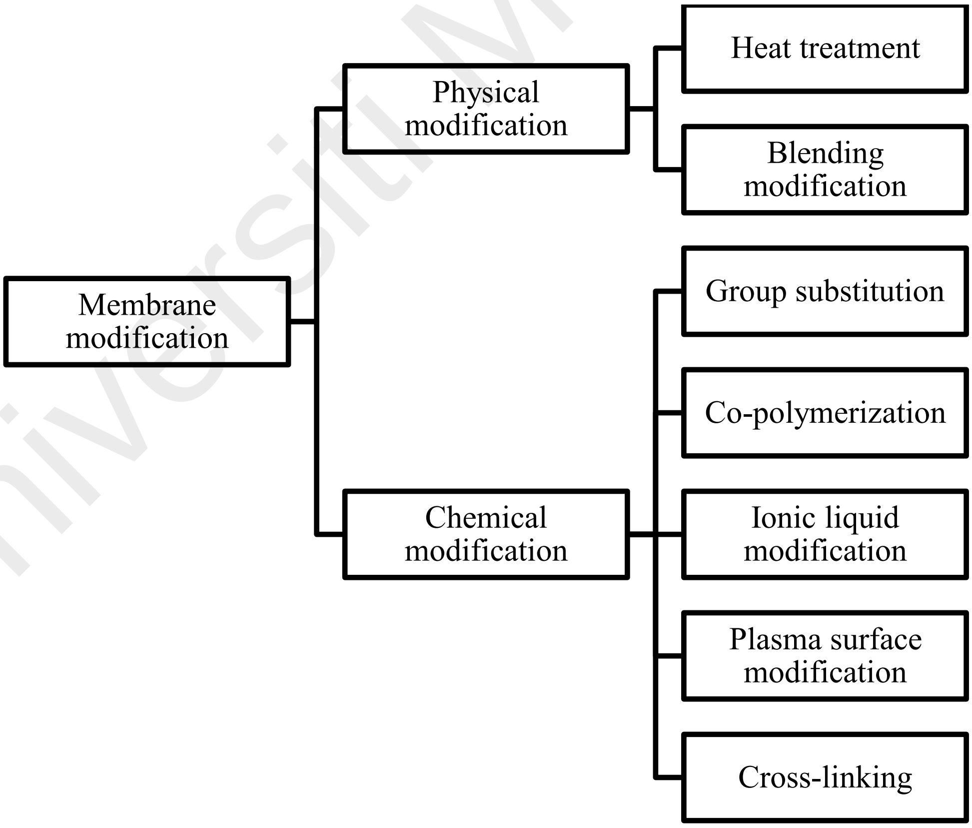


Figure 2.3: Methods of membrane modification

2.4.1 Physical Modification

2.4.1.1 Heat Treatment

One of the methods of physical modification is heat treatment where the membrane undergoes thermal treatment at a certain temperature for a period of time (Yuan et al., 2016). Heat treatment may cause a change in the arrangement of the polymer molecules which can increase the flexibility and degree of density of the membrane (Yuan et al., 2016). However, the studies on this approach are limited due to the struggle in setting the reaction time for the modification (Yuan et al., 2016). A study reported on a significant improvement of the separation properties after a PVDF membrane was thermally treated at 393.2 K for 12 minutes which led to the increase in the number of carbonyl (C=O) and hydroxyl (C-OH) on the membrane surface and therefore enhanced the surface polarity of the membrane (He et al., 2006). The modifications resulted in significant improvement in separation performance (He et al., 2006). Moon et al. (2019) studied on H_2/CO_2 separation performance of thermally treated PBI and polymer blends. Moon et al. (2019) reported that H_2 permeability of thermally treated compatibilized PBI at 400 °C remained the same while there is a decrease in CO_2 permeability, hence the enhancement of H_2/CO_2 selectivity by 82 %. The H_2/CO_2 selectivity of thermally treated HAB-6FDA-CI/PBI (20/80 wt %) compatibilized blend also significantly increased from 17 to 42 (Moon et al., 2019). The increase in H_2/CO_2 selectivity upon heat treatment is stemmed by densification and reduction in free volume of the PBI matrix phase (Moon et al., 2019).

2.4.1.2 Blending Modification

Blending is considered as the most popular approach of physical modification because of its reproducibility, cost-effectiveness, and simplicity in operation where they are prepared by solution mixing, melt mixing, extrusion, or molding processes (Hafiz A

Mannan et al., 2013; Yong & Zhang, 2020). Polymers which differ in separation and physicochemical properties are blended together to achieve more advanced properties that are not possessed by individual polymers (Figure 2.4) (Hafiz A Mannan et al., 2013). Polymer blends are classified into two categories according to their phase behavior which are miscible and phase-separated blends (Hafiz A Mannan et al., 2013). Miscible blends refer to two polymers which dissolve completely to form a homogenous solution (Hafiz A Mannan et al., 2013). On the other hand, in phase-separated blends, the two polymers are partially dissolved and separated by an interface between the two phases (Hafiz A Mannan et al., 2013). The phase behavior of blends can be ascertained by the glass transition temperature T_g, light or X-ray scattering, or by microscopy (Hafiz A Mannan et al., 2013). A single T_g proves that the blend is miscible, meanwhile immiscible blend shows two different T_g (Hafiz A Mannan et al., 2013). Partially miscible blends have been utilized for gas separation applications where their performance relies on membrane morphology, specific volume fraction, and size and shape of the dispersed and continuous phase (Hafiz A Mannan et al., 2013).

Visser et al. (2007) conducted a study on blending modification using PI Matrimid blended with either co-polyimide (co-PI) P-84 or PES. The result indicated that the O_2 permeability and O_2/N_2 selectivity of Matrimid/P-84 enhanced by 78 % and 16 % respectively (Visser et al., 2007). On the contrary, Matrimid/PES experienced a decrease in permeability and selectivity since different functional groups were introduced to the membrane (Visser et al., 2007). An imide group within the Matrimid/P-84 membrane provides stronger interaction with O_2 compared to the sulfone group present within the Matrimid/PES membrane (Visser et al., 2007). Subsequently, Hamid et al. (2019) developed an asymmetric PSf/P84 (50/50 wt %) membrane for H_2/CO separation with 42 % enhancement on H_2/CO_2 selectivity compared to pure P84. Hence, a suitable blending material is important to promote the performance of the gas separation membrane.

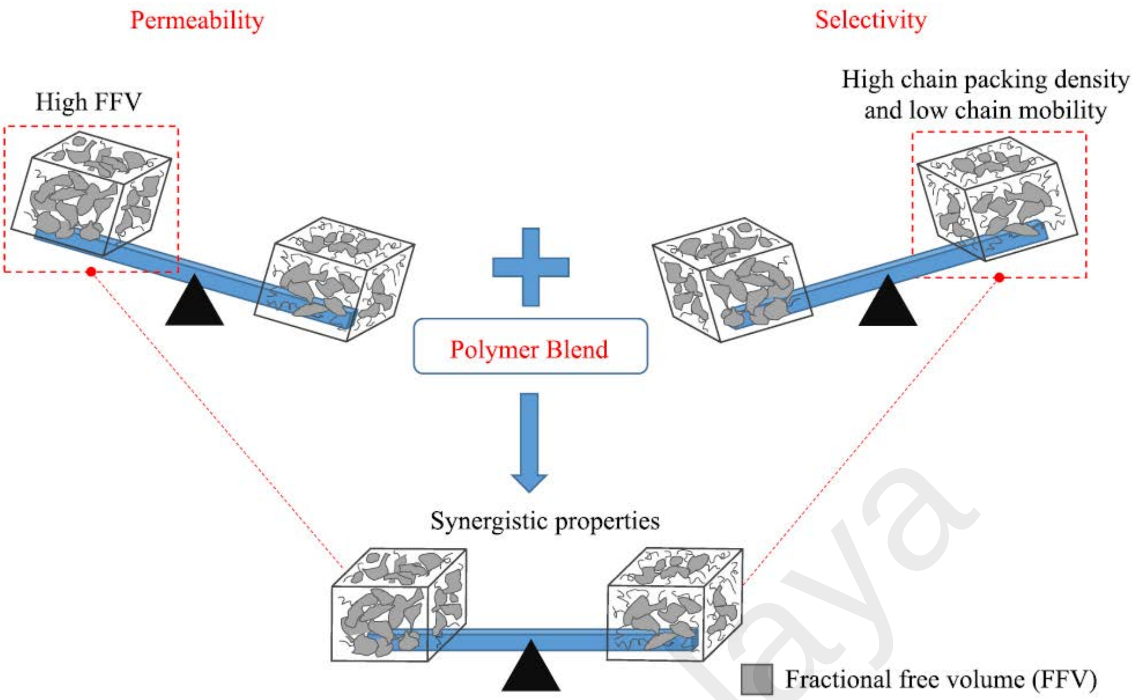


Figure 2.4: Schematic diagram of polymer blend (Yong & Zhang, 2020)

Blending with a polymer of higher plasticization resistance can overcome the pressure-induced plasticization phenomenon. For example, PI has a good correlation between permeability and selectivity but has a low plasticization resistance. Therefore, Visser et al. (2007) blended PES and co-PI P-84 which have higher plasticization resistance, with PI. The study showed that PI/PES achieved the highest plasticization resistance (16 bar), followed by PI/P-84 membrane (~10 bar) and pure PI membrane (4 bar) when tested with CH_4/CO_2 (2/8,v/v) mixed gas as feed (Visser et al., 2007).

2.4.2 Chemical Modification

2.4.2.1 Group Substitution

Group substitution has the potential to enhance the gas separation efficiency of membranes. Group substitution includes samination, bromination, sulfonation, and benzoylation (Yuan et al., 2016). Several researches have been done on surface modification by group substitution to boost the gas separation properties of PPO membrane (Figure 2.5(a)). Cong et al. (2007) studied on bromination of poly(2,6-diphenyl-1,4-phenylene oxide) (Figure 2.5(b)) and discovered an increase in CO_2 permeability (78 Barrer) and selectivity. Bhole et al. (2007) reported that nitration and amination of PPO (Figure 2.5(c)) led to an increase in chain stiffness and packing density and a decrease in thermal stability. Yet, this approach suffers the drawback of degradation possibility of the main polymer chain at high temperatures or long reaction time (Zhao et al., 2013).

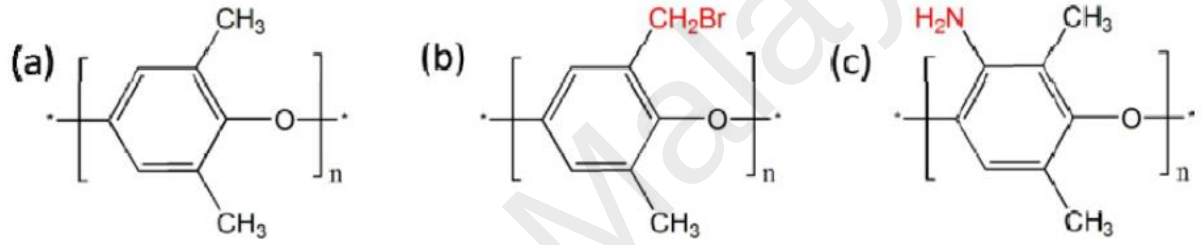


Figure 2.5: Structure of chemically modified PPO: (a) PPO; (b) BPPO; (c) PPO-NH_2 (Yuan et al., 2016)

2.4.2.2 Co-polymerization

Block co-polymers possess exquisite nanostructures which give them the potential to be utilized in membrane technology. Husken et al. (2010) studied on gas permeation performance of poly(ethylene oxide) (PEO)-based segmented block copolymers containing monodisperse amide segments. They discovered that the gas permeability and the gas transport values were influenced by both the dispersed hard segment concentration and the polyether segment length (Husken et al., 2010). Research on a series of phase-separated polyether-*b*-polyamide segmented block copolymers was conducted by Bondar et al. (2000) where they found that the polymers improved substantially significantly in CO_2/H_2 and CO_2/N_2 selectivity. They concluded that the amount of polyether (PE) component in the block copolymer and the polarity of the PE backbone elements directly affect the permeability performance (Bondar et al., 2000). According to Yuan et al. (2016), it is difficult to control the grafting density which is crucial as it affects the separation performance of the modified membrane.

2.4.2.3 Ionic Liquid Modification

Ionic liquids (IL) are organic salts made from cations and anions which are liquid at room temperature. They have drawn attention to many researchers due to their superior physicochemical properties such as high chemical and thermal stability, negligible volatility and high ionic conductivity (S.-C. Lu et al., 2016; Hafiz Abdul Mannan et al., 2016). IL have been widely utilized as reagent for gas separation membrane attributable to their affinity for CO_2. Therefore, once a flue gas stream passes through the membrane, CO_2 selectively diffuses its way through the membrane due to its high affinity for the IL (S.-C. Lu et al., 2016).

Cong et al. (2012) have synthesized four types of ionic liquid modified poly(2,6-dimethyl-1,4-phenylene oxide) (IPPO) from PPO (Figure 2.6). They found that IPPO improved in CO_2 solubility compared to pure PPO as they have CO_2-philic ionic liquid groups in the structure (Cong et al., 2012). Meanwhile, PyIPPO possesses superior CO_2 solubility and diffusivity among the four IPPOs, thus having the best CO_2/N_2 separation performance (Cong et al., 2012). Nevertheless, this method is not cost-effective because of the high cost of IL and there has not been any studies conducted on this method to enhance H_2 gas permeability in H_2/CO_2 separation.

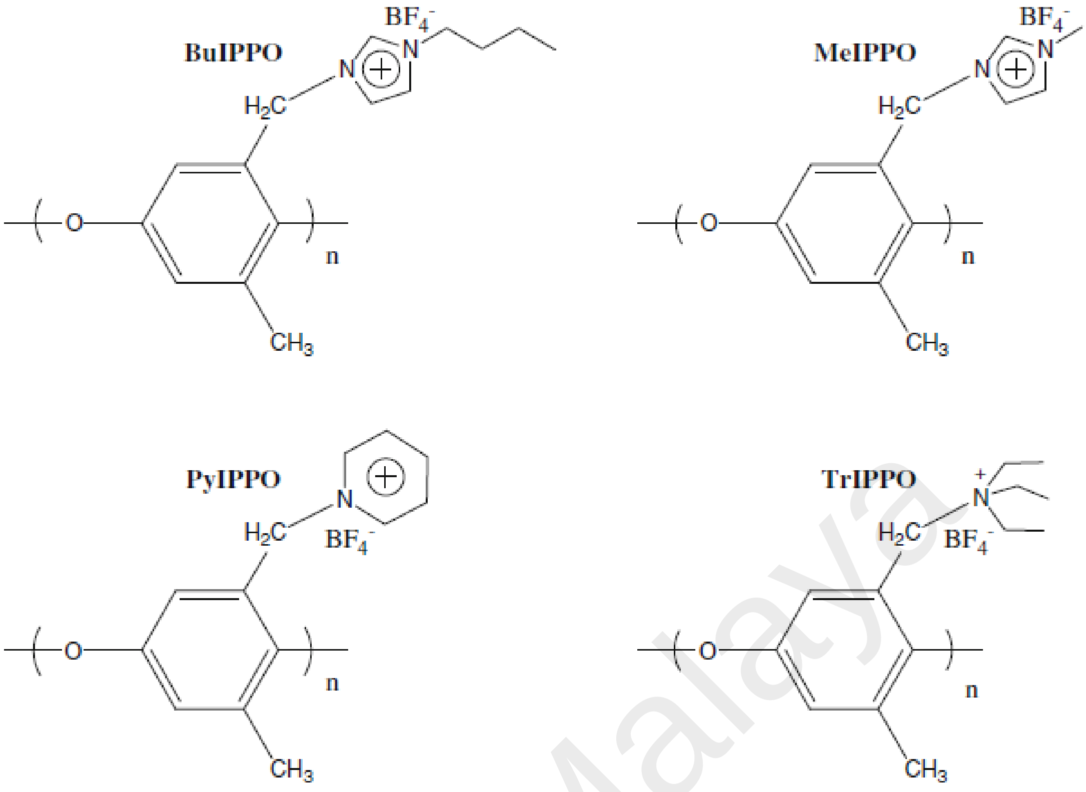


Figure 2.6: Structure of IPPO

2.4.2.4 Plasma Surface Modification

Plasma treatment is an effective method of surface modification for polymeric membranes (Yuan et al., 2016). Low-temperature plasma treatment has been applied to prepare highly selective composite membranes as it can alter the degree of modification (Yuan et al., 2016). Borisov et al. (1997) conducted a study on the surface fluorination of poly[1-trimethylsilyl-1-propyne] (PTMSP) and poly(vinyl trimethylsilane) (PVTMS) films. The control of the fluorine atom density in the discharge and density of fluorine atoms flux on the modified surface was used to increase their selectivity in gas separation (Borisov et al., 1997). In spite of that, the equipment utilized in this method is quite expensive. This method also shows other disadvantage in terms of the time dependency of the modification induced from plasma treatment (Zhao et al., 2013).

2.4.2.5 Cross-linking

Currently, diamino crosslinking is among the most promising approach for the improvement of H_2/CO_2 selectivity of PI membranes due to the method simplicity and cost effectiveness despite showing a significant enhancement on H_2/CO_2 permselectivity. It was first discovered by Hayes (1991) to improve O_2/N_2 selectivity and then further developed to enhance the separation performance of other gas pairs (Chung et al., 2006; Y. Liu et al., 2001; Low et al., 2008; Shao et al., 2005; Shao et al., 2004; Shao et al., 2008; Tin et al., 2003). Shao et al. (2004) were the first to discover the improvement in H_2/CO_2 selectivity of 6FDA-durene films upon modification with diaminobutane dendrimer at 35 ^{0}C for 60 minutes where there was a 265 % increase of H_2/CO_2 selectivity (Figure 2.7).

A series of aliphatic diamines comprising ethylene diamine (EDA), 1,3-diaminopropane (PDA), and 1,4-diaminobutane (BuDA) was studied for modification of PI membranes for H_2/CO_2 separation (Chung et al., 2006; Shao et al., 2005; Shao et al., 2008; Tin et al., 2003). Chung et al. (2006) discovered that PDA is superior as a crosslinking agent for PI membranes for H_2/CO_2 selectivity enhancement. The crosslinked 6FDA-durene membranes in 10 minutes reaction time exhibit a dramatic increase in H_2/CO_2 selectivity from 1 to 101 (Figure 2.8) (Chung et al., 2006). Meanwhile, the modification of 6FDA-ODA/NDA copolyimide membranes with PDA also enhance the H_2/CO_2 selectivity by 146 % (Low et al., 2008).

According to Chung et al. (2006), the effectiveness of the crosslinking reagents is most likely associated with the molecular lengths as EDA, PDA and BuDA possess the similar molecular width (3 Å). The long molecular length of BuDA (8 Å) may reduce the reaction rate because of the restriction of diffusion into PI membranes (Chung et al., 2006). On the other hand, the short molecular length of EDA (5.5 Å) may hinder the reaction due to the mutual influence between the two functional groups (-NH_2) (Chung et al., 2006). Meanwhile, PDA with the medium molecular length (6.7 Å) attains the balance between the two hindrances and therefore promotes better crosslinking reaction (Chung et al., 2006).

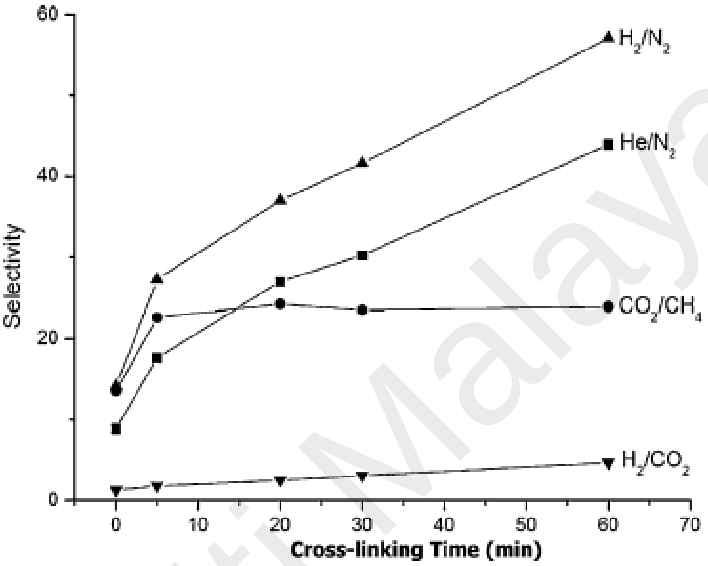


Figure 2.7: Effect on dendrimer (DAB-AM-4) crosslinking on the selectivity of PI membranes at 35 ^{0}C for various gas-pairs (Shao et al., 2004)

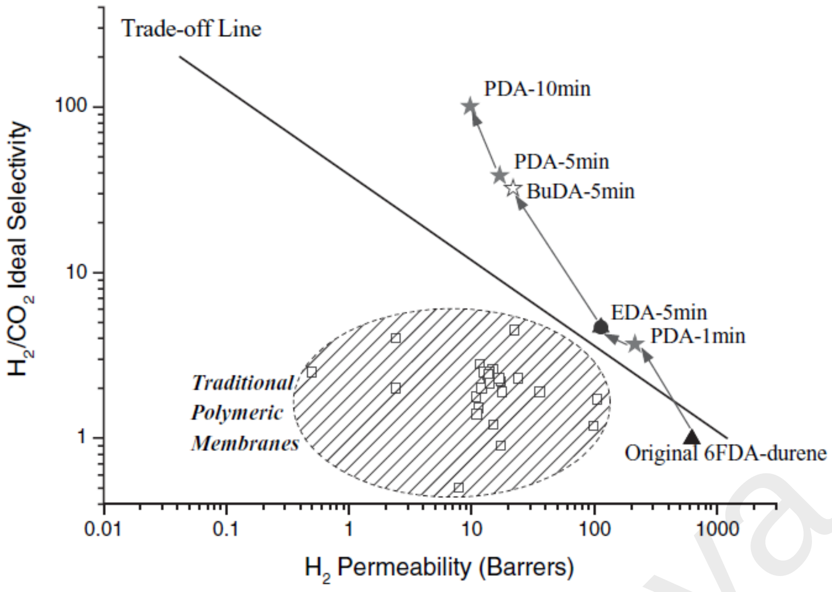


Figure 2.8: H_2/CO_2 selectivity of 6FDA-durene membranes crosslinked by different diamines in different reaction time (Chung et al., 2006)

The change in the membranes' separation performance is due to the alteration of the membranes' physicochemical structures upon diamino crosslinking. The modification causes the decrease in the interchain spacing between the polymer chains and thereby constricts the passage for the gases to pass through (C. H. Lau et al., 2010). Since the kinetic diameter of CO_2 (3.3 Å) is larger than that of H_2 (2.89 Å), the degree of decline in CO_2 permeability is more prominent than that of H_2 (C. H. Lau et al., 2010). As a result, an improvement on H_2/CO_2 selectivity is observed.

2.5 Summary of literature review

The demand for H_2 as a source of energy has led to the importance of H_2 purification. Among the conventional techniques, membrane technology has drawn attention in H_2 separation market as it exhibits greater energy efficiency, ease of operation, smaller equipment size, portability, eco-friendly as well as cost-effective. Polymeric membranes such as PIs are commonly used as commercial membranes for H_2/CO_2 because of their rigid structures and good permselectivity. However, conventional polymeric membranes suffer from the performance trade-off between permeability and selectivity. Membrane modification is an approach to overcome these limitations. Various methods have been employed for membrane modification such as heat treatment, blending modification, group substitution, co-polymerization, ionic liquid modification, plasma surface modification, and cross-linking. Most of the methods have not been widely researched for H_2/CO_2 separation except cross-linking. The blending of PES and P84 followed by crosslinking the polymer blend can alter the physicochemical properties of the membranes and thereby contribute to the enhancement of H_2/CO_2 separation performance.

CHAPTER 3: MATERIALS AND METHODS

Figure 3.1 depicts the flow diagram of research methodology of this study whereas the list of chemicals and reagents used for the study are tabulated in Table 3.1.

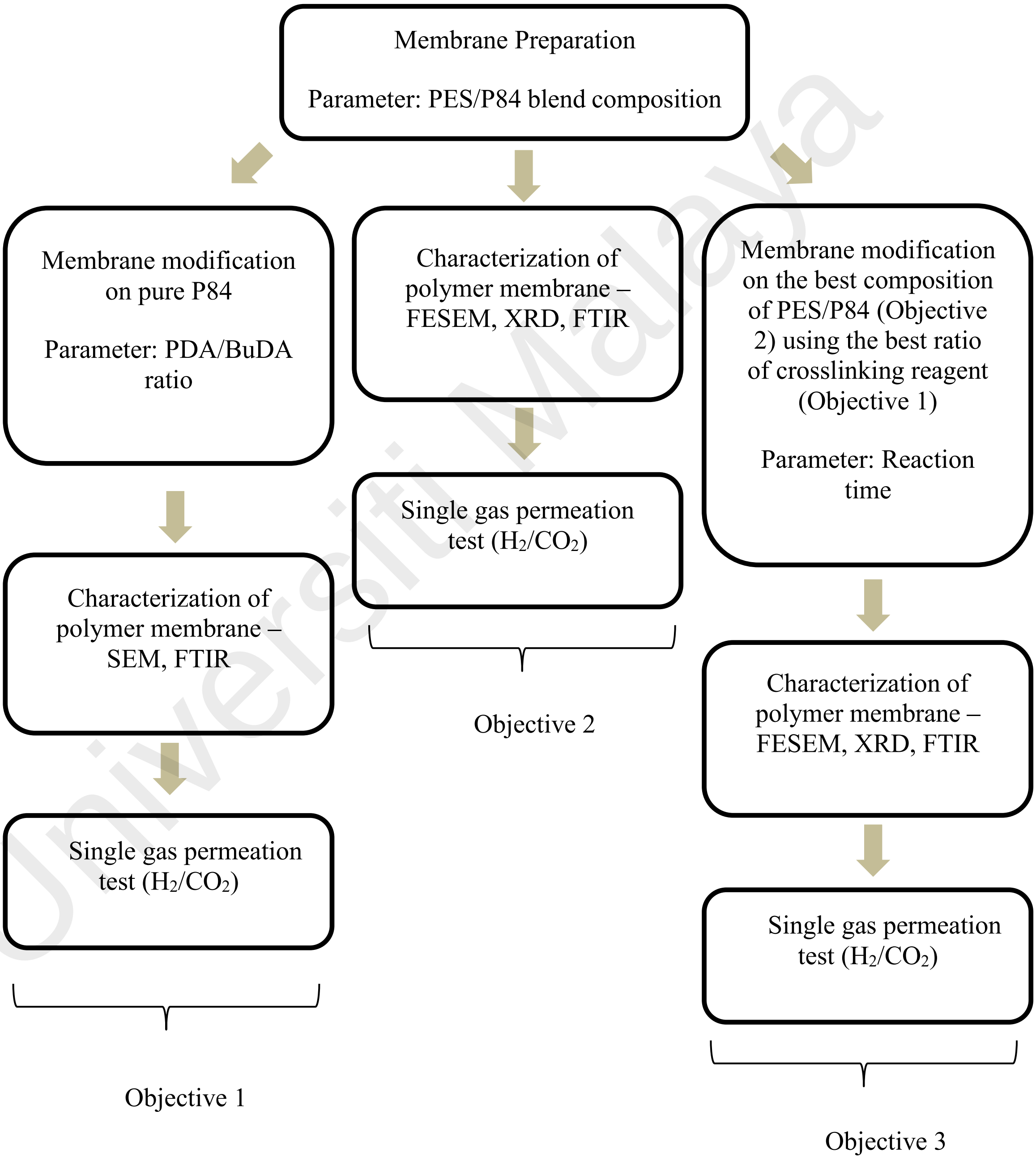


Figure 3.1: Flow diagram of research methodology

Table 3.1: List of chemicals and reagents applied for the research

Chemical/ Reagent	Supplier	Purpose of use
Polyimide P84	Goodfellow Ltd.	Membrane fabrication
Polyethersulfone	Goodfellow Ltd.	
N-methyl-2-pyrrolidone (NMP)	Merck	
Tetrahydrofuran (THF)	Merck	
Deionized water	Particle Lab	
1,3-diaminopropane (PDA)	Merck	Membrane modification
1,4-diaminobutane (BuDA)	Merck	
Methanol	R&M Chemicals	
Carbon dioxide (CO_2)	Gaslink Industrial Gases	Gas permeation test
Hydrogen (H_2)	Gaslink Industrial Gases	
Nitrogen in liquid form	Gaslink Industrial Gases	Sample analysis

3.1 Membrane Preparation

The polymer membrane was prepared via dry-wet phase inversion method where PES and P84 were weighed according to the composition in Table 3.2 to produce asymmetric PES/P84 membrane as well as pure P84 with A4 size (148 mm x 210 mm). NMP and THF were used as solvents with the ratio of 2:1 mol mol^{-1} to produce a dope solution and were weighed using A&D Weighing GF-400 Milligram Balance. P84 was first mixed in NMP at 60 °C and 500 rpm where the P84 was added gradually into the solvent (Figure 3.2). After P84 was dissolved, the weighed PES and THF were added into the mixture followed by continuous stirring until it forms a homogenous dope solution. Subsequently, the dope solution went through degasification using an ultrasonic bath Fisherbrand

FB15055 for 30 minutes to remove microbubbles trapped inside the solution (Hamid et al., 2019).

Table 3.2: Blend composition of polymer membranes

Membrane Sample	Polymer Composition (wt. %)	
	PES	**P84**
PP-1	25	75
PP-2	50	50
PP-3	75	25
P84	-	100

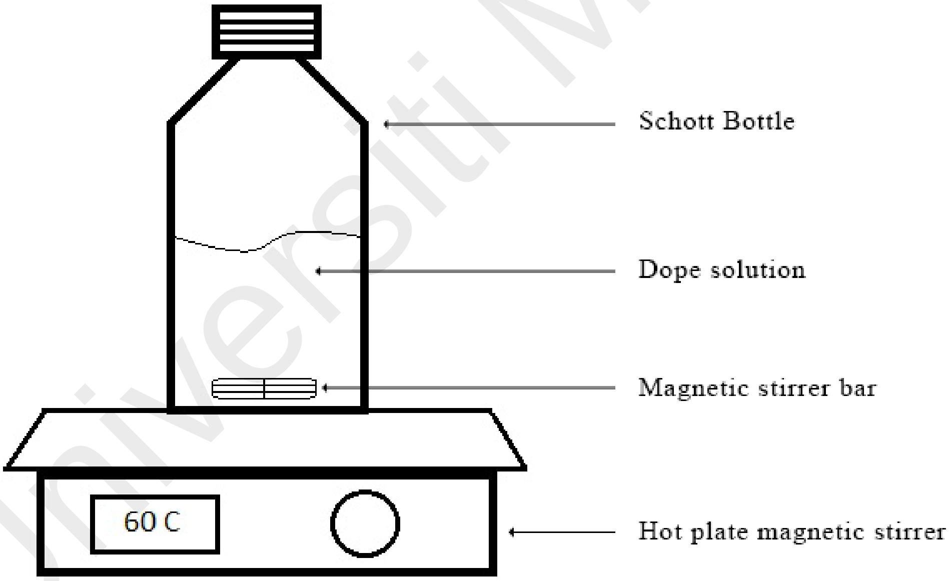


Figure 3.2: Schematic diagram of dope solution preparation

After that, the dope solution was cast onto a glass plate using Elcometer 4340 Automatic Film Applicator with a casting knife of 0.3 mm gap at room temperature (Hamid et al., 2019). Upon 60 seconds of evaporation time, it is immersed in a coagulation bath containing deionized water overnight for a solvent-exchange process, followed by one-day drying process in an oven at 60 °C, to form a flat sheet membrane (Hamid et al., 2019).

3.2 Membrane Modification

PDA and BuDA obtained from Merck were used as received. The chemical structures are illustrated in Figure 3.3 and Figure 3.4 respectively. Cross-linking reagents comprising PDA and BuDA were prepared with different concentration ratios as shown in Table 3.3 in methanol solution. The surface modification was performed by immersing pure P84 membrane films into PDA-BuDA crosslinking solution for 5 minutes (Chung et al., 2006). The modified membrane film was washed with fresh methanol immediately after taking out from the solution to clear off the residual solutions on membranes (Chung et al., 2006). Then, the membrane was dried naturally at room temperature for 1 day (Chung et al., 2006).

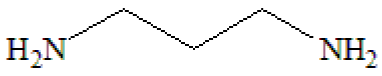


Figure 3.3: Chemical structure of PDA

Figure 3.4: Chemical structure of BuDA

Table 3.3: Composition of crosslinking agents in crosslinking solution

PDA/BuDA (% w/w)	Concentration (g/g of methanol)	
	PDA	BuDA
0/100	0.00	0.18
20/80	0.03	0.15
40/60	0.05	0.11
60/40	0.07	0.09
80/20	0.04	0.12
100/0	0.00	0.15

The best ratio of diamine was used for the modification of polymer blend membrane. Diamine solution was prepared by diluting PDA in methanol to produce 1 mol L^{-1} PDA:methanol (Omidvar et al., 2019). The prepared membrane underwent modification through immersion in PDA:methanol in different reaction times as tabulated in Table 3.4 (Omidvar et al., 2019). The range of reaction time was selected based on the previous literatures (C. H. Lau et al., 2010; Shao, Lau, et al., 2009). The membrane was then washed off with fresh methanol to eliminate the residue and left to dry at room temperature before use (Omidvar et al., 2019).

Table 3.4: Diamine modification reaction time

Membrane Sample	Reaction time (minutes)
PP-3	0
PP-3-M5	5
PP-3-M10	10
PP-3-M15	15
PP-3-M30	30

3.3 Membrane Characterization

The fabricated membrane samples were characterized using several analytical techniques to study their physical and chemical properties. The analytical equipments employed in this study includes Scanning Electron Microscope (SEM), Field Emission Scanning Electron Microscope (FESEM), X-ray diffraction (XRD) and Fourier-Transform Infrared Spectroscopy (FTIR).

3.3.1 Scanning Electron Microscope (SEM) and Field Emission Scanning Electron Microscope (FESEM)

The surface and cross-section of the membranes were physically characterized via Phenom ProX SEM (Thermo Scientific, United States) and Quanta FEG 450 FESEM (Oxford Instruments, Netherlands). For sample preparation, the membranes were fractured using liquid nitrogen beforehand to ensure clean cuts. Next, the membranes were cut into small pieces and placed onto the sample holders. The samples were coated with a thin gold layer to inhibit surface charging (Junaidi et al., 2014).

3.3.2 X-ray Diffraction (XRD)

XRD analysis was conducted using Philips X'pert-MPD X-ray diffraction system (Philips, Netherlands) to quantify the inter-chain spacing of the membranes before and after modification. The scanning was performed at 40 kV and 30 mA with the scan ranging from 4° to 70° and a step increment of 0.04° /s (Hosseini et al., 2008). The d-spacing was calculated using Bragg's equation (Equation 3.1).

$$n\lambda = 2d\sin\theta \qquad \text{(Equation 3.1)}$$

where n is an integral number, λ is the X-ray wavelength, d is the d-spacing between two polymer chains and θ is the diffraction angle.

3.3.3 Fourier-Transform Infrared Spectroscopy (FTIR)

Perkin Elmer FTIR-Spectrum 400 (Perkin Elmer, United States) was used to attain FTIR spectra of all fabricated membranes to study their functional groups as well as the possible reaction upon diamino crosslinking. The spectra were obtained from wavenumbers ranging from 450 to 4000 cm^{-1}.

3.4 Single Gas Permeation Test

The gas permeation test rig was set up as illustrated in Figure 3.5. The gases were purchased from local companies with a purity greater than 99 %. The single gas permeation test was conducted through a constant pressure system where the upstream pressure was set between 1 to 5 bar whereas the downstream pressure remained atmospheric. This pressure range was chosen because of the favorable low-pressure condition for the bio-H_2 purification upon POME fermentation (Hamid et al., 2019). Flat sheet membrane discs with a diameter of 4.1 cm and an effective area of 13.2 cm^2 were tested. The volumetric flow rate of permeate was measured using a soap bubble flow meter (Junaidi et al., 2014). Each set of data was repeated thrice to obtain the average value. The ideal gas permeability was determined using Equation 3.2 below:

$$P_i = \frac{Q_i L}{A \Delta p_i} \qquad \text{(Equation 3.2)}$$

where P_i is the gas permeability in Barrer unit (1 Barrer =10^{-10} cm^3 STP.cm /cm^2 s cmHg), Q is volumetric flow rate of permeate in cm/s, L is the average thickness of the dense layer of the membrane obtained from FESEM, A is the membrane surface area in cm^2 and Δp_i is the pressure difference across the membrane. The ideal H_2/CO_2 selectivity was calculated using Equation 3.3 below:

$$\alpha_{H_2/CO_2} = \frac{P_{\mathrm{H_2}}}{P_{\mathrm{CO_2}}} \qquad \text{(Equation 3.3)}$$

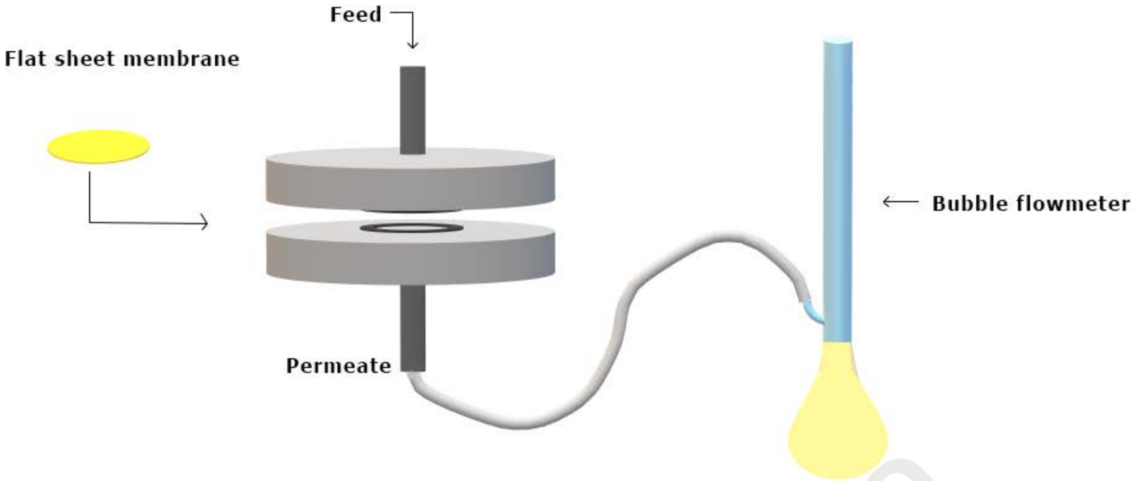


Figure 3.5: Schematic diagram of gas permeation rig

CHAPTER 4: RESULTS AND DISCUSSION

4.1 The effect of different types of diamine as crosslinking agents on P84 membrane characteristics and H_2/CO_2 separation performance

4.1.1 Physical Characterization

The morphology of the membrane was investigated by observing the surface and cross-sectional view of the membrane using SEM analysis as shown in Figure 4.1. The membrane cross-sectional view could be visualized and the SEM images demonstrated that P84 membranes yield asymmetric structures. The observation in Figure 4.1 (c) revealed that the fabricated P84 membrane possessed a denser top layer, sponge-like and finger-like sublayers. The evaporation step during preparation of membrane forced a delayed liquid-liquid demixing process which resulted in the formation of the denser top layer. Meanwhile, THF which is a volatile solvent reduced interaction between solvent and non-solvent, promote the sponge-like structure formation after the dense top layer, which is analogous with the reported literatures (Hamid et al., 2019; Junaidi et al., 2013).

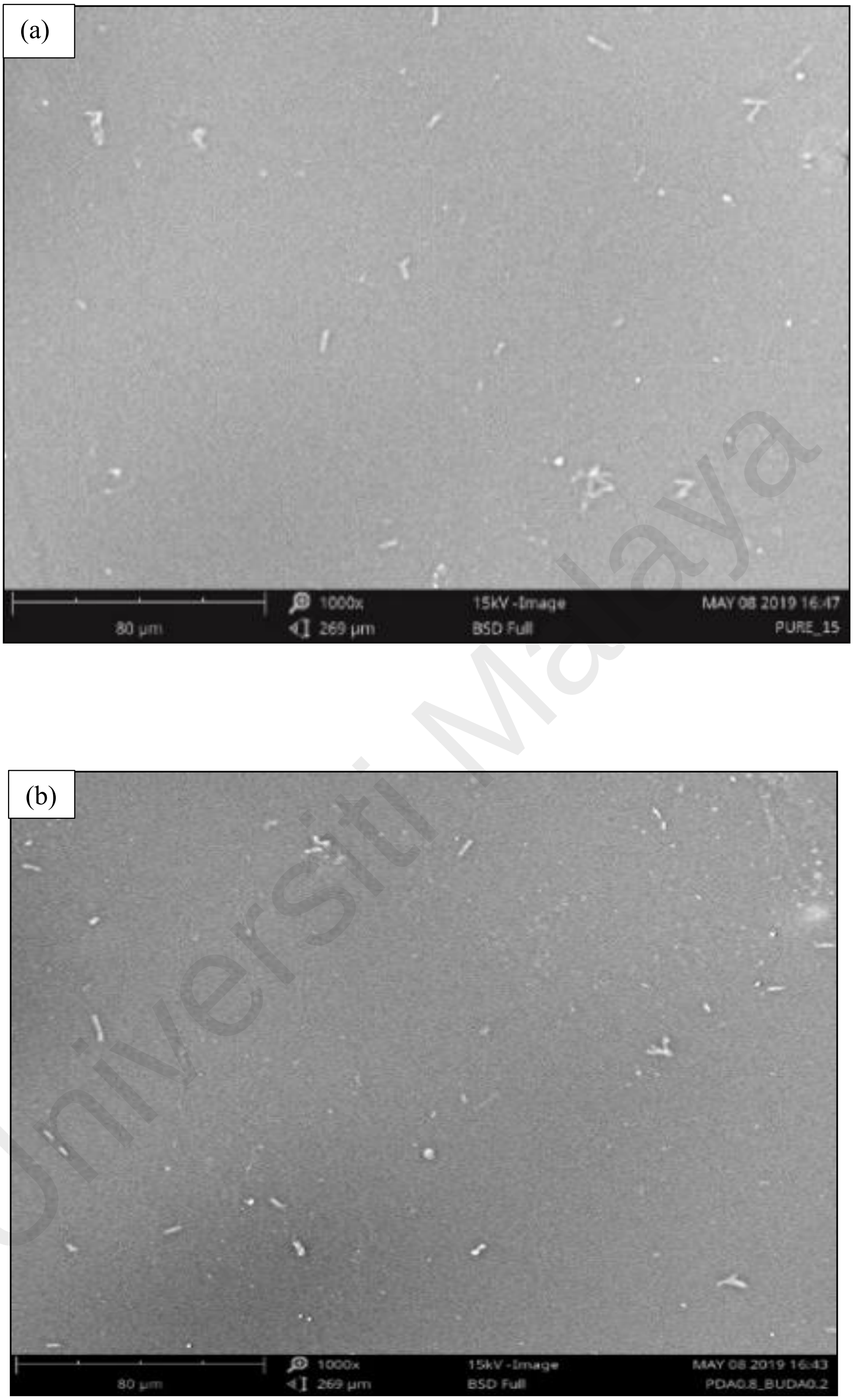


Figure 4.1: Morphology of surface and cross section of pure and crosslinked membranes. (a) Pure P84-surface; (b) 0.8 PDA:0.2 BuDA crosslinked P84-surface; (c) Pure P84-Cross section

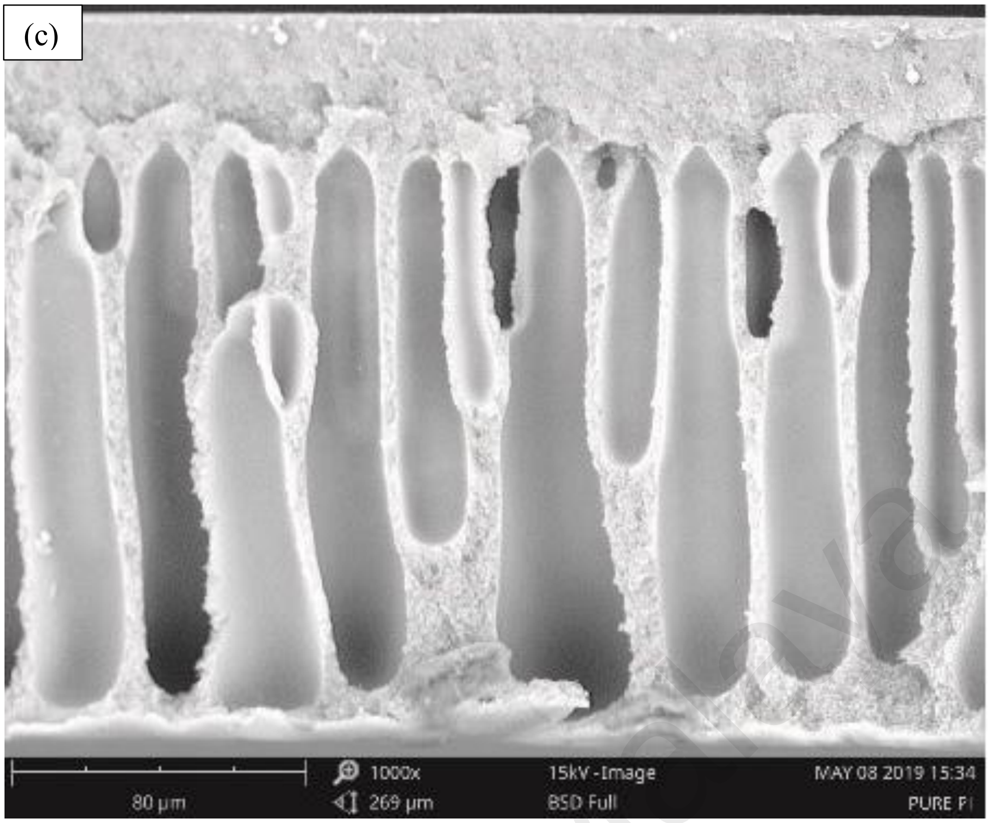


Figure 4.1, continued

4.1.2 Chemical Characterization

Interaction between polymer of the membrane was studied by using FTIR. The peaks that appeared in the FTIR spectrum proved the existence of functional groups formed during surface modification of membrane. Figure 4.2 shows FTIR spectra of original and modified P84 asymmetric membranes. For both original and crosslinked membranes, Imide groups which include C=O asymmetric stretch (1778.02 cm^{-1}), C=O symmetric stretch (1717.15cm^{-1}) and C-N (1366.29cm^{-1}) were detected. In a surface modification reactor, PDA and BuDA crosslinking agents were able to attack the macromolecules as the asymmetric P84 membrane has a thin skin layer and porous structure (Chung et al., 2006; R. Liu et al., 2005). Thus, the characteristic peaks for imide groups in crosslinked membranes are lower compared to the original P84 membrane as shown in Figure 4.2. Among crosslinked membranes with different ratios of BuDA and PDA crosslinking solution, the characteristic peaks of amide groups in 0.8 PDA: 0.2 BuDA of the modified membrane is the lowest. It showed that 0.8 PDA:0.2 BuDA mixed crosslinking solutions give a stronger attack to the macromolecules. Thus, it induces a higher degree of crosslinking reaction and gives the lowest imide peaks among crosslinked membranes.

Besides, the peak detected at 1652.94 cm^{-1} and 1528.62 cm^{-1} proved the presence of C=O stretching in amide group and strong amide bands (bend of N-H) and characterized the thermodynamic cross-linking reactions between P84 and crosslinking agents (Chung et al., 2006).

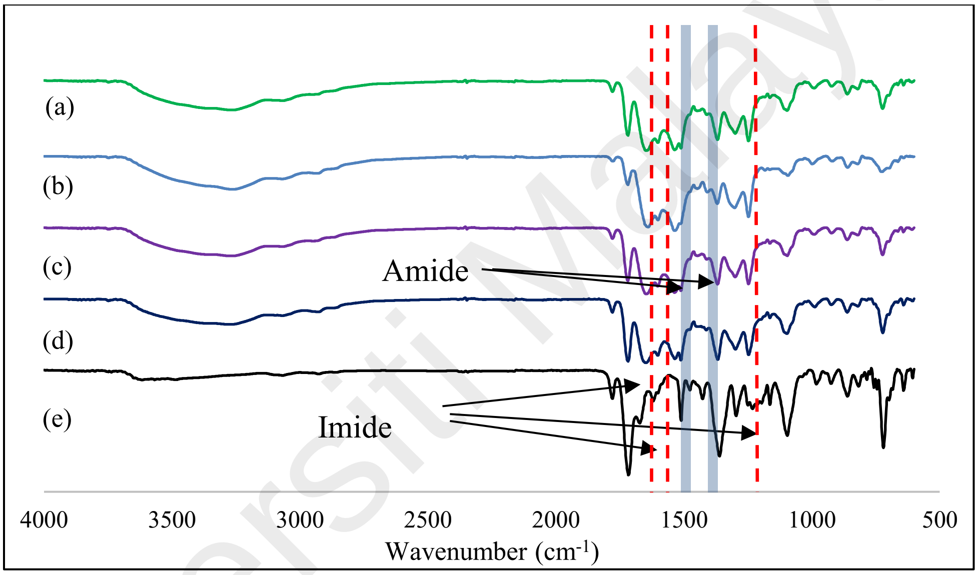


Figure 4.2: FTIR spectra of original P84 membrane and crosslinked membranes. (a) 100 % PDA; (b) 0.8 PDA:0.2 BuDA; (c) 0.4 PDA:0.6 BuDA, (d) 100 % BuDA, (e) P84-original.

4.1.3 Ideal Gas Permeation Properties

Ideal gas separation membrane specifically focuses on single gas molecule permeability and selectivity as crucial parameters for separation performance evaluation (Li et al., 2015). Greater selectivity will result in greater efficiency and therefore reduces the driving force needed for a separation to occur and leads to low operation cost. Moreover, higher permeability will lessen the membrane area required which should lower the capital cost of the system. Hence, any small improvement in separation efficiency is significant as it could result in substantial cost reduction.

Cross-linking modification for P84 membrane was carried out with different ratios of PDA-BuDA crosslinking solutions. H_2 and CO_2 permeation tests were also conducted to investigate the effect of blending two crosslinking agents on the gas separation performance. H_2 permeance and ideal selectivity of H_2 over CO_2 were obtained before and after crosslinking modification processes and the changes on both parameters are shown in Figure 4.3 in terms of percentage improvements. For instance, P84 crosslinked with 0.8 PDA: 0.2 BuDA achieved 110.08 % improvement on H_2/CO_2 selectivity with 62 % decrement on H_2 permeability.

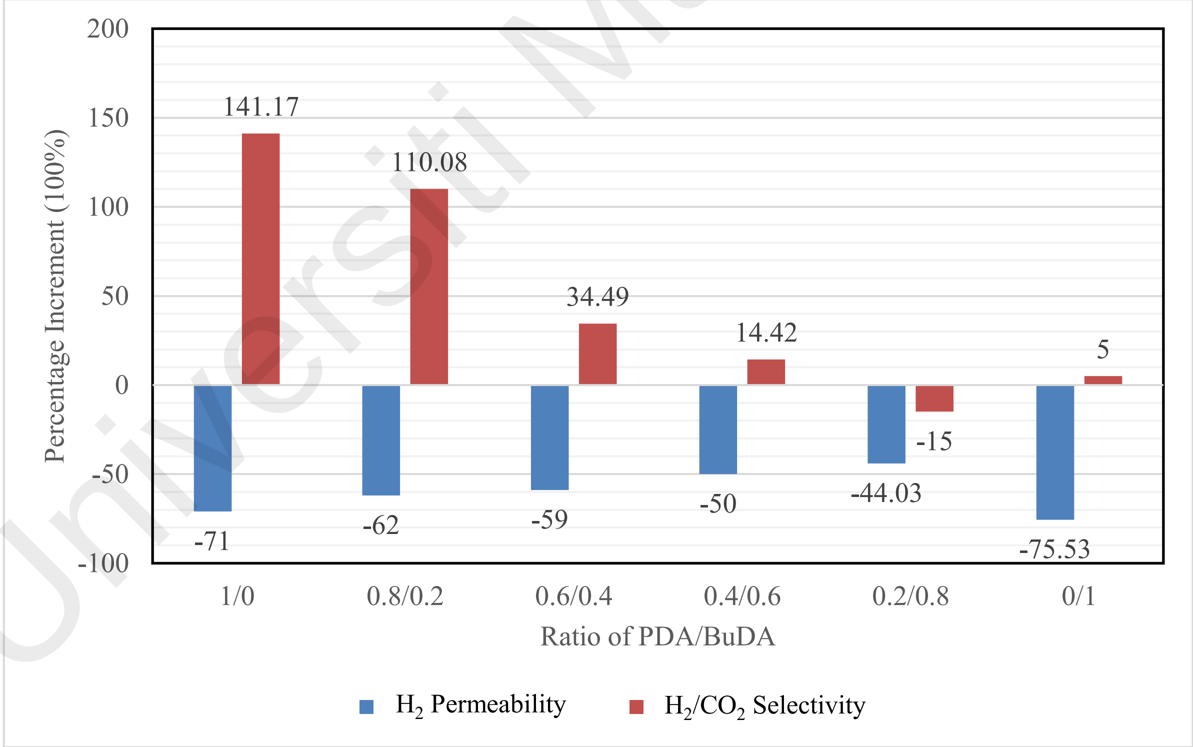


Figure 4.3: Gas separation improvement after crosslinking modification with different ratios of PDA-BuDA diamine solutions.

The hydrogen permeability after crosslinking modification deteriorates with increasing PDA concentration (= decreasing concentration of BuDA) in crosslinking solutions. Meanwhile, the ideal selectivity improved tremendously after modification with higher PDA concentration. This is because the molecular length of crosslinking reagents influences the gas penetration process. The decrease in gas permeability upon diamino crosslinking is anticipated due to the tightening of polymer chains which constricts the channel for gases to pass through (Hosseini & Chung, 2009). Since the kinetic diameter of H_2 (2.89 Å) is smaller than CO_2 (3.3 Å), it is expected for the degree of reduction in CO_2 permeance to be greater than H_2 permeance, hence the corresponding increase in H_2/CO_2 selectivity (C. H. Lau et al., 2010). PDA (molecular length=6.7Å) has shorter molecular length compared to BuDA (molecular length=8Å). PDA may promote mutual influence between 2 $-NH_2$ functional groups and thermodynamically restrict gas diffusion into PI membranes (Chung et al., 2006). On the other hand, although PDA has shorter molecular length, the closer chain packing, and smaller linear structure induce faster crosslinking rate and thus higher improvement on H_2 selectivity over CO_2 with a higher concentration of PDA.

Hence, 100 % PDA as crosslinking agent is proven to demonstrate the most significant H_2/CO_2 selectivity improvement which is up to 141.17 % despite the minor drop on H_2 permeability and therefore is used for the modification of polymer blend membrane in the next procedure.

4.2 The effect of polymer blend ratio and diamine crosslinking towards PES/P84 membrane characteristics and H_2/CO_2 separation performance

4.2.1 Physical Characterization

The morphological analysis of the membrane for the surface and cross-sectional view was conducted using FESEM analysis as shown in Figure 4.4 and Figure 4.5. The cross-sectional view of the membranes (Figure 4.4) depicted that each membrane possesses asymmetric structures where a thin dense skin layer is supported by thick sponge-like substructure for PP-1 and PP-2 whereas PP-3 and the modified membrane consist of finger-like sublayer. The formation of asymmetric structure with sponge-like substructures depicted by PP-1 and PP-2 are due to the delayed liquid-liquid demixing process induced by the evaporation step during membrane preparation and the use of THF which diminished the interaction between solvent and non-solvent. Similar structures were also observed in previous literature (Aroon et al., 2010; Hamid et al., 2019; A. F. Ismail & Lai, 2003; Junaidi et al., 2014). However, as the composition of PES increases, the finger-like sublayer is more likely to form. This is because of the characteristic of PES being greater polarity and affinity to water. This observation is in agreement with the reported literature (Barth et al., 2000).

The dense layer thickness which ranges from 0.16 µm to 0.92 µm is favorable since a top thin dense layer enhances the gas permeability of the asymmetric structured membranes by minimizing the penetration resistance (G. Liu et al., 2019). The highly porous substrate as shown in the figure also contributes in facilitating the gas transport (G. Liu et al., 2019). Meanwhile, the surface morphologies of the membranes as illustrated in Figure 4.5 show that the membranes are defect-free. Hence, the gas transport occurs via solution-diffusion mechanism that involves three consecutive steps, (a) sorption of the preferential permeate at the upstream, (b) activated diffusion through the dense top layer membrane, and (c) desorption at the end of the dense layer to the downstream side (Shao, Low, et al., 2009).

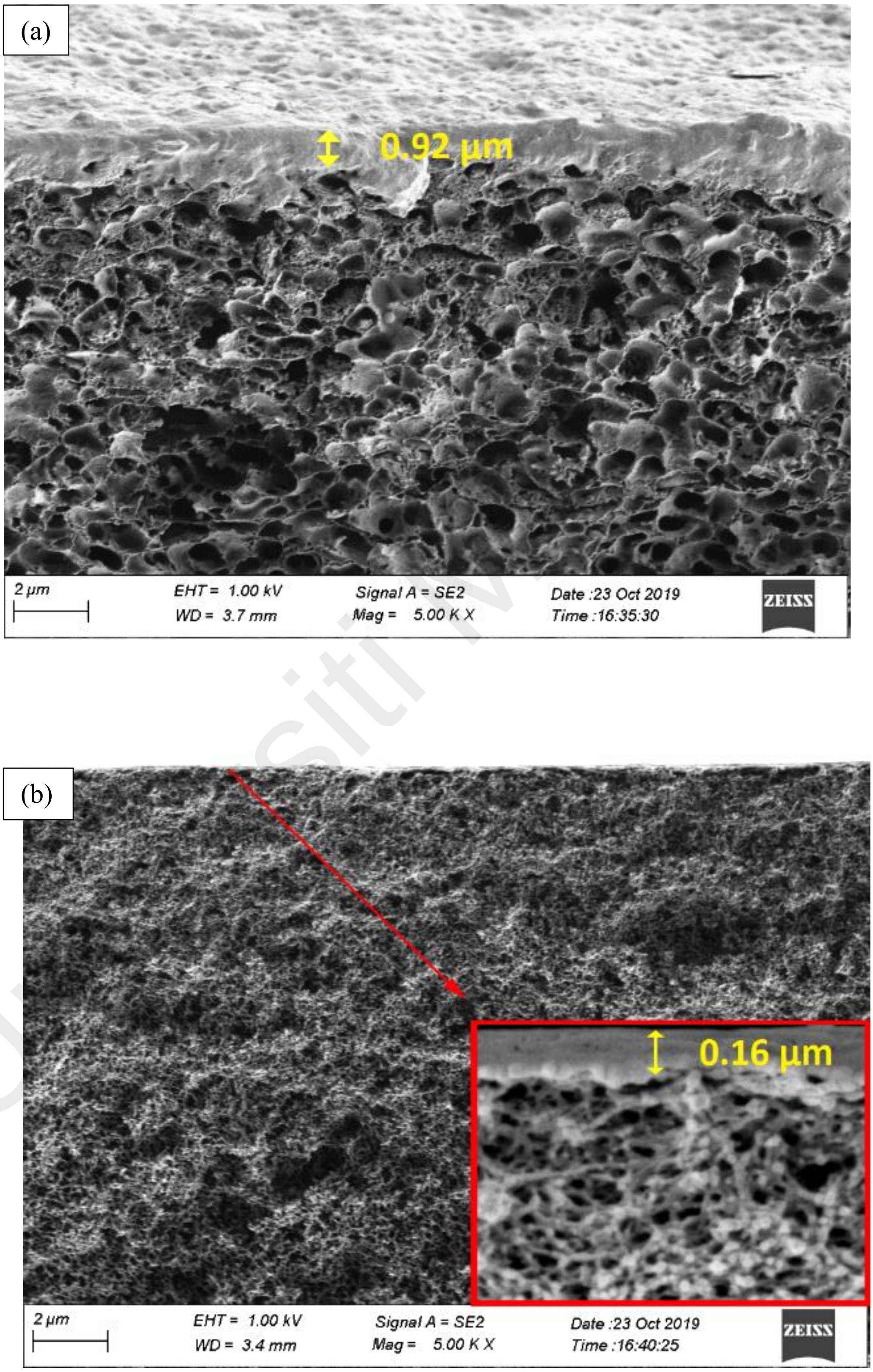


Figure 4.4: Cross sectional morphologies of polymer blend membranes where the yellow arrows indicate the dense layer thickness (a) PP-1; (b) PP-2; (c) PP-3; (d) PP-3-M15.

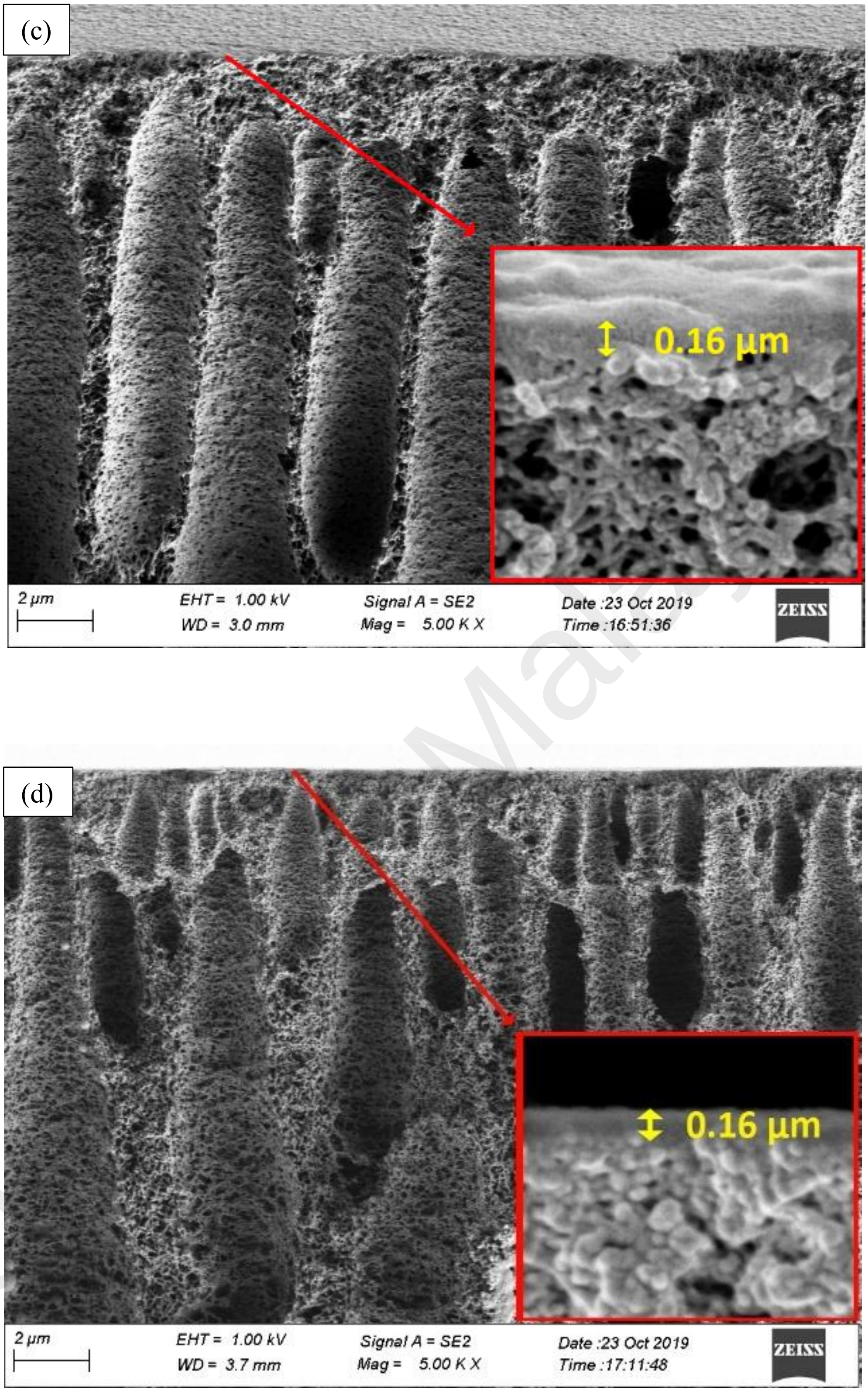


Figure 4.4, continued

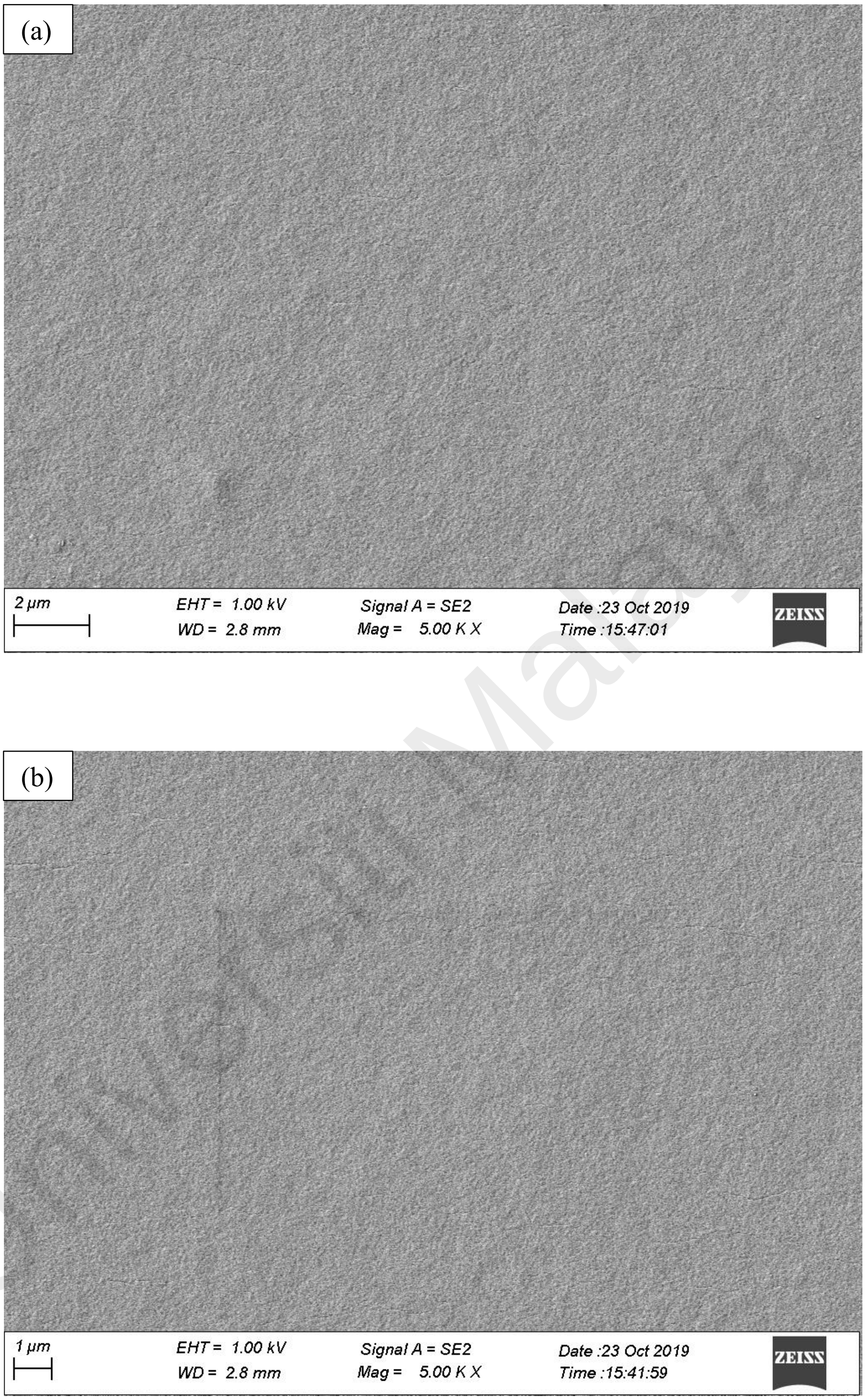


Figure 4.5: Surface morphologies of polymer blend membranes. (a) PP-1; (b) PP-2; (c) PP-3; (d) PP-3-M15.

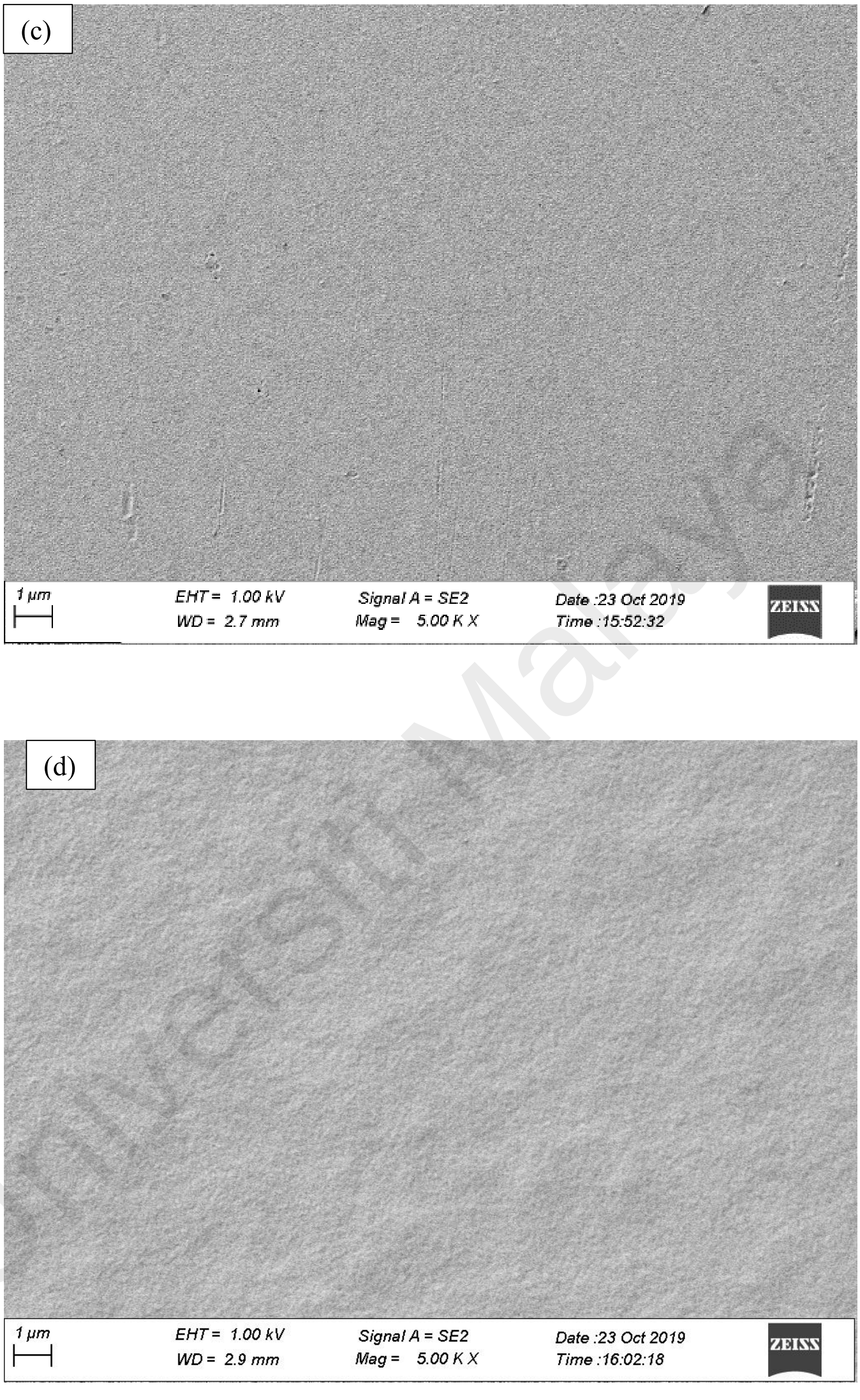


Figure 4.5, continued

Figure 4.6 and 4.7 shows the results of XRD of polymer blends with different compositions as well as uncrosslinked and diamine-crosslinked membrane which were performed to determine the d-spacing values. XRD patterns of different composition of polymer blends show that each of the peaks appears at almost the same loci which implies that there is no significant difference in the average d-spacings. On the other hand, there is a great difference in peak intensities of the polymer blends where the intensities increase as the composition of P84 increases. The increase in peak intensities signifies greater regularity and packing order which justifies the trend in permeation performance in Section 4.2.3 (Hosseini & Chung, 2009).

Meanwhile, Figure 4.7 illustrates that the d-spacing of the membrane upon modification decreases compared to before modification which is from 5.04 Å to 4.9 Å. The size decrement indicates that the diamino crosslinking alters the packing conformation of the polymer chains which thereby tightens the membrane microstructures and therefore affects the H_2/CO_2 separation performance (Shao, Lau, et al., 2009).

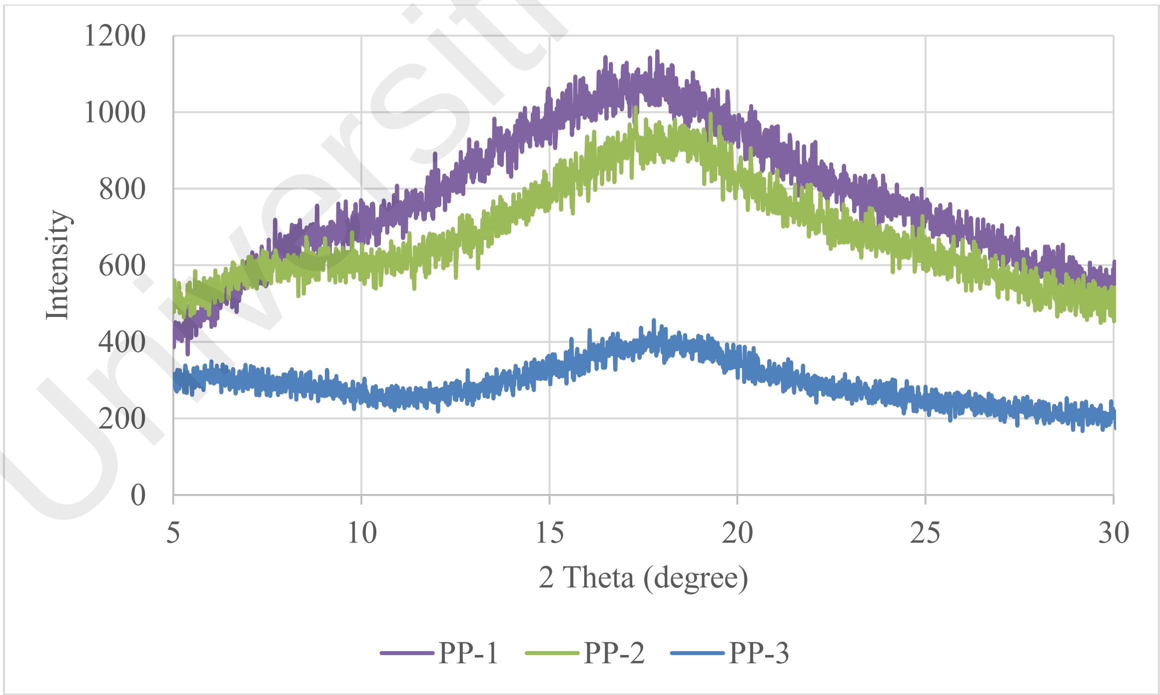


Figure 4.6: XRD spectra of polymer blends with different compositions

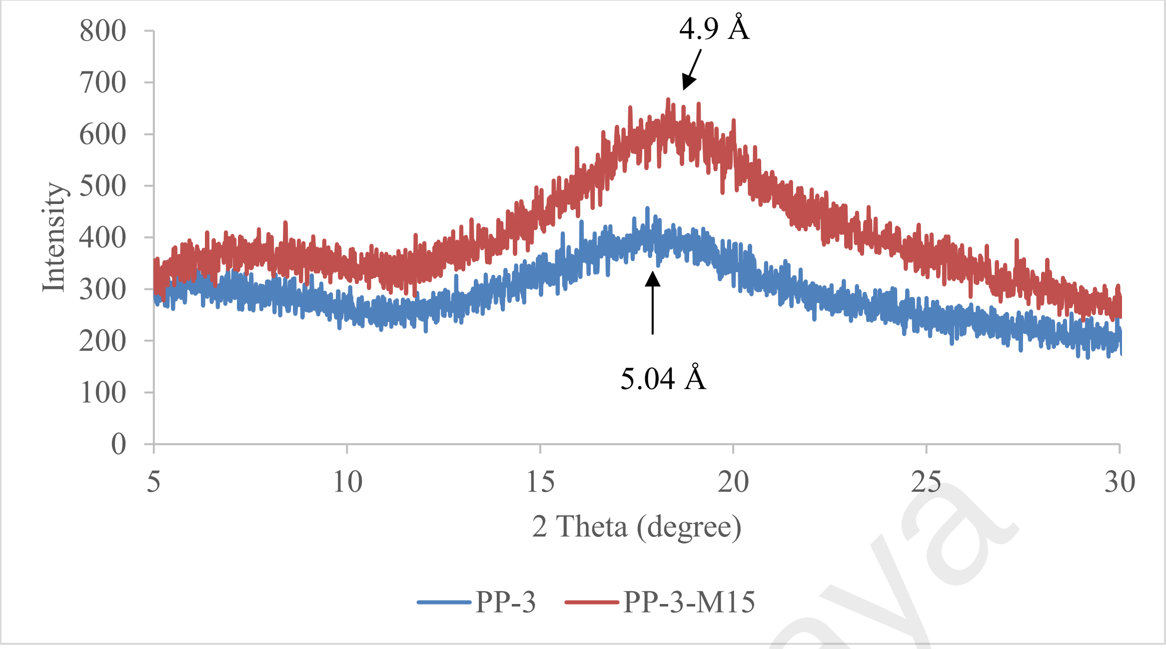


Figure 4.7: XRD spectra of uncrosslinked membrane and diamine-crosslinked membrane

4.2.2 Chemical Characterization

Figure 4.8 depicts FTIR spectra of PES/P84 with different blend compositions to study the interaction between the two polymers. The peaks at 1105 cm^{-1} and 1325 cm^{-1} are attributed to sulfone groups of PES. Meanwhile, aromatic ether (-C-O-C-) of PES displays the stretching vibration at 1245 cm^{-1} (Han et al., 2010). Aromatic benzene ring shows absorption bands at 1487 cm^{-1} and 1579 cm^{-1} (Han et al., 2010). The appearance of peaks at 1778 cm^{-1} and 1727 cm^{-1} are due to carbonyl group (-CO-N-CO-) whereas the peaks at 1200 cm^{-1} and 1360 cm^{-1} are associated with C-N bond from imide groups of P84 (Han et al., 2010). As the composition of PES increases, the peaks attributed to characteristics of PES increases in intensities and vice versa. The change of intensities in IR spectra proves the interaction of PES and P84 at the molecular level, and thus confirming the compatible nature of PES/P84 blend (Hamid et al., 2019).

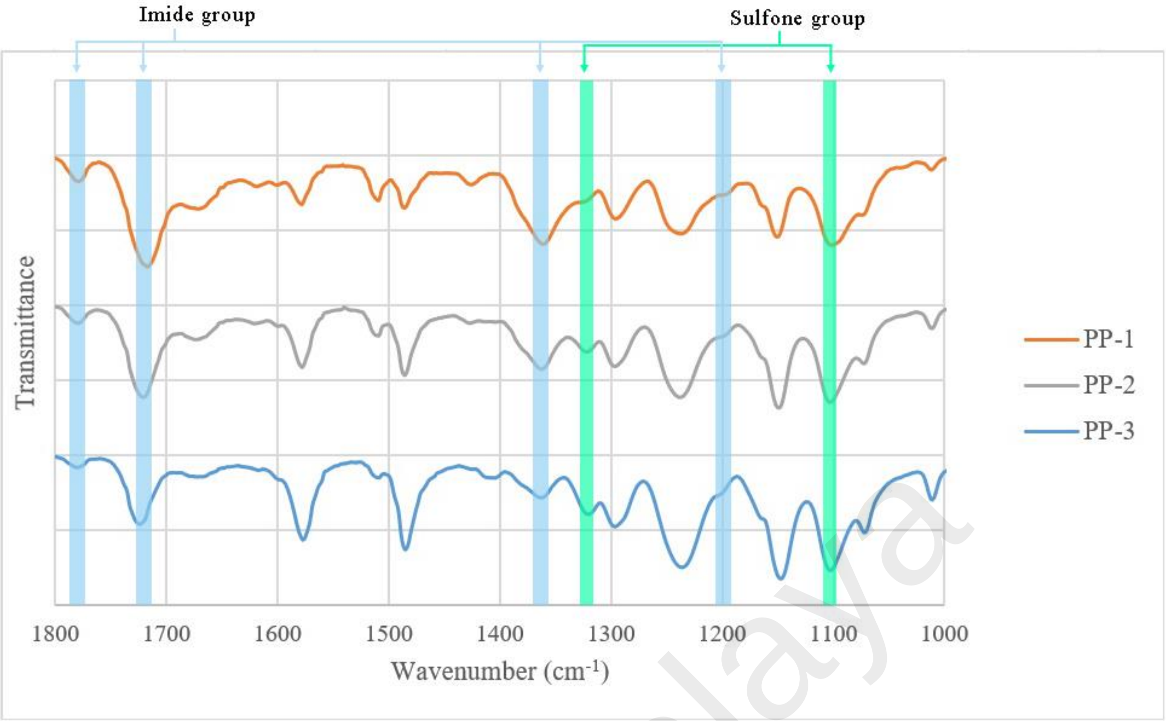


Figure 4.8: FTIR spectra of PES/P84 with different blend composition

Figure 4.9 portrays a comparison of FTIR spectra of PES/P84 before and after diamino crosslinking. As summarized in Table 4.1, the imide groups from pure P84 are detected through the peaks at 1781 cm^{-1} and 1725 cm^{-1} which signifies C=O asymmetric stretch and C=O symmetric stretch respectively (C. H. Lau et al., 2010; Shao et al., 2008). The peaks at 1360 cm^{-1} and 1200 cm^{-1} are attributed to C-N bond from imide groups as well (Chatzidaki et al., 2007; Han et al., 2010; Wijenayake et al., 2013). After modification with diamine, the peaks from imide groups disappear with the emergence of new peaks indicating amide groups, at 1644 and 1528 cm^{-1} which correspond to C=O stretch and C-N stretch bands, respectively. The disappearance of imide groups along with the emergence of amide groups occur gradually with the increase of reaction time. This proves that the chemical reaction occurred between P84 and PDA which is the conversion of imide group of P84 to an amide group where the imide ring is opened due to the nucleophilic attack of PDA (Chung et al., 2006; Mangindaan et al., 2014; Wijenayake et al., 2013). Meanwhile, the peaks representing the sulfone groups of PES at 1105 and 1300 cm^{-1} remain upon modification which implies that the sulfone groups are inert to the attack. The proposed reaction mechanism is illustrated in Figure 4.10.

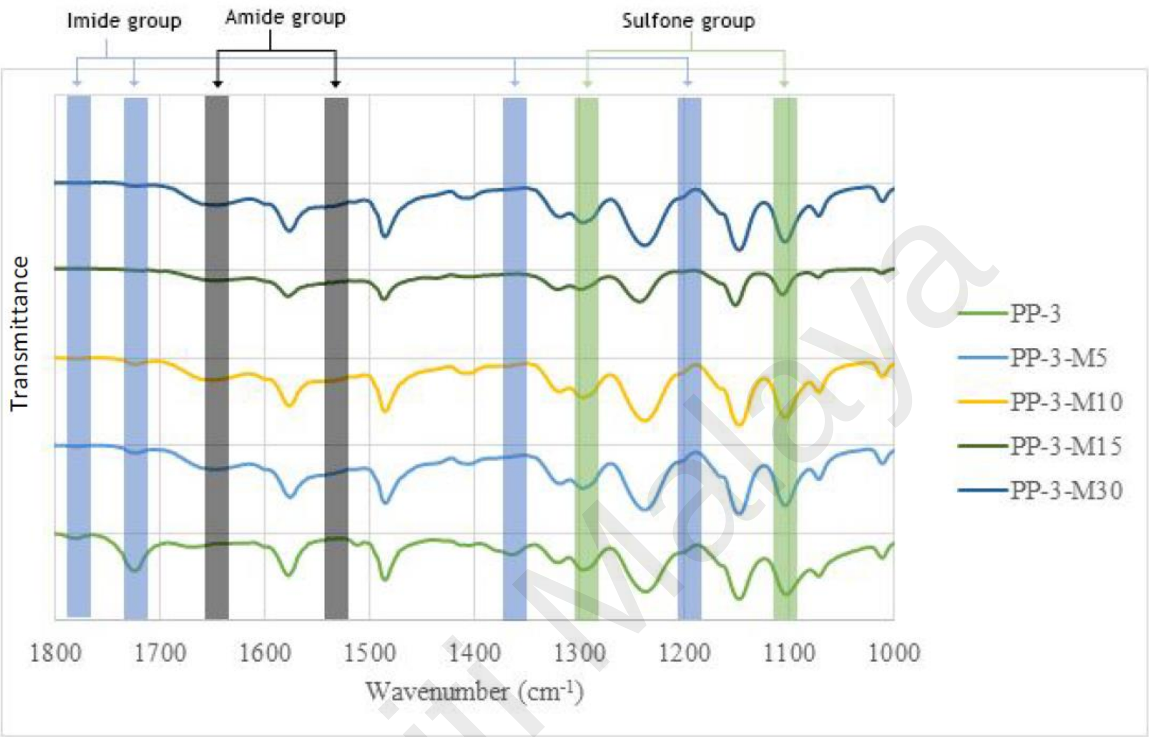


Figure 4.9: FTIR spectra of the original and PDA-modified membranes in different reaction time

Table 4.1: Functional groups detected in FTIR spectra

Functional group		**Wavenumber (cm^{-1})**
Imide group	C=O asymmetric stretch	1781
	C=O symmetric stretch	1725
	C-N	1360
		1200
Amide group	C=O stretch	1644
	C-N stretch	1528
Sulfone group	O=S=O	1105
		1300

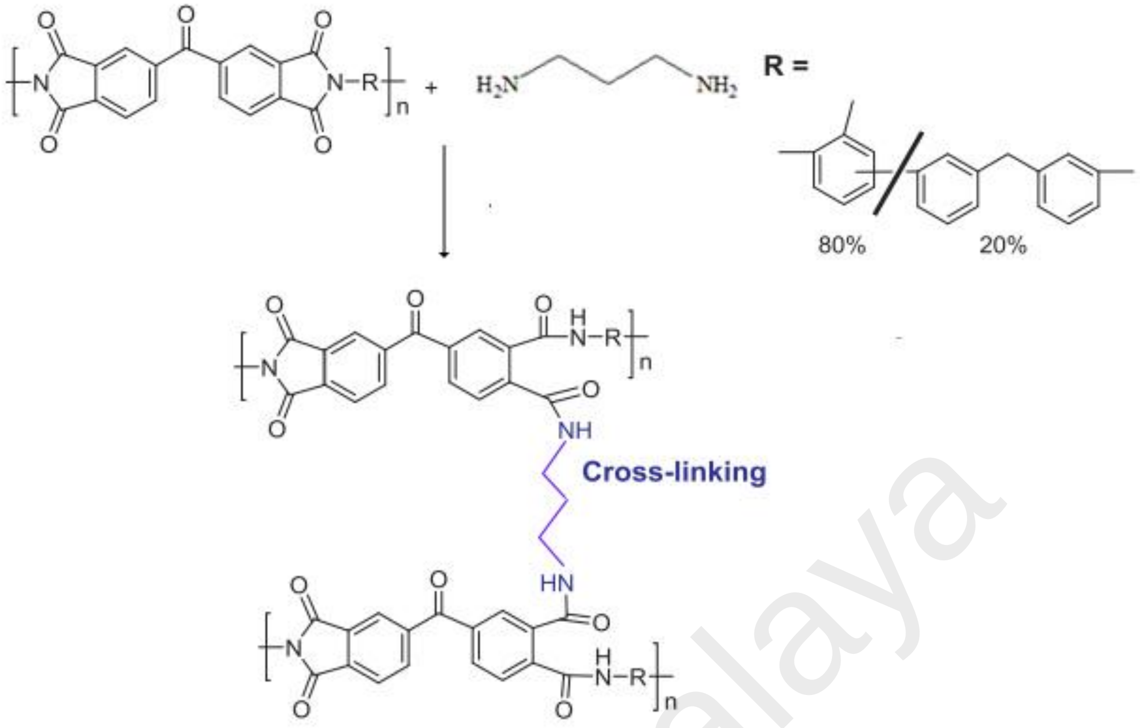


Figure 4.10: Possible reaction mechanism between imide group from P84 and diamine

4.2.3 Ideal Gas Permeation Properties

The fabricated membranes with blend composition of three different ratios are tested for their gas permeation properties and the results are summarized in Table 4.2. From the table, it can be seen that the increase in PES concentration results in a greater H_2/CO_2 separation performance. Even though the change in H_2/CO_2 selectivity is not quite prominent, the H_2 permeability of PP-3 increases by about fourfold from the one obtained by PP-1. This shows that the blend composition of the membranes significantly influences the gas permeation properties. The highest H_2 permeability demonstrated by PP-3 might be related to the least regularity and packing order compared to PP-2 and PP-3 which was discussed in Section 4.2.1 according to the XRD spectra shown in Figure 4.6.

Table 4.2: Gas permeation properties of polymer blend with different ratios

Membrane Sample	H_2 Permeability (Barrer)	CO_2 Permeability (Barrer)	H_2/CO_2 Selectivity
PP-1	39.66	12.7	3.12
PP-2	42.86	12.46	3.44
PP-3	187.3	53.7	3.49

Since PP-3 shows the best H_2/CO_2 separation performance, diamine modification on the polymer blend is, therefore, conducted with this ratio. The polymer blend is immersed in PDA:methanol solution in a stipulated period of time to study the effect of reaction time on H_2/CO_2 separation efficiency where the results is compiled in Table 4.3. With 5 minutes and 10 minutes of diamine reaction time, both gases permeabilities increase with the increment of the reaction time. Meanwhile, the H_2/CO_2 selectivity observed gradual improvement. The reaction time increment causes a further increment in the crosslinking density and the reduction of free volume as verified by FTIR analysis, which eventually leads to the gradual improvement of H_2/CO_2 selectivity for PP-3-M5 and PP-3-M10. The result shows that H_2 permeability decreases dramatically while H_2/CO_2 selectivity increases by 96.9 % upon 15 minutes of immersion in diamine solution (Figure 4.11). This is due to the changes in physicochemical structures caused by diamino modification where the interstitial spacing between the polymer chains is tightened which is validated via XRD analysis explained in Section 4.1. The performance behaviour of PP-3-M15 membrane is inline with the observation obtained by Chung et al. (2006) when they increased the reaction time of diamine modification on 6FDA-Durene membrane where the membranes show the loss of H_2 permeability with a dramatic increase of H_2/CO_2 selectivity. The difference in kinetic diameter of H_2 (2.89 Å) and CO_2 (3.3 Å) plays an important role in the improvement of H_2/CO_2 selectivity. As the tightening of the interstitial spacing occurs, the channel for gases to pass through becomes more restricted

(Hosseini & Chung, 2009). The restricted channel causes the gas permeability to decrease. However, the decrement in CO_2 permeability is greater than H_2 due to a bigger kinetic diameter of CO_2 which thereby, results in H_2/CO_2 selectivity increment (C. H. Lau et al., 2010). The highest H_2/CO_2 selectivity achieved by PP-3-M15 signifies that 15 minutes is the best reaction time obtained in this work for the alterations in physicochemical structures of modified membrane for H_2/CO_2 separation. During the first 15 minutes, the crosslinking restricts the inter-chain spacing while maintaining the backbone rigidity since most of the imide rings remain which contribute to the mechanical integrity of the polymer network (Low et al., 2008). However, longer reaction time which is 30 minutes opens up most of the imide rings forming amide groups which thereby reduces the backbone rigidity despite restricting the inter-chain spacing (Low et al., 2008). The reduction of backbone rigidity causes the mobility of the polymer chains to increase, hence the depletion of H_2/CO_2 selectivity (Low et al., 2008; Omidvar et al., 2019).

Table 4.3: Effect of reaction time on H_2/CO_2 selectivity

Membrane Sample	**H_2 Permeability (Barrer)**	**CO_2 Permeability (Barrer)**	**H_2/CO_2 Selectivity**
PP-3	187.3	53.7	3.49
PP-3-M5	288.48	76.12	3.79
PP-3-M10	310.78	70.16	4.43
PP-3-M15	105.60	15.36	6.87
PP-3-M30	122.43	30.90	3.96

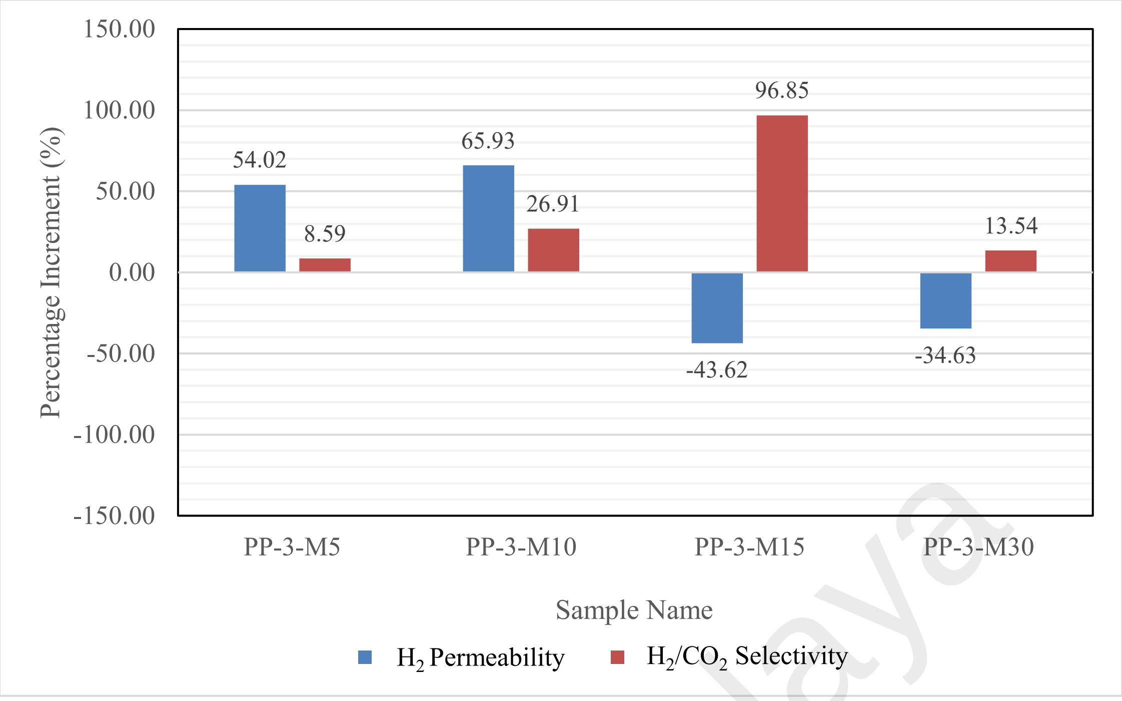


Figure 4.11: Percentage increment of gas separation performance after crosslinking modification in different reaction time

4.2.4 Robeson's Upper Bound Curve for H_2/CO_2 Separation

Figure 4.12 portrays permeation characteristics of membrane films from this study plotted against Robeson H_2/CO_2 upper bound curve showing the separation performance of conventional polymeric membranes in terms of permeability and selectivity trade-off limits whereas Table 4.4 tabulates the data points close to the present upper bound along with the ones from this study (Robeson, 2008). Based on the figure, PP-3-M5, PP-3-M10 and PP-3-M15 samples have surpassed the present upper bound. In comparison to pure PES reported by Farrokhnia et al. (2015), PP-3-M10 has shown an improvement of H_2 permeability and H_2/CO_2 selectivity. Meanwhile, by comparing with P84 reported by Omidvar et al. (2019), PP-3-M10 has managed to surpass the P84 H_2 permeability performance, despite the reduction loss of H_2/CO_2 selectivity by 26.2 %. PP3-M-15 has transcended the performance of both P84 and PES in terms of H_2 permeability and H_2/CO_2 selectivity. Overall, it can be described that PP-3-M15 exhibits the most satisfactory separation performance as it achieves an adequate balance between the permeability and selectivity while succeeding to surpass the present upper bound. Therefore, this study has been successfully demonstrated as a promising approach to develop membranes with high separation performance.

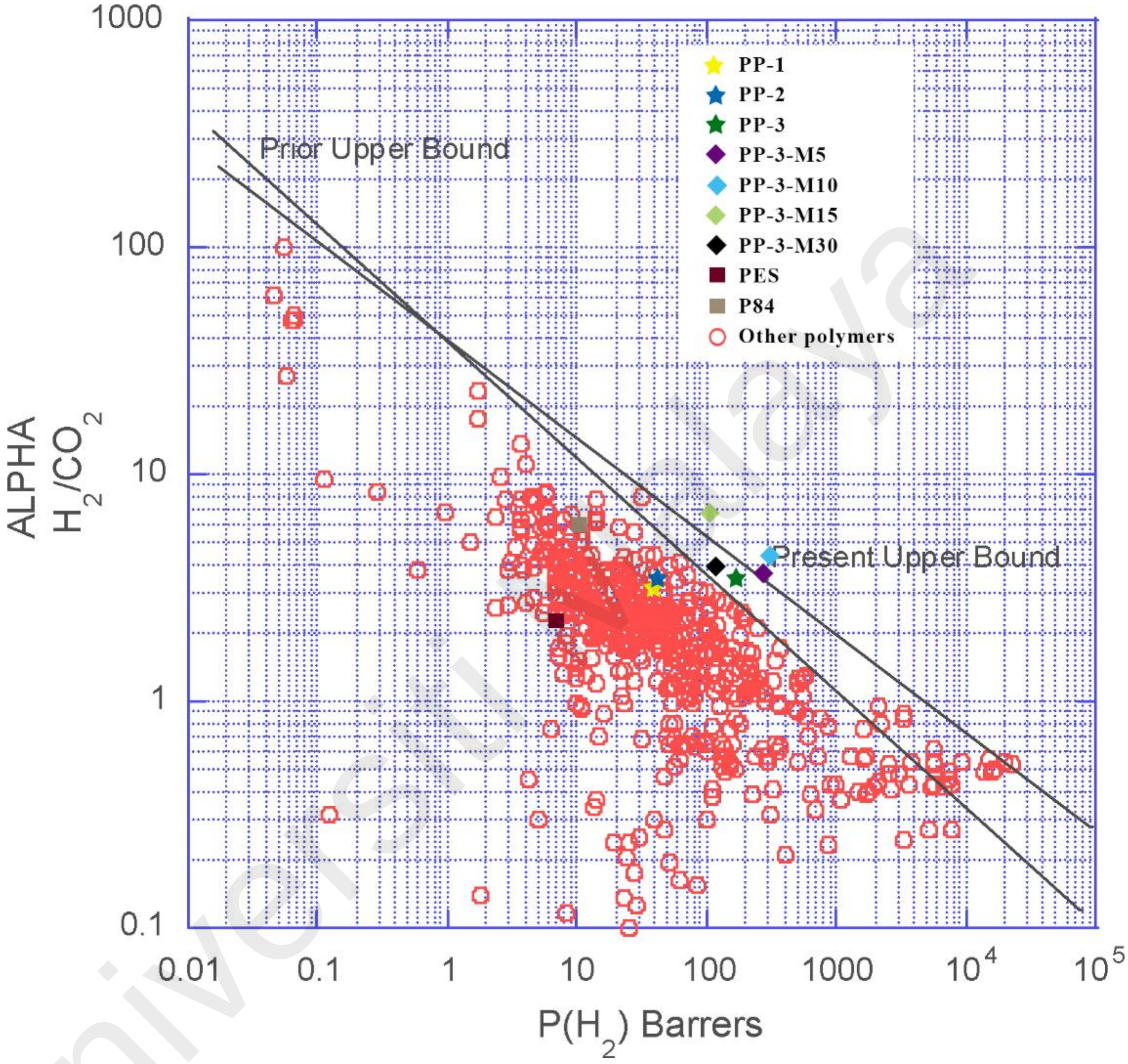


Figure 4.12: Permeation characteristics of blended and diamine modified PES/P84 over Robeson's upper bound (Robeson, 2008)

Table 4.4: Data points close to the present upper bound as well as data points from this study

Polymer	H_2 Permeability	H_2/CO_2 Selectivity	Reference
Liquid crystalline polyester (HBA/HNA 30/70)	0.0545	100.9	Weinkauf and Paul (1992)
Polyaniline (redoped)	1.753	23.1	Illing et al. (2005)
Polyimide(1,1-6FDA-DIA)	31.4	8.05	Rezac and Schöberl (1999)
Poly(trimethylsilylpropyne)	13900	0.495	Nagai et al. (1994)
Poly(trimethylsilylpropyne)	16200	0.489	Savoca et al. (1993)
Poly(trimethylsilylpropyne-cophenylpropyne) (95/5)	20400	0.538	Nagai et al. (1995)
Poly(trimethylsilylpropyne)	23300	0.53	Nagai et al. (1995)
PP-1	39.66	3.12	This study
PP-2	42.86	3.44	This study
PP-3	187.3	3.49	This study
PP-3-M5	288.48	3.79	This study
PP-3-M10	310.78	4.43	This study
PP-3-M15	105.60	6.87	This study
PP-3-M30	122.43	3.96	This study

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Asymmetric P84 membrane was successfully synthesized via dry-wet phase inversion and chemically crosslinked with mixed PDA-BuDA of different ratios. Chemical structure changes before and after modification were validated using FTIR. 1,3-diaminopropane is a superior crosslinking agent by demonstrating the highest H_2/CO_2 selectivity improvement by 141.2 %. This is because of the tighter chain packing, and smaller linear structure which promotes faster crosslinking rate, and thereby enhancing the improvement on H_2 selectivity with a higher concentration of PDA.

Asymmetric miscible blend membranes in three different ratios were synthesized to study the effect of blend composition of PES/P84 towards the membrane characteristics and its H_2/CO_2 separation performance. The compatibility nature of PES and P84 was verified via FTIR. Hydrogen permeabilities significantly increased with increasing concentration of PES where PES/P84 (75/25 wt. %) achieved 187.3 Barrer with H_2/CO_2 selectivity of 3.49. This is because of the changes in regularity and packing order as the composition was altered.

The influence of diamine surface modification parameters towards membrane properties in terms of chemical, physical and separation properties had been studied. PES/P84 (75/25 wt. %) which showed superior H_2/CO_2 separation performance had been further modified with PDA solution. The changes in the physical and chemical structure after diamine modification had been verified by FTIR, FESEM and XRD. The highest improvement on H_2/CO_2 selectivity (up to 96.9 %) had been achieved using a 15-minutes crosslinked-membrane due to the tightening of the polymer chain and the reduction in free volume. Meanwhile, the overall finest performance had been achieved by the PP-3-

M15 (i.e. diamine-crosslinked membrane in 15 minutes) and it was able to surpass Robeson's upper bound curve with the highest enhancement of H_2/CO_2 selectivity.

5.2 Recommendations

Based on the present study, the following recommendations are suggested to be employed for further studies and development in the membrane technology for H_2 purification:

i. In this study, a newly developed polymer blend crosslinked with diamine was successfully studied in terms of pure H_2 and CO_2 permeation properties. However, a mixed gas permeation test is necessary to evaluate real industrial application. Hence, a study on mixed gas permeation test for this newly developed membrane is recommended for future work.

ii. PES/P84 crosslinked with diamine from this study exhibited a good H_2/CO_2 separation performance. It is recommended to explore other gas pairs for biogas applications to utilize the fabricated membrane such as H_2/CH_4 separation.

iii. The present study developed the membrane in a flat sheet form. However, a hollow fibre membrane module is more attractive since it possesses a larger effective surface area which leads to better productivities. Therefore, it is suggested to fabricate the membrane in a hollow fibre form.

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

1. Nasir, N. A. A., Ling, J. H., Junaidi, M. U. M., Hashim, N. A., Hizzaddin, H. F., Rabuni, M. F., Abidin, M. I. I. Z., & Rohani, R. (2020). 1, 3-Propane Diamine/1, 4-Butane Diamine Cross-linking Modification of Polyimide Membrane for Hydrogen Selective Separation: Effect of Diamine Mixture Ratio. *Asia-Pacific Journal of Chemical Engineering*, *15*(3), e2411. (Published) https://doi.org/10.1002/apj.2411
2. Nasir, N. A. A., Alshaghdari, A. G. A., Junaidi, M. U. M., Hashim, N. A., Rabuni, M. F., Rohani, R. (2020). Miscible Blend Polyethersulfone/ Polyimide Asymmetric Membrane Crosslinked with 1,3-Diaminopropane for Hydrogen Separation. *Journal of Polymer Engineering*. (Published) https://doi.org/10.1515/polyeng-2020-0316