

**INTERFACIAL ENHANCEMENT OF MIXED
MATRIX MEMBRANE USING IONIC LIQUID
FOR CO₂ SEPARATION**

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UNIVERSITI SAINS MALAYSIA

2020

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by

NOR NAIMAH ROSYADAH BINTI AHMAD

**Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy**

April 2020

ACKNOWLEDGEMENT

In the name of Allah S.W.T., the Most Gracious and the Most Merciful. First and foremost, I am grateful to Allah who bestowed me the strength and courage to complete this thesis. Without His guidance and help, I will not be able to finish this challenging journey. Special thanks to my parents, Haji Ahmad bin Chin and Hajjah Aishah binti Jusoh and other family members for their prayers and support throughout my life. Their prayers and encouragement have spurred me on to reach the success.

I would like to convey highly appreciation to my supportive supervisor Assoc. Prof. Ir. Dr. Leo Choe Peng for her non-stop guidance and knowledge sharing throughout my study. I would also like to thank my co-supervisor Prof. Abdul Latif Ahmad for his support. I am truly grateful for the research experience under their supervision.

My deepest gratitude goes to my lab mates and friends under supervision of Assoc. Prof. Ir. Dr Leo Choe Peng (Nor Aini, Usman, Hani, Haziyana, Izyatul and Melvin, Why Ling and Hoi Fang) for their helps, comments and ideas given throughout my research. I would like to thank Suhaili, Syahida, Shazlina, Athiah, Wani, Muthmirah, Izzati, Nurul Aini, Nazierah and Ain Najihah for the beautiful moments that we spent together in USM. I am thankful for the all the support and friendships.

I would like to extend my appreciation to all management staff and technicians in School of Chemical Engineering especially Mr. Ismail, Mr, Arif, Mr. Raqib, Mr. Faiza, Mr. Shamsul, Mdm. Aswani and Mdm. Latiffah for their kindness and technical

supports. My appreciation also goes to the technical staff from School of Material Engineering (Mr. Rasyid, Mr. Zaini and Mr. Khairi).

Finally, I would like to thank Ministry of Education Malaysia (MOE) for the MyPhD scholarship. The research funding support granted by Institute of Climate Change UKM-Sime Darby Foundation (IPI-UKM 304/PJKIMIA/050334/U124), Membrane Science and Technology Cluster (1001/PSF/8610013) and LRGS (203.PJKIMIA.6726101) are fully appreciated.

Nor Naimah Rosyadah Ahmad

April 2020

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LIST OF SYMBOLS

%	Percentage
°C	Temperature in degree Celcius
T_g	Glass transition temperature
wt. %	Weight percentage
Å	Angstrom (10^{-10} m)
α	Gas selectivity
l	Effective membrane thickness or skin layer thickness
vol. %	Volume percentage
P	Gas permeability
D	Gas diffusion coefficient
S	Gas solubility coefficient
N	Gas flux across a membrane
p_o	Pressure at upstream side of membrane
p_l	Pressure at downstream side of membrane
C_o	Gas concentration in membrane (faces the upstream side)
C_l	Gas concentration in membrane (faces the downstream side)
Q_{STP}	Volumetric flow rate of permeate gas at standard temperature and pressure
Δp	Pressure difference across a membrane
A	Effective membrane area
\emptyset	Time lag
$E_T(30)$	Polarity parameter
P/P_o	Relative pressure
q	Volume of the permeate gas

LIST OF ABBREVIATIONS

[Ac]	Acetate anion
Ag	Silver
Al	Aluminium
[Ala]	Alanate anion
AlCl ₃	Aluminium chloride
Al (i-C ₃ H ₇ O) ₃	Aluminum tri-isopropylate
APDMES	3-aminopropyldimethylethoxysilane
APMDES	3-aminopropylmethyldiethoxysilane
APTES	3-aminopropyltriethoxysilane
APTMS	3-aminopropyltrimethoxysilane
[BF ₄]	Tetrafluoroborate anion
BET	Brunauer-Emmett-Teller
[bmim]	1-butyl-3-methylimidazolium cation
CCS	Carbon capture and storage
[CF ₃ SO ₃]	Trifluoromethanesulfonate anion
CH ₄	Methane
CHA	Chabazite
CH ₃ MgBr	Methylmagnesium bromide
[Cl]	Chloride anion
CNF	Carbon nanofiber
CNT	Carbon nanotubes
CO ₂	Carbon dioxide
CrO ₃	Chromium(VI) oxide
[dca]	Dicyanamide anion

DMAc	Dimethylacetamide
DMS	Disordered mesoporous silica
DSC	Differential scanning calorimeter
EDX	Energy dispersive X-ray
[emim]	1-ethyl-3-methylimidazolium cation
EtOH	Ethanol
ETS-10	Microporous titanosilicate
FTIR	Fourier transform infrared spectrometer
[Gly]	Glycinate anion
GO	Graphene oxide
GPU	Gas permeation unit
H ₂	Hydrogen
H ₂ O	Water
HKUST	Hong Kong University of Science and Technology
HMA	2-hydroxy 5-methylaniline
[hmim]	1-hexyl-3-methylimidazolium cation
H ₃ PO ₄	Ortho-Phosphoric acid
H ₂ S	Hydrogen sulfide
IL	Ionic liquid
ISA	Integrally skinned asymmetric
ITQ	Instituto de Tecnologia Quimica Valencia
LTA	Linde Type A
LMOG	Low molecular organic gelator
LMWM	Low molecular weight material
MCM	Mobil Composition of Matter
Me	Methoxy
MeOH	Methanol

Mg ²⁺	Magnesium ion
MMM	Mixed matrix membrane
MOF	Metal organic framework
8-MR	Eight membered ring
MWCNT	Multi-walled carbon nanotubes
N ₂	Nitrogen
Na ⁺	Sodium ion
NaCl	Sodium chloride
O	Oxygen
P	Phosphorus
PC	Polycarbonate
PDMS	Polydimethyl siloxane
Pebax®	Polyether-block-amide
PEO	Poly(ethylene oxide)
PES	Polyethersulfone
[PF ₆]	Hexafluorophosphate anion
PI	Polyimide
PIL	Poly(ionic liquid)
PIM	Polymer of intrinsic microporosity
[Pro]	Prolinate anion
PSf	Polysulfone
PVDF-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
[P ₆₆₆₁₄]	Trihexyl(tetradecyl)phosphonium cation
RTIL	Room temperature ionic liquid
SAPO	Silicoaluminophosphate
SEM	Scanning electron microscope
Si	Silicon

SILM	Supported ionic liquid membranes
SLM	Supported liquid membrane
SOCl ₂	Thionyl chloride
SWNT	Single walled carbon nanotubes
TAP	2,4,6-triaminopyrimidine
TEAOH	Tetraethylammonium hydroxide
TFC	Thin film composite
[Tf ₂ N]	Bis(trifluoromethylsulfonyl)imide anion
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TSIL	Task specific ionic liquid
XRD	X-ray diffractometer
ZIF	Zeolitic imidazolate framework
ZSM	Zeolite Socony Mobil

PENINGKATAN ANTARA MUKA MEMBRAN MATRIKS CAMPURAN MENGUNAKAN CECAIR ION UNTUK PEMISAHAN CO₂

ABSTRAK

Penggunaan membran matriks campuran (MMM) muncul sebagai pendekatan yang berpotensi dalam aplikasi pemisahan CO₂ disebabkan oleh kesan bersinergi bahan polimer dan bukan organik. Walau bagaimanapun, keserasian yang lemah di antara partikel bukan organik dan polimer sering menyebabkan kecacatan antara muka yang mengurangkan prestasi pemisahan gas MMM. Dalam kajian ini, MMM tidak simetri terdiri daripada polisulfon (PSf) dan zeolit SAPO-34 telah dihasilkan melalui penyongsangan fasa kering-basah. Pertamanya, kandungan zeolit SAPO-34 dalam rumusan MMM telah dibezakan dari 5 ke 15 wt.% untuk mengkaji kesan kandungan zeolit terhadap ciri-ciri MMM dan prestasi pemisahan gas CO₂. Peningkatan kandungan zeolit telah meningkatkan telapan CO₂ dalam MMM tetapi mengurangkan kepilihan CO₂/N₂ berbanding membran PSf yang tulen. Penggabungan zeolit SAPO-34 dalam membran PSf telah menghasilkan pembentukan lompong pada sentuhan antara muka polimer/ pengisi seperti yang ditunjukkan oleh imej mikroskop elektron imbasan. Cecair ionik (IL) yang selektif terhadap CO₂ digunakan dalam kajian ini untuk mengubah suai MMM dengan memalam kecacatan antara muka dalam membran. Dua pendekatan yang berbeza iaitu pra-pengubahsuaian dan pasca-pengubahsuaian telah digunakan dalam pengubahsuaian MMM. Keputusan menunjukkan bahawa kaedah pasca-pengubahsuaian dengan IL telah meningkatkan sentuhan antara muka polimer/zeolit serta prestasi pemisahan gas MMM berbanding pendekatan pra-pengubahsuaian. Kaedah pasca-pengubahsuaian diteruskan dengan

mengkaji kesan kepekatan IL, kandungan zeolit, sifat-sifat pelarut dan IL. Kajian mendapati bahawa pasca-pengubahsuaian bagi MMM yang mengandungi 5 wt. % zeolit telah meningkatkan kepilihan CO₂/N₂ sekitar 820% berbanding MMM yang tidak diubahsuai dengan meningkatkan kepekatan IL/etanol daripada 0.2 kepada 0.4 M. Kepilihan CO₂/N₂ juga boleh ditingkatkan apabila pelarut yang lebih kutub seperti metanol digunakan dalam pasca-pengubahsuaian MMM melibatkan kepekatan IL yang rendah (0.2 M). Telapan CO₂ dan kepilihan CO₂/N₂ bagi MMM yang diubahsuai dengan IL masing-masing telah diperbaiki kepada 4.93-7.19 GPU dan 26.63-35.21 dengan menggunakan IL yang mempunyai berat molekul yang besar kerana pengurangan keliangan zeolit dapat diminimumkan. Analisa parameter pengangkutan gas mendedahkan bahawa penggabungan IL ke dalam MMM telah meningkatkan kebolehlarutan CO₂ dalam membran tetapi peningkatan dalam kepilihan CO₂/N₂ lebih disebabkan oleh kepilihan kemeresapan. Prestasi pemisahan gas bagi MMM yang diubahsuai dengan IL telah diperhatikan tetap kekal apabila didedahkan kepada keadaan gas lembap. Oleh itu, pendekatan pasca-pengubahsuaian MMM menggunakan IL boleh menjadi strategi alternatif dalam pembangunan membran bagi aplikasi pemisahan CO₂.

INTERFACIAL ENHANCEMENT OF MIXED MATRIX MEMBRANE USING IONIC LIQUID FOR CO₂ SEPARATION

ABSTRACT

The use of mixed matrix membrane (MMM) appears to be a promising approach in CO₂ separation application due to the synergistic effects of polymer and inorganic materials. However, poor compatibility between inorganic particles and polymer often results in interfacial defects that reduce the MMM gas separation performance. In this study, asymmetric MMMs comprises of polysulfone (PSf) and SAPO-34 zeolite were fabricated via dry-wet phase inversion. The loading of SAPO-34 zeolite in the MMM formulation was first varied from 5 to 15 wt.% to study the effect of zeolite loading to the characteristics of the MMMs and CO₂ gas separation performance. Increasing the zeolite loading has enhanced the CO₂ permeance of the MMM but reduced the CO₂/N₂ selectivity as compared to the neat PSf membrane. The incorporation of SAPO-34 zeolite in the PSf membrane has resulted in the voids formation at the polymer/filler interface contact as shown by scanning electron microscopy images. Ionic liquid (IL) which selective towards CO₂ was used in this study to modify the MMM by sealing the interface defects in the membrane. Two different approaches namely pre-modification and post-modification were applied in the MMM modification. Results showed that the post-modification method with IL has improved both polymer/zeolite interface contact and gas separation performance of the MMM as compared to the pre-modification approach. The post-modification method was further explored by studying the effects of IL concentration, zeolite loading, solvent and IL properties. It was found that the post-modification of the MMM incorporated with 5 wt. % zeolite loading has enhanced the CO₂/N₂ selectivity about 820 % over the unmodified MMM

by increasing the concentration of the IL/ethanol solution from 0.2 to 0.4 M. The CO₂/N₂ selectivity can also be increased when more polar solvent such as methanol was used in the post-modification of MMM involving low IL concentration (0.2 M). The CO₂ permeance and CO₂/N₂ selectivity of IL-modified MMM was improved to 4.93-7.19 GPU and 26.63-35.21 respectively by using IL with large molecular weight since the reduction in zeolite porosity could be minimized. Analysis of the gas transport parameters revealed that the incorporation of IL into the MMM has increased the CO₂ solubility of the membrane but the improvement in the CO₂/N₂ selectivity was mainly contributed by the diffusivity selectivity. The gas separation performance for the IL-modified MMM was observed to sustain when being exposed to the humid gas condition. Thus, the post-modification approach of MMM using IL can be as an alternative strategy in membrane development for CO₂ separation application.

CHAPTER 1

INTRODUCTION

1.1 Carbon Dioxide (CO₂) Separation

Global warming due to the increasing emission of carbon dioxide (CO₂) has become one of the great issues today. This issue requires urgent task to mitigate the CO₂ emission into the atmosphere. It was reported that in 2017, 73 % of total greenhouse gas is coming from CO₂ (Olivier and Peters, 2018). Coal fired power plants, cement manufacturing and petrochemicals industries have been identified to contribute about 56 % to the amount of CO₂ emitted (Change, 2014). Meanwhile, the fuel combustion has resulted in 32.8 Gtonnes of worldwide CO₂ emission in 2017 (IEA, 2019). The CO₂ concentration in the atmosphere has increased since the preindustrial times which led to the rise of the earth' surface temperature of about 0.6-0.7 °C during the past century (Pera-Titus, 2013).

In Malaysia, the CO₂ emission has been recorded to increase every year. Figure 1.1 represents the trend of total CO₂ emission in Malaysia within 10 years starting from 2009 until 2018 (YCharts, 2019). It can be observed that the CO₂ emission has been elevated about 30 % for the past 10 years. According to MESTECC (2018), the major source of CO₂ emission is due to the energy industries such as electricity, petroleum refining and natural gas processing plant in Malaysia. Therefore, Malaysia has set the target to reduce about 45 % of its CO₂ emission by 2030 to combat the climate change impact (Babatunde et al., 2018).

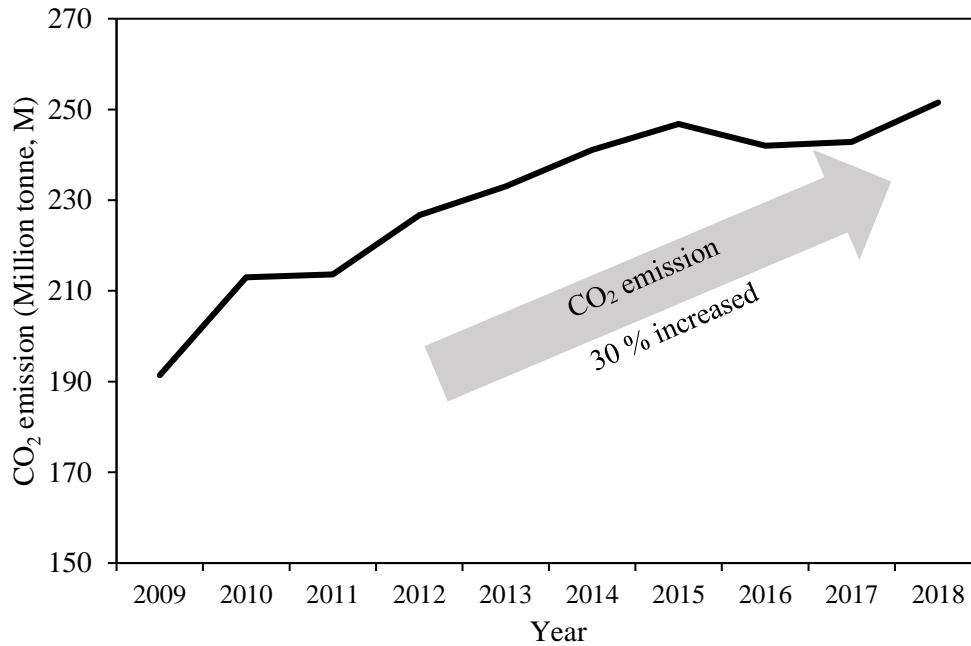


Figure 1.1 CO₂ emission in Malaysia (YCharts, 2019)

Carbon capture and storage (CCS) technology has been developed to reduce the CO₂ emission into the atmosphere (Arellano et al., 2016). CCS technology can be divided into two main approaches which are CO₂ capture from fossil fuel power plant and CO₂ removal from industrial processes such as natural gas and biogas purification (He, 2018). Since the fossil fuel power plant is the major source of global CO₂ emission, the development of the CO₂ capture technology is urgently needed to suppress the CO₂ emission level from this source. Basically, the flue gas emitted from coal-fired power plant may contain 72-77 % N₂, 12-14 % CO₂, 8-10 % H₂O and 3-5 % O₂ by volume (Song et al., 2004). The low CO₂ partial pressure in the flue gas explains why the CO₂ capture process from flue gas stream is quite challenging.

The CO₂ capture from power plant comprises of three main strategies namely, pre-combustion capture, oxyfuel processes and post-combustion capture (Gargiulo et al., 2016). Among these approaches, post-combustion capture is preferable to reduce the CO₂ emission since it does not require modification on the plant architecture (Erto

et al., 2015). Various CO₂ separation methods have been developed for the post-combustion strategies including amine absorption, adsorption, membrane and cryogenic separation (Vinoba et al., 2017). Amine absorption is the most commonly used, but it possesses several drawbacks such as high energy consumption, corrosion and low thermal stability (Dilshad et al., 2017). Among these technologies, membrane-based separation has been appeared as a promising technology due to its simple design, low capital investment, and high product recovery (Mannan et al., 2013).

1.2 Membrane for Gas Separation

The potential of membranes in gas separation has been discovered since 1950s (Mohshim et al., 2013). However, the application of gas separation membranes in the industries only initiated 40 years ago. Permea (now parts of Air Product) was the first company to launch the gas separation membrane for industrial application in 1980 (Baker, 2002). Such advancement in membrane history has further promoted the growth of membrane development for gas separation application.

Polymeric membrane is the first generation of membrane which has been developed in 1980s to separate gas mixture (Chuah et al., 2018). The fast growth of polymeric membrane application is driven by its low production cost and ease for upscaling (Vinoba et al., 2017). The ease of fabrication which involves various choices of polymer materials and tunable membrane configuration further promote the utilization of polymeric membranes in CO₂ separation field. In general, there are two types of polymer materials which are known as rubbery and glassy polymers (Ismail et al., 2009). Rubbery polymers have flexible structure due to the highly intra-segmental mobility. They operate above their glass transition temperature (T_g) and has high gas permeability but low selectivity. By contrast, glassy polymers have rigid

structure and work below their T_g . Currently, the glassy polymers have been extensively used in membrane gas separation owing to their good mechanical properties and high selectivity (Bastani et al., 2013). Polysulfone (PSf) is one of the commonly used glassy polymers in the fabrication of membrane for CO_2 separation. It has high T_g value, around $190\text{ }^\circ\text{C}$. PSf possesses good mechanical strength, high chemical stability as well as good thermal resistance due to the presence of stable diphenylene sulfone as repeating in its structure as illustrated in Figure 1.2 (Gomez-Coma et al., 2016). Moreover, PSf is also considered as a cost effective polymeric material and it can resist the plasticization effect under high pressure (Rafiq et al., 2012). Similar to most polymeric membranes, polysulfone membrane also faces limitation in term of “trade-off” between the selectivity and permeability which is membranes with higher selectivity usually have lower permeability (Goh et al., 2011).

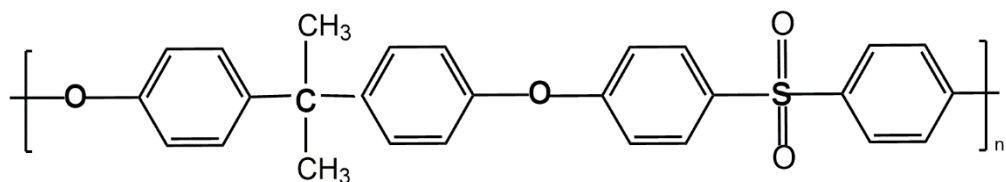


Figure 1.2 Polysulfone monomer structure

Inorganic membranes are another class of membrane that has been developed for gas separation application. In comparison to polymeric membranes, inorganic membranes possess higher gas selectivity and higher permeability (Jusoh et al., 2016). Furthermore, inorganic membranes are attractive due to their chemical and thermal stabilities as well as longer lifespan (Vinoba et al., 2017). Inorganic membranes can be categorized into two groups, namely dense and porous inorganic membranes. Silver, zirconia and palladium are examples of dense inorganic membranes.

Meanwhile, numerous porous inorganic membranes have been developed for gas separation application which include carbon molecular sieve, silica, zeolite and metal organic frameworks (MOF) (Jusoh et al., 2016). Zeolite is one of the commonly used inorganic materials for membrane development in gas separation application due to its high porosity, uniform pore size, excellent thermal and chemical stability (Kosinov et al., 2016). The framework of zeolites consists of AlO_5^{4-} and SiO_4^{4-} tetrahedral linked to each other by sharing of one Al or Si atom at the center and oxygen atoms in each corner of the tetrahedron (Flanigen EM, 2010). Silicoaluminophosphate-34 (SAPO-34) is one of the promising zeolite for CO_2 separation due to their CO_2 adsorption affinity (Junaidi et al., 2013, Sen and Das, 2017). This zeolite family consists of chabazite (CHA) framework structure (Figure 1.3) which contains eight membered ring (8-MR) channels with the pore size of 0.38 nm. Therefore, its small pore opening is suitable for the CO_2 separation from N_2 or CH_4 gases (Kim et al., 2014, Chew et al., 2018). Despite the excellent gas separation property of the inorganic membranes such as SAPO-34, it is difficult to scale-up the inorganic membrane and the production cost of inorganic membranes is expensive which limits their application for large scale gas separation process.

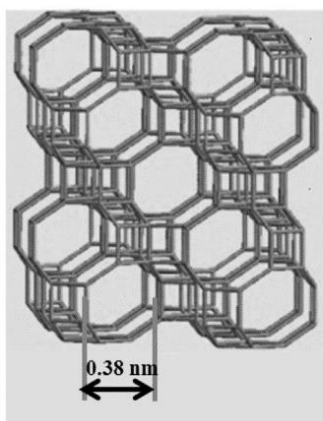


Figure 1.3 Framework structure of CHA (Hu et al., 2017)

Mixed matrix membrane (MMM) has been developed for CO₂ separation application to overcome the limitations faced by polymeric and inorganic membranes. The structure of MMM consists of polymeric material as the continuous phase and inorganic particles as the dispersed filler (Figure 1.4). The first generation of MMMs was reported in 1970s which 5A zeolite was blended with polydimethyl siloxane (PDMS) to form the MMM for gas separation (Paul and Kemp, 1973). Theoretically, the incorporation of inorganic fillers into the polymer matrix helps to enhance the permeability of the resulting MMM in relative to neat polymeric membrane (Bastani et al., 2013). The selectivity improvement can also be achieved since the presence of porous fillers in the MMM can act as a molecular sieve which favour the transport of small gas molecules and hinder the diffusion of larger gas molecules (Aroon et al., 2010). Beside the gas separation properties, the fabrication of MMM is attractive since it retains the processability of the polymer matrix (Chuah et al., 2018). Various inorganic particles such as silica (Ahn et al., 2008), zeolite (Dorosti et al., 2011), metal organic framework (Ban et al., 2015) and carbon material (Kim et al., 2007) have been embedded into the polymeric membrane to form MMMs. These MMMs especially zeolite-based MMMs have demonstrated significant improvement in gas separation over the neat polymeric membranes. Zeolite-based MMMs have been extensively studied in recent years owing to the uniform pore size and the great porosity of zeolite that allow the selective permeation of CO₂. Apart from the promising gas separation properties of the MMM, the issue regarding poor compatibility between the inorganic fillers and the polymer matrix has become one of the challenges that need to be addressed in the MMM fabrication (Aroon et al., 2010). In view of the poor polymer/filler compatibility issue, various attempts have been made in recent years to modify the MMM which include the incorporation of the ionic liquid as the third

component in the MMM. The coverage of IL around the filler can act as a wetting medium that improve the interaction between the polymer and inorganic filler in MMM (Hudiono et al., 2010).

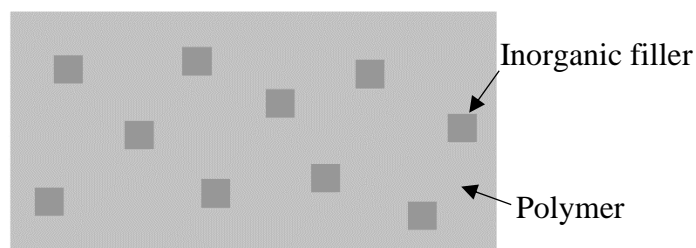


Figure 1.4 Structure of mixed matrix membrane

1.3 Ionic Liquid

In recent years, ionic liquids (ILs) have emerged as promising absorbent for CO₂ capture. ILs are salts made of cation and anion which appear in liquid form at room temperature. Figure 1.5 displays the examples of cations and anions of the ILs. The low intermolecular interactions and poor packing of their ions are the reasons why ILs remain as liquid at room temperature (Tome and Marrucho, 2016). ILs are attractive due to their negligible vapour pressure, good thermal stability and high CO₂ solubility. Moreover, the ILs properties such as viscosity, solubility and hydrophobicity can be adjusted by altering the combination of anion and cation (Lozano et al., 2011). Among the ILs, imidazolium-based ILs have been commonly investigated in literatures (Ramdin et al., 2012). In general, ILs can be categorized into two types which are room temperature ionic liquids (RTIL) and task-specific ionic liquids (TSIL). RTILs are conventional type of ILs which absorb the CO₂ via physisorption. For instance, tetrafluoroborate ([BF₄]), dicyanamide ([dca]), chloride ([Cl]) and hexafluorophosphate ([PF₆]) are examples of anion in RTILs group.

Meanwhile, TSILs have been developed to enhance the CO₂ absorption capacity of the ILs. TSILs can be designed by functionalizing the ILs using various basic anions such as carboxylates and amino acids. Unlike conventional RTILs which interact with CO₂ via physisorption and prefer high pressure, TSILs absorb the CO₂ via chemisorption at low CO₂ partial pressure (Dai et al., 2016c). Acetate-based IL is one of the commonly investigated TSILs for CO₂ separation. In the last decades, supported ionic liquid membranes (SILM) have been developed to utilize the potential of ILs for CO₂ separation process. SILM comprises of porous supports which pores are filled with the ILs. Despite high selectivity of SILM, the insufficient membrane stability for long time operation has become one of the major constraints of SILM (Yan et al., 2019). The limitation of SILM has led to development of another type of IL-based membranes which include ionic liquid-mixed matrix membrane.

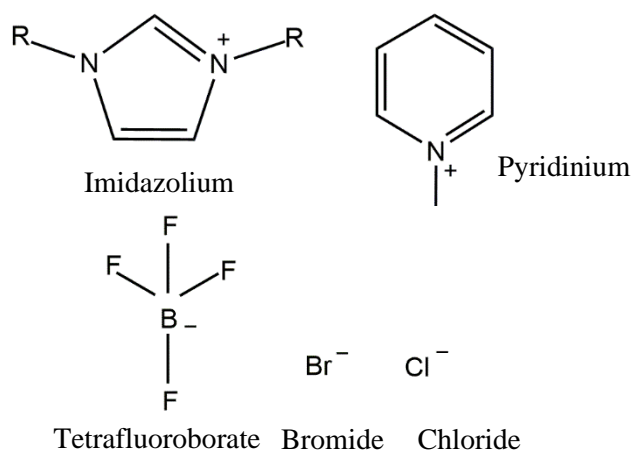


Figure 1.5 Examples of cation and anion of ionic liquid

1.4 Problem Statement

Polymeric membrane such as polysulfone possesses limitation in terms of “trade-off” between permeability and selectivity. Therefore, MMM has been developed for the purpose to enhance the gas separation properties of polysulfone

membrane. Small pore zeolite including SAPO-34 is one of the promising inorganic fillers in the MMM fabrication. Its affinity towards CO₂ and small pore size (0.38 nm) are suitable for the CO₂ separation from N₂ gas (Carter et al., 2017). Incorporation of SAPO-34 is expected to enhance the CO₂ separation properties of the membrane. Meanwhile, the development of membrane with asymmetric structure which consists of a thin selective layer is required for enhancing the membrane productivity (Dechnik et al., 2017). Nevertheless, not much studies have been focused on the fabrication of MMM containing SAPO-34 fillers especially in the form of asymmetric structure. Furthermore, it is essential to get a fundamental understanding on how SAPO-34 fillers affecting the characteristics of the asymmetric MMM and its gas transport properties in order to further develop the membrane. However, the gas transport parameters in asymmetric MMM were not much explored in previous studies. Thus, investigation on the effect of SAPO-34 incorporation towards the MMM characteristics, CO₂ separation properties as well as the gas transport parameters is required.

The poor compatibility between the inorganic fillers and polymer often results in the formation of interfacial defects. These defects are undesirable in the fabrication of the MMM since it will cause the non-selective gas permeation across the membrane. In recent years, ionic liquid (IL) has drawn a lot of attention in the gas separation application due to its high CO₂ solubility and tunable chemical/physical properties. IL is commonly immobilized into the porous support which is known as supported ionic liquid membrane (SILM), but SILMs always face the challenges to retain IL in long operation (Dai et al., 2016c). Furthermore, the application of IL in membrane gas separation is limited by the high production cost and viscosity. The incorporation of IL into the MMM formulation can be an interesting alternative way to utilize the potential of IL for gas separation application. At the same time, the presence of IL in

MMM can help to improve the interfacial compatibility at polymer/filler contact. Previous study has observed that IL can act as a wetting agent around the filler which improve the interaction of polymer/filler interface (Hudiono et al., 2010). Therefore, the use of imidazolium-based IL with higher CO₂ affinity such as TSIL is attractive for MMM modification since it can enhance both polymer/filler compatibility and CO₂ solubility of the membrane. So far, not many studies have been focused on the exploration of the TSILs in the MMM modification probably due to the high cost of TSILs compared to conventional ILs. Furthermore, in IL-modified MMM fabrication, conventional approach such as pre-treatment of filler with IL prior to embedment in MMM has been commonly used. Since most of the imidazolium-based ILs are hygroscopic in nature (Mohammad, 2012), entrapping such IL-modified filler in the asymmetric membrane during phase inversion in water bath might result in water-IL interaction. However, the effect of such pre-treatment method on morphology and gas separation properties of asymmetric MMM is still unclear and requires a systematic investigation. Apart from the conventional approach in MMM modification using IL, new strategy to further improve the gas separation properties of MMM is required. Post-modification method of membrane can be as an alternative but this technique has never been applied yet in IL-modified MMM fabrication. Hence, it is interesting to compare the characteristics and gas separation properties of the IL-modified MMMs which prepared using pre-modification and post-modification approaches.

Lack of understanding towards the concept of MMM modification with IL can lead to poor design of IL-modified MMM. Parameters such IL concentration, zeolite loading, solvent and IL properties can affect the gas separation of IL-modified MMM. Among the previous works which reported on the IL-modified MMMs, limited studies have been investigated to understand how these parameters can be used to tailor the

membrane properties as well as the gas permeation and selectivity. Thus, the study on these parameters is essential to contribute to the knowledge of the art of membrane modification that will benefit to the gas separation property.

The gas separation properties of IL-modified MMM should be further explored under various operating condition to study the durability or stability of this membrane in CO₂ separation. Previously, it was reported that the presence of moisture in the feed gas stream can lead to the formation of water clusters within the IL which further influence the stability of the SILM (Neves et al., 2010). However, the effect of the humid feed gas to the MMM incorporated with IL is rarely reported. Other factors that might affect the stability of the IL in the membrane is the feed pressure. Under high pressure, the IL might be leached out from the pores of the membrane which greatly reduce the gas separation properties. In addition, the temperature can also affect the membrane selectivity due to the changes in polymer chains mobility. Hence, the stability of developed IL-modified MMM should be investigated when the membrane is subjected to feed gas stream with moisture, high pressure and temperature. This is important to understand the CO₂ separation properties of the membrane under severe operating conditions.

1.5 Objectives

This study is mainly designed to address the problems mentioned earlier. The main objectives of this study are as follows:

1. To synthesis, characterize and evaluate the CO₂ separation properties as well as gas transport parameters of asymmetric PSf/SAPO-34 MMM at different SAPO-34 loading.

2. To compare the effect of IL pre-treatment and post-treatment methods on SAPO-34 and PSf/SAPO-34 MMM characteristics and CO₂ separation properties.
3. To investigate the effects of the modification parameters such as IL concentration, zeolite loading, solvent and IL properties on the characteristics and CO₂ separation properties of PSf/SAPO-34 MMM.
4. To investigate the effect of operating condition including pressure, humidity and temperature on the CO₂ separation properties of the IL-modified MMM.

1.6 Scope of Thesis

The present study mainly focuses on the development of PSf/SAPO-34 MMM and its modification using IL for the CO₂ separation from N₂. In the first objective of the study, the scope covers the preparation of neat asymmetric PSf and PSf-based MMM incorporated with SAPO-34. SAPO-34 zeolite was chosen as the inorganic filler in this study since it can serve as a molecular sieve to separate the CO₂ molecules from N₂. This zeolite was synthesized via microwave heating method. Its characteristics such as morphology, crystal structure, functional groups and porosity were studied using scanning electron microscope (SEM), X-ray diffractometer (XRD), Fourier transform infrared spectrometer (FTIR) and Brunauer-Emmett-Teller (BET) surface area analyser. The synthesized SAPO-34 zeolite was then added into PSf dope solution at different zeolite loading (5-15 wt. %) to obtain the MMM via dry-wet phase inversion. The maximum limit of zeolite loading used in this study was limited up to 15 wt. % since zeolites loading which higher than that amount can lead to severe particles agglomeration (Junaidi et al., 2014a). The compatibility between the filler and polymer matrix at different weight loading was examined using scanning electron

microscope. This is to understand the effect of zeolite loading towards the interfacial defects that may formed in the membrane. Meanwhile, the single gas separation properties of the membranes were tested using pure CO₂ and N₂ gas. The gas transport parameters such diffusivity and solubility were also evaluated.

In the second part of this work, the MMM was further modified using IL to seal the interfacial defects and improve the CO₂ separation properties. 1-butyl-3-methylimidazolium acetate was selected as the IL to modify the MMM since it belongs to TSIL group which possesses high CO₂ affinity. The zeolite loading was fixed at 5 wt. % since the objective in this part was to investigate the effect of different modification methods using IL towards the MMM characteristics and gas separation properties. Furthermore, MMM with 5 wt. % zeolite loading has possessed the least interfacial defects in the membrane as compared to that of 10 and 15 wt. % zeolite loading which was observed from the first part of this work. Two types of modification methods were applied in the MMM modification namely pre-treatment and post-treatment. The pre-treatment method was carried out by pre-modifying the zeolite particles with IL prior to embedment into the MMM dope solution preparation whereas the post-treatment was done by modifying the fabricated MMM using IL solution after the phase inversion process. All the modified MMMs were characterized and the CO₂/N₂ separation properties were compared. The modification method which significantly improved the polymer/filler compatibility as well as CO₂ separation properties of the MMM was then selected for further investigation.

The selected modification method was further applied in the parametric study. Several parameters in preparation of IL-modified MMM such as IL concentration, zeolite loading, solvent and types of IL were investigated to fundamentally understand how these factors can be used to tailor the gas separation properties. The modified

MMMs were characterized using scanning electron microscope, X-ray diffractometer, Fourier transform infrared spectrometer, thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to study the effect of IL on the membrane properties. The gas permeance and CO₂/N₂ selectivity was analysed for each membrane.

Finally, the IL-modified MMM with the highest CO₂/N₂ separation among the fabricated membranes prepared in this study was selected to be tested under various operating conditions such as under different operating pressure, humid gas as well as temperature. Since the IL-modified MMM in this work was developed for CO₂/N₂ separation that has potential application for CO₂ capture from post-combustion process, thus it is essential to investigate the CO₂ separation under more severe operating conditions. For example, the flue gas stream after desulphurization process in a power plant may contain some moisture and its temperature can be around 50°C (Zhao et al., 2008). Furthermore, the flue gas stream is usually at atmospheric pressure and it need to be compressed to produce the driving force for CO₂ permeation (Khalilnejad et al., 2017). Therefore, the investigation on the CO₂ separation under wet gas condition and at high operating temperature (up to 60°C) as well as at high pressure is useful to explore the stability of the membrane.

1.7 Organization of Thesis

This thesis is divided into five chapters. A general overview of each chapter is described as follow:

Chapter one gives a brief introduction on the global issues related to CO₂ emission into the atmosphere. The focus in this chapter is to give the overview on membrane for gas separation. Different classes of membrane materials such as

polymeric, inorganic and mixed matrix membrane are being explained in this chapter. In addition, the introduction of ionic liquid as promising CO₂ absorbent has been included in this chapter to give a fundamental view on its potential for application in membrane gas separation. The problem statements are also being discussed to highlight the problems of this study. Meanwhile, the objectives on this research are listed and the scope of study are further explained.

Chapter two discusses on the comprehensive literature review which covering the topics related to mixed matrix membrane development for CO₂ separation. Different types of polysulfone and zeolite-based mixed matrix membrane are reviewed in the beginning of the chapter. The issues and challenges in mixed matrix membrane fabrication which included the poor adhesion at the polymer/filler interface are also discussed. In the subsequent subsection of the chapter, various modification methods in MMM fabrication which based from previous studies to the recent one is reviewed. Then, the ionic liquid-based membrane is discussed in depth including the challenges of conventional supported ionic liquid membrane. The development of ionic liquid-based mixed matrix membrane is further discussed with emphasis is given on the modification techniques that has been reported in literatures. The effect of operating condition on the gas separation properties is also elaborated. At the end of this chapter, the fundamental transport parameters which involved in gas separation membrane are reviewed.

Chapter three describes the detail information on the materials used in this research. The experimental procedure for the fabrication of the mixed matrix membrane as well as the membrane modification with ionic liquid are described in this chapter. In addition, the characterization methods of the samples and procedure for the gas permeation test are explained.

Chapter four presents the experimental data collected in this research which corresponds to the objectives that have been outlined in chapter one. The experimental data are discussed in detail which covering the sample characterization and CO₂ gas separation properties. The gas transport parameters such diffusivity and solubility are also being discussed. In addition, some of the results are being compared with the data reported in current literatures and discussed.

Chapter five summarizes the main findings obtained from this research. The recommendations for future works are also given for improvement and development of the present research.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane for CO₂ Separation

Membrane technology is attractive since it offers many advantages over conventional separation technologies. This includes high energy efficiency, simple design, easy and low-cost operation (Chuah et al., 2018). Therefore, the development of membrane technology for CO₂ gas separation has attracted vast interest over past few decades. Basically, membrane can be described as a thin layer material which functioning as a selective barrier that allow one component to pass through while another component is retained. Figure 2.1 shows the illustration of typical membrane separation. The component that can pass through a membrane is known as permeate while the component which remained in another side is known as retentates. In gas separation membrane, concentration and pressure gradient across the membrane are the driving force that allow the gas components to be separated (Ismail et al., 2009). In general, the performance of gas separation membrane is evaluated in terms of permeation and selectivity. The permeability can be interpreted as the ability of a gas component to permeate across a membrane and it also indicates how fast the transport of a gas component in that membrane. Meanwhile, the selectivity is defined as the permeability ratio between two components. For instance, the CO₂/N₂ selectivity is referring to the ratio of CO₂ permeability to N₂ permeability. High CO₂/N₂ selectivity reflects that a membrane is more selective towards CO₂ rather than N₂. Therefore, the selectivity can also be used to describe the separation efficiency (Xie et al., 2018). The enhancement in both permeability and selectivity is the main target in the development of a membrane. This is because membrane with high permeability of desired gas

component just requires a small membrane area for the gas separation which is beneficial in terms of space needed for membrane unit installation. Moreover, the use of membrane with high selectivity is also important since this will result in high purity of desired gas.

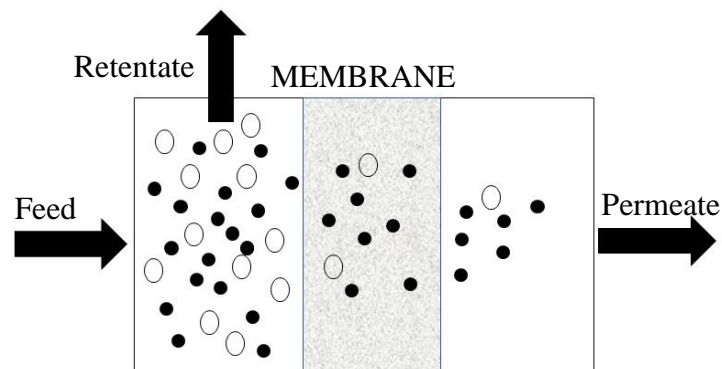


Figure 2.1 Illustration of typical membrane separation

2.1.1 Membrane structure

Generally, the membrane can be categorized based on structures namely, symmetric and asymmetric membrane as displayed in Figure 2.2. The membrane with symmetric structure can be referred to the dense membranes. However, the thickness of symmetric membrane which usually higher than $50\ \mu\text{m}$ has imparted more resistance for the gas transport which resulted in membrane with low permeability (Dong et al., 2013). Meanwhile, a membrane with asymmetric structure consists of a very thin dense layer ($0.1\text{-}1.0\ \mu\text{m}$) on a top of porous sublayer (Aroon et al., 2010). It shall be noted that the asymmetric membranes have been developed in gas separation studies due to industrial demand which requires membrane with high productivity (Rezakazemi et al., 2014). The asymmetric membrane can be further classified as integrally skinned asymmetric (ISA) and thin film composite (TFC) membranes (Chuah et al., 2018). For

ISA membrane, both thin dense layer and the porous sublayer are comprised of the same material and fabricated via single membrane fabrication step such as dry-wet phase inversion. On the other hand, the thin dense layer and porous support in TFC membranes consist of different materials. Basically, the porous sublayer in the asymmetric membrane only acts as a mechanical support for the thin dense layer and has no effects on the gas separation properties of the membrane. The gas separation property in asymmetric membrane is governed by the thin dense layer which functioning as the selective barrier (Aroon et al., 2010). Since the thickness of the thin dense layer is difficult to be measured, the permeation property of an asymmetric membrane is commonly be expressed in terms of permeance, not permeability (Chen et al., 2018). The permeance which is represented by gas permeation unit (GPU) is inversely proportional to the thickness of the membrane. In other words, the thinner the selective layer, the higher the permeance value of a membrane. It was reported that membrane with high permeance (> 2000 GPU) and CO_2/N_2 selectivity (50) can offer a cost-efficient CO_2 capture process which is desirable in industrial application (Roussanaly and Anantharaman, 2017).

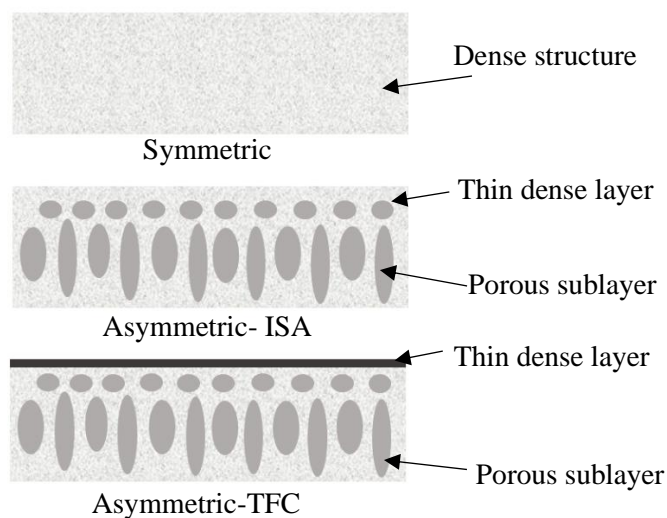


Figure 2.2 Symmetric and asymmetric membrane structure

2.1.2 Polysulfone membrane

Most of the membranes for gas separation are fabricated using glassy polymers due to high selectivity and good mechanical properties. Glassy polymers are classified as rigid structured polymers which containing small free volume (Kim and Lee, 2013). PSf is one of the glassy polymers that have been used as the commercial membrane materials for industrial scale application. For instance, the PSf hollow fiber membranes was used by Air Products in 1980 for hydrogen recovery from the purge gas stream in ammonia plant. The commercial PSf membrane exhibited good H₂/N₂ separation with selectivity falls in the range of 50 to 150 (Baker and Low, 2014). In 1984, Dow Chemical also utilized the PSf hollow fiber membrane to separate the O₂ from N₂ (Chen et al., 2018).

PSf can be easily processed into different membrane configuration with excellent mechanical, thermal and chemical properties (Jeon and Lee, 2015, Gomez-Coma et al., 2016, Sanders et al., 2013). Its excellent properties have further promoted more researches and development on this polymer material for membrane gas separation such as for CO₂/CH₄ and CO₂/N₂ separation. For example, Ismail et al. (2003) have developed the asymmetric PSf membrane and investigated its CO₂ and CH₄ permeation. Their fabricated PSf membranes were coated with a thin layer of silicone rubber to heal the skin defects. It was found that the application of silicone rubber coating on the membrane surface has greatly decreased the CO₂ permeance about 68 % but improved the CO₂/CH₄ selectivity about 81 %. Over the past several years, various strategies have been implemented to further enhance the gas separation properties of the PSf membrane. This includes the blending of PSf with other polymer materials such as polyimide (PI) and polyethersulfone (PES) (Basu et al., 2010, Rafiq et al., 2011, Abdul Mannan et al., 2016). However, the more common strategies which have been

widely reported in literatures is the incorporation of inorganic particles into the PSf membrane. The combination of PSf membrane and inorganic fillers is then called as mixed matrix membrane.

2.2. Mixed Matrix Membrane (MMM)

Mixed matrix membranes (MMMs) have attracted vast interest in CO₂ removal due to their integrated properties. MMMs usually consist of polymeric material as the continuous phase and inorganic particles as the dispersed phase. Since the polymeric membranes were commonly limited by the trade-off between permeability and selectivity (Robeson, 2008), the incorporation of inorganic fillers with great porosity and molecular sieving ability into the polymeric membrane is expected to promote high gas separation performance of the MMM. Besides gas separation properties, the integration of both materials can enhance the mechanical properties and thermal stability of the membranes (Dong et al., 2013).

Numerous types of inorganic particles have been used as the dispersed fillers in the PSf-based MMMs. This includes the use of silica (eg. DMS, MCM-41, MCM-48) (Reid et al., 2001, Kim et al., 2006, Kim and Marand, 2008, Park et al., 2014), metal organic framework (MOF) (eg. ZIF-8, ZIF-301, MIL-53(Al)) (Sorribas et al., 2014, Sarfraz and Ba-Shammakh, 2016b, Chang and Chang, 2018) and zeolite (eg. zeolite 4A, zeolite-T, ZSM-5 and ITQ-29) (Dorosti et al., 2011, Pakizeh and Hokmabadi, 2017, Casado-Coterillo et al., 2012, Mohamad et al., 2016). The inclusion of these fillers into PSf matrix has resulted in MMMs with various gas separation properties, depending on the nature of the fillers.

2.2.1 Zeolite as filler in MMM

Among the porous inorganic materials, zeolites have been widely used as CO₂ adsorbent and fillers in the fabrication of MMM (Dong et al., 2013). This could be attributed to the superior gas separation performance of zeolites and their low cost in comparison to other fillers such as MOF and carbon nanotubes (CNT). Zeolites are attractive since they contain pore dimension between 0.5 to 1.2 nm which be able to separate molecules with almost similar kinetic diameters as displayed in Table 2.1 (Chuah et al., 2018). Furthermore, their high thermal and chemical stability as well as commercial availability explain why the use of zeolites remains as one of the concerns in MMM development (Dong et al., 2013, Chuah et al., 2018, Dechnik et al., 2017). Combination of molecular sieving property of zeolite and easy processability of polymer can result in improved properties of MMM. Most of the MMMs embedded with zeolites have presented enhancement in terms of gas separation performance over the pure polymeric membrane. Generally, zeolites are crystalline aluminosilicate with structure of three-dimensional framework. The properties of zeolite such as polarity are dependent on its chemical composition. For instance, zeolite with high Al content (low Si/Al ratio) is more polar and thus it has stronger interaction with CO₂ which possesses large quadrupole moment (Kosinov et al., 2016).

Table 2.2 shows several types of zeolites that have been applied as fillers in MMM fabrication found in literatures. Dorosti et al. (2011) studied the effect of ZSM-5 zeolite loading to gas separation properties of dense MMM fabricated from PSf and PSf/PI mixture. It was found that the CO₂ permeability of the MMM containing 10 and 20 wt.% of ZSM-5 was increased about 18 and 29 % respectively as compared to the pure PSf membrane. They suggested that the enhancement in the gas permeability was due to the zeolite effect which caused the increase in free volume of the membrane.

Similar improvement in the CO₂ permeability was observed by Ilyas et al. (2018) who blended 30 wt.% of zeolite-4A into dense PSf membrane. The CO₂ permeability of PSf/30 wt.% zeolite 4A around 17.5 Barrer is 60 % higher than the CO₂ permeability of neat PSf membrane. The effect of zeolite loading to the gas transport parameters such as CO₂ solubility and diffusivity were also investigated. Increasing the zeolite loading from 10 to 30 wt.% has resulted in the slight decrease of CO₂ solubility of the MMM but greatly increased the CO₂ diffusivity. They proposed that the molecular sieve of zeolite-4A with pore dimension close to kinetic diameters of CO₂ (3.3 Å) and N₂ (3.64 Å) increased the porosity in the membrane which promotes more diffusion of CO₂ molecules.

Table 2.1 Physical properties of CO₂, N₂ and CH₄ (Bastani et al., 2013)

Gas molecule	Kinetic diameter (Å)	Density (g/L)
CO ₂	3.30	1.98
N ₂	3.64	1.25
CH ₄	3.80	0.72

Table 2.2 Example of zeolites for gas separation

Zeolite	Pore size (Å)	Reference
Zeolite A	3.2-4.3	(Dong et al., 2013)
ITQ-29	4.0	(Bastani et al., 2013)
NaY	7.4	(Yong et al., 2001)
ZSM-5	5.4-5.6	(Dorosti et al., 2011)
Zeolite -13X	7.4	(Yong et al., 2001)
SAPO-34	3.8	(Peydayesh et al., 2013)

Besides zeolite-4A, silicoaluminophosphate (SAPO-34) zeolite has also been extensively studied in recent years for CO₂ removal (Chew et al., 2018, Mu et al., 2019, Liu et al., 2019). This microporous zeolite with pore size of 3.8 Å is promising in for CO₂ separation from N₂. Moreover, SAPO-34 zeolite is attractive due to its strong CO₂ affinity (Peydayesh et al., 2013). Previously, SAPO-34 zeolites have been combined with different polymeric materials to form the MMMs for CO₂ separation. For instance, MMM comprised of polyimide (PI) and SAPO-34 zeolites at various loadings were investigated for CO₂/CH₄ separation (Peydayesh et al., 2013). The MMM integrated with 20 wt.% of SAPO-34 displayed a significant enhancement of CO₂ permeability from 4.45 to 6.90 Barrer in comparison to pristine PI membrane. Similarly, the CO₂/CH₄ selectivity was greatly improved about 97 %. The improvement could be attributed to the shape selective nature of SAPO-34 which allow the permeation of small molecules of CO₂ but restricted the CH₄ transport across the MMM. Meanwhile, the separation of CO₂/N₂ and CO₂/CH₄ mixture using polyether-block amide (Pebax[®])/SAPO-34 MMMs were studied by Rabiee et al. (2015b). Owing to the integration of molecular sieving and CO₂ affinity of SAPO-34, the CO₂/CH₄ and CO₂/N₂ selectivity of Pebax[®]/SAPO-34 MMM was increased by 70 % and 15 % respectively by increasing zeolite loading up to 20 wt.%. The gas separation properties of several MMMs fabricated from PSf or SAPO-34 is summarized in Table 2.3.