DEVELOPMENT OF ASYMMETRIC POLYSULFONE AND ZEOLITIC
IMIDAZOLE FRAMEWORK 8 MIXED MATRIX MEMBRANE
FOR CARBON DIOXIDE AND METHANE SEPARATION

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For my beloved mother and father,

my brothers and sisters,

colleagues, and friends.

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ABSTRACT

Metal-Organic Framework (MOF) materials such as Zeolitic Imidazole Framework 8 (ZIF-8) have been considered among ideal filler in mixed matrix membrane (MMM) due to their good compatibility with various polymer matrices. However, limitations suffered by ZIF-8 such as commercially expensive and hardly available in small particle size and poor intrinsic separation properties have hindered its great potential. To address these issues, this study aims to synthesize and characterize ZIF-8, followed by fabricating and evaluating the performances of ZIF-8 loaded asymmetric flat sheet polysulfone (PSf) MMM for CO_2/CH_4 separation. ZIF-8 was prepared via the method of aqueous room temperature media with base-type additive, triethylamine (TEA), with ratio ranging 0-0.007 to assist ZIF-8 formation. The synthesized ZIF-8s were characterized with respect to their phase crystallinity, particle size and thermal stability. The synthesis approach is considerably attractive due to relatively lower metal/ligands/solvent ratio requirement, rapid process, and high yield while retaining its intrinsic properties. The PSf/ZIF-8 MMMs incorporated with as-synthesized and heat-treated (100°C for 12 hours) ZIF-8 with different particle sizes (~100 nm, ~300 nm, and ~500 nm) were prepared via dry/wet phase inversion. The prepared membranes were evaluated with respect to their morphology, mechanical and thermal properties, and gas separation performance. Pure phase ZIF-8s were obtained with TEA/total mole ratios of 0.004-0.007 and its particle size decreased with increasing TEA ratios. The membrane characterizations as well as gas permeation test results showed that the heat-treated ZIF-8 with ~100nm particle size provided good interaction with PSf matrix. MMM loaded with 0.5wt% of heat-treated ZIF-8 produced the optimum CO_2 permeance (29.22 GPU) and CO_2/CH_4 selectivity (23.16), while higher loading deteriorated the separation performances. Modification of ZIF-8 particle with 25mL and 50mL ammonium hydroxide solution at ice bath temperature, room temperature and 60°C was found to significantly improve its properties, i.e. phase crystallinity, pore properties and BET surface area, while preserving its overall structure. PSf/ZIF-8 MMM loaded with 0.5wt% ZIF-8 modified under 25mL ammonium hydroxide solution at 60°C increased CO_2/CH_4 selectivity 72% higher than neat PSf membrane, without diminishing CO_2 permeance. Hence, the promising results obtained in this study demonstrates the potential of MOF, especially ZIF-8 based MMM for gas separation, specifically CO_2 separation and thus warrants further investigation.

ABSTRAK

Logam-Organik Berangka (MOF) seperti Imidazolat Berangka Zeolitic 8 (ZIF-8) merupakan calon yang ideal sebagai bahan pengisi dalam Membran Campuran Matrik (MMM) kerana keserasiannya yang baik dengan kebanyakan jenis polimer. Walaubagaimanapun, potensi ZIF-8 sebagai bahan pengisi terbatas kerana mahal, sukar untuk diperoleh dalam saiz partikel yang kecil dan pemisahan intrinsik yang rendah. Untuk menangani isu tersebut, kajian ini bertujuan untuk mensintesis dan mencirikan ZIF-8, diikuti dengan penghasilan dan penilaian polisulfona (PSf) MMM untuk pemisahan CO_2/CH_4. ZIF-8 telah disediakan melalui kaedah media akueus pada suhu bilik dengan bahan tambahan bersifat alkali, triethylamina (TEA), dengan nisbah 0-0.007 untuk membantu pembentukan ZIF-8. ZIF-8 yang disintesis dicirikan dari segi fasa ketulenan, saiz partikel dan kestabilan termanya. Kaedah ini merupakan langkah yang menarik dengan kurangnya nisbah logam/ligan, tindak balas yang pantas dan kadar penghasilan yang tinggi serta mengekalkan sifat asalnya. Membran PSf/ZIF-8s dengan ZIF-8 yang terhasil setelah melalui rawatan haba (100°C selama 12 jam) pada saiz partikel yang berlainan (~100 nm, ~300 nm, dan ~500 nm) telah disediakan melalui kaedah fasa pembalikan basah/kering. MMM kemudiannya dinilai bagi mengenalpasti struktur membran, kestabilan mekanikal dan haba, dan prestasi pemisahan gas. Fasa tulen ZIF-8 berjaya diperoleh pada nisbah TEA/jumlah mol 0.004-0.007 dan saiz partikelnya mengecil dengan peningkatan jumlah TEA. Pencirian membran dan ketelapan gas telah menunjukkan bahawa ZIF-8 yang melalui rawatan haba dengan partikel size ~100 nm berinteraksi baik dengan matriks PSf. PSf/ZIF-8 yang diisi dengan 0.5wt% ZIF-8 yang melalui rawatan haba menghasilkan kadar ketelapan CO_2 (29.22 GPU) dan pemilihan CO_2/CH_4 (23.16) yang optimum, manakala pengisian ZIF-8 yang lebih tinggi menyebabkan prestasi pemisahan membran merosot. Pengubahsuaian ZIF-8 dengan menggunakan larutan ammonia hidroksida sebanyak 25mL dan 50mL pada suhu takat beku, suhu bilik dan 60°C telah meningkatkan fasa ketulenan, sifat liang, dan luas permukaan BET sambil mengekalkan struktur keseluruhannya. MMM dengan 0.5wt% ZIF-8 yang diubahsuai dengan 25mL larutan ammonia hidroksida pada 60°C telah meningkatkan kadar pemilihan CO_2/CH_4 sebanyak 72% lebih baik berbanding membran PSf tulen tanpa mengurangkan ketelapan CO_2. Oleh itu, keputusan yang memberangsangkan dari kajian ini telah membuktikan potensi MOF, terutamanya ZIF-8, sebagai bahan pengisi dalam MMM khususnya untuk pemisahan CO_2 dan dengan itu memerlukan kajian lanjut yang terperinci.

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LIST OF ABBREVIATIONS

2-MeIM	-	2-methylimidazole
AIPO	-	Aluminophosphate zeolite
ATR-IR	-	Attenuated total reflectance infrared spectroscopy
BDA	-	Benzene-1,4-dicarboxylic acid
BET	-	Brunauer–Emmett–Teller surface area
BTC	-	Benzene-1,3,5-tricarboxylic acid
BTDA	-	3,3'-4,4'-benzophenone tetracarboxylic dianhydride
CA	-	Cellulose acetate
CM	-	Carbon membrane
CMS	-	Carbon molecular sieve
CNT	-	Carbon nanotube
CSD	-	CO_2 supercritical drying
CTA	-	Cellulose triacetate
CVD	-	Chemical vapour deposition
DAPI	-	Diaminophenylindane
DDR	-	Deca-dodecasil 3R
DEA	-	Diethanolamine
DEF	-	Diethylformamide
DMF	-	Dimethylformamaide
DMSO	-	Dimethyl sulfoxide
DSC	-	Differential scanning calorimeter
EDX	-	Energy dispersion X-ray spectrometer
FAU	-	Faujasite-type zeolite
FESEM	-	Field emission scanning electron microscopy
HKUST	-	Hong Kong University of Science and Technology
MCMB	-	Mesocarbon microbeads
MDEA	-	Methylethanolamine

MEA	-	Monoethanolamines
MIL	-	Matériauxs de l'Institut Lavoisier
MMM	-	Mixed-matrix membrane
MMSCFD	-	Million metric standard cubic feet per day
MOF	-	Metal-organic framework
MSS	-	Mesoporous silica sphere
MWCNT	-	Multiwall carbon nanotube
NMP	-	*N,N*-methylpyrrolidone
NMR	-	Nuclear magnetic resonance
PBI	-	Polybenzimidazole
PDMS	-	Polydimethylsiloxane
PE	-	Polyethylene
PEBAX	-	Polyether block polyamide
PI	-	Polyimide
PIM	-	Polymer of intrinsic microporosity
PMPS	-	Polymethylphenylsiloxane
PP	-	Polypropylene
PPEES	-	Poly(1,4-phenylene ether-ether-sulfone)
PSA	-	Pressure swing adsorption
PSf	-	Polysulfone
PVDF	-	Polyvinylidenefluoride
PXRD	-	Powder X-ray diffraction
SAPO	-	silico-alumino-phosphate
SBU	-	Secondary building unit
SEM	-	Scanning electron microscopy
SSZ	-	Aluminosilicate
SWCNT	-	Single-wall carbon nanotube
TEA	-	Triethylamine
TEM	-	Transmission electron microscopy
TGA	-	Thermal gravimetric analysis
THF	-	Tetrahydrofurane
TSA	-	Temperature swing adsorption
VOC	-	Volatile organic compounds
XRD	-	X-ray diffraction

| ZIF | - | Zeolitic imidazole framework |
| ZSM | - | Zeolite socony mobil |

LIST OF SYMBOLS

Å	-	Angstroms
A	-	Membrane effective area
b	-	Langmuir's affinity constant
C	-	Total sorption capacity
C_D	-	Henry's sorption parameter
C_H	-	Saturation sorption concentration
d	-	Distance of atoms in crystal lattice at different plane
D_D	-	Gas diffusivity on Henry site
D_H	-	Gas diffusivity on Langmuir site
D_i	-	Diffusivity coefficient of gas i
δ	-	Chemical shift scales in NMR
K	-	Combination of sorption parameters
K_D	-	Henry's law constant
P_c	-	Critical pressure
P_i	-	Permeability of gas i
$P_{Plasticization}$	-	Plasticization pressure
Qi	-	Volumetric flowrate of gas i
S_i	-	Solubility coefficient of gas i
T_c	-	Critical temperature
T_g	-	Glass transitional temperature
T_{bp}	-	Boiling point temperature
α	-	Gas pair selectivity
β	-	Beta cages
Δp	-	Transmembrane pressure difference
θ	-	Diffraction angle
λ	-	Wavelength of x-ray radiation

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CHAPTER 1

INTRODUCTION

1.1   Background of study

Natural gas is hydrocarbon gas mixture consists of mainly methane (CH_4) which formed after decaying of organic matters in intense heat and pressure over thousands of years. Natural gas is preferable world's energy source because it provides clean-burning combustible fuel, economical, and reliant compared to coal and fuel combustion. The natural gas was subjected to purification process before being used as energy source to minimize the impurities contents. However, the challenges arise as continuous depletion of natural gas resources as well as depletion of natural gas quality accompanied by wide range of impurities would increase the challenges to maximize natural gas purification. It was reported that the natural gas composition consist of up to 80% of impurities, depending on geographical factors (Tom Cnop *et al.*, 2007). Among the impurities presences in natural gas, the removal of CO_2 is considered the most crucial species to be intensively removed. Aside from environmental issue such as the main culprit of climate change, the presence of CO_2 in the process streams would decrease the heating value, pipeline corrosion, and consequently leads to increase operational and maintenance cost.

Challenges arise to ensure the presence of CO_2 in pipeline in below 0.2% based on U.S. pipeline specifications before the product was delivered to customers. There are several established processes that have been currently applied to address

this issue such as amine based absorption, potassium carbonate based absorption, cryogenic separation, and membrane separation. Each of the processes offers different separation mechanisms with certain advantages and limitations. For example, chemical-based absorption provides high CO_2 removal by chemically reacts with absorbents, while phase separations through cryogenic distillation are suitable for high CO_2 content in the feed stream. However, related-problems such as high solvent loss, high energy consumption to regenerate solvent and requirement of storage tank (Wappel *et al.*, 2011) in chemical-based absorption, while high energy requirement for cooling in cryogenic separation (Chiesa *et al.*, 2011) have encourage researchers to explore new approaches.

Polymeric membrane is emerging technology over the years with high performance separation while offering lower operating cost. It is widely applied for wastewater treatment, gas separation, seawater desalination, distillation, dialysis and many more. Polymeric membrane is considered as preferable separation media to replace the conventional separation method since its separation are based on molecular size, modest energy requirement and modular equipment requirement. Polymeric membrane, using high feed pressure as a driving force for membrane permeation, are favorable to be implemented in pressurized plant such as natural gas processing hence no additional compression needed. Despite those advantages, polymeric membranes are bounded by the Robeson trade-off limit between permeability and selectivity (Robeson, 2008). The trade-off limit depicted as highly permeable membranes are accompanied with low selective properties and vice versa. This factor commonly regard as the main factor that hindered its potential application in separation processes.

Hence, research has been focused on a new class of membrane called mixed-matrix membrane (MMM). MMM is a combination between polymeric membrane as continuous phase and inorganic nanoparticles as dispersed phase. The development of MMM aims to improve separation properties, mechanical strength and thermal stability of the conventional polymeric membrane. The embodiment of fillers into polymer matrices would improves gas separation properties by (1) introducing molecular sieving mechanism (Junaidi *et al.*, 2014a), (2) increased specific

interaction with penetrant (Kwon *et al.*, 2011), (3) disruption on polymer chains (Beatriz Zornoza *et al.*, 2011b), and/or (4) provide tortuous permeation path that hinder larger molecule to permeates (Hudiono *et al.*, 2010). Hence, the improvement in permeability and/or selectivity of resulted MMM is expected.

Selections of continuous and dispersed phase in MMM are equally crucial factors to develop high performance MMM. Polysulfone (PSf) is one of preferable candidates for continuous phase. The presence of phenylene unit in PSf, linked with isopropylidene, ether and sulfone, provides the polymer with good chemical resistance, thermal stability and mechanical strength. For CO_2/CH_4 separation aspect, PSf possess excellent balance between permeability and selectivity towards CO_2. Although it is lacking in term of rigidity and separation properties, PSf possess high plasticization pressure ($P_{plasticization} \sim 34$ bar (Bos *et al.*, 1999)) while relatively cheaper materials has compensate itself as preferable continuous phase. For dispersed phase, there it is ideal that their intrinsic separation properties are superior than polymer matrix. Ideal filler for MMM are advised to possess these characteristic, (1) high intrinsic separation properties, (2) high mechanical and thermal stability, and most important, (3) good interaction with polymer. Numerous inorganics dispersed phase such as zeolite, carbon nanotube (CNT), carbon molecular sieve (CMS), activated carbon and metal organic framework (MOF) has been reported over the years and have demonstrated to improve membrane performances.

Polymer-filler compatibility is often being addressed as a challenge in MMM development since it directly reflects on the membrane performances. Poor polymer-filler compatibility would cause voids interface that are easily accessible for larger molecules and hence deteriorate gas pair selectivity. Therefore, filler surface modifications are often employed to improve polymer-filler compatibility. Compared to other filler class, metal-organic framework (MOF) has shown to have good affinity towards polymer matrices without surface modification. MOF is crystalline compound with metal ion and organic ligands as repetitive unit, arranged systematically as framework. The presence of the organic ligands within its structure

provides good interaction with polymer matrices, hence minimize the interfacial defects.

Among MOFs, Zeolitic Imidazole Framework 8 (ZIF-8) is one of most matured MOF available. ZIF-8 is crystalline compound consist of Zn ion bridged by 2-methylimidazole (2-MeIM), having sodalite topology with β-cages with 11.6Å opening connected to 6-membered ring window with 3.4Å aperture with permanent porosity (Park *et al.*, 2006, Tan *et al.*, 2010). ZIF-8 is commonly synthesized by three (3) major approaches; solvothermal, microwave-assisted solveothermal, and aqueous room temperature system. For solvothermal and microwave-assisted, reactants were dissolved into organic solvent before placed in autoclave under elevated temperature. The synthesis requires highly diluted solvent, high ligands to metal ratio, high reaction time (up to days), and high synthesis temperature in order to ease the reaction between metal ion and ligands. Base-type additive such as triethylamine (TEA) is commonly employed using these two synthesis approach to ease the ligands deporotonation.

ZIF-8 possesses high surface area close to 2000 m^2/g, high adsorption capacity and highly permeable. Although the intrinsic separation properties of ZIF-8 is not convincing for gas separation application, numerous studies on ZIF-8-based MMM has been demonstrated over the years and the benefits of the fillers in assisting gas separation performance have been established. The role of ZIF-8 on gas separation properties of membrane has been reported as; (1) enhancement of CO_2 diffusivity coefficient through polymer chain disruption exceeding CH_4 (Qilei Song *et al.*, 2012); (2) interaction between quadrupole moment of CO_2 with the weak electrostatic field of ZIF-8 (Basu *et al.*, 2011); and/or (3) molecular sieving induced by ZIF-8 (Ordoñez *et al.*, 2010). These improvements are observed since interfacial defects between polymer and ZIF-8 are absence. This is due to good interaction between polymer matrices with the imidazole ligands in ZIF-8, which rarely reported in other class of filler. Most notable is the work by Ordoñez *et al.* (2010) where 50wt% (total solids) of ZIF-8 was incorporated in Matrimid®. They achieved CO_2/CH_4 selectivity of 124.89, which is 187% better than the neat MatrimidR membrane. This level of high ZIF-8 loading is typical of dense MMMs without

suffering from defective polymer-filler interface and the dispersed ZIF-8 can be fully utilized to facilitate the separation performance.

1.2   Problem statement

However, ZIF-8 MMMs are commonly reported as dense configuration. Since dense configuration having poor membrane flux, it is rarely attractive for industrial aspect. Asymmetric membrane configuration is more relevant for practical applications since it is more permeable and mechanically stable compared to dense membrane. Moreover, the ZIF-8-based asymmetric MMMs are still rarely reported since ZIF-8 material is relatively new and focus is more on its synthesis. In addition, the thickness of selective layer within asymmetric membrane commonly in the range 100-500 nm (Baker, 2004) would hardly accommodate large filler particle. Hence, it is necessary to investigate the common problems in asymmetric MMM preparation such as filler size, filler loading and membrane preparation since it would affect membrane performance differently from that reported in dense MMM.

As-synthesized MOF, in general, possessing low surface area compared to activated counterpart due to the presence of guest molecules in the pores has limited the pore accessibility. Common activation steps commonly involve of highly polar, weak polar and non-polar solvents, consecutively to extract residue reactant and solvent that may resides within MOF's pores. The activation also could be done through heat treatment with temperature enough to evaporate residue solvent. Common temperature used for activation is normally ranging from 250 - 300°C, depending on the guest molecule species and thermal stability of the MOF. However, it should be noted MOF with no permanent porosity will form into amorphous or dense molecule after losing its residual solvent. In addition, excessively high heat treatment could cause structural collapsing and leads to formation of amorphous materials (Pan *et al.*, 2011a).

Despite having the characteristics of an ideal MMM's filler, the limitations possessed by ZIF-8 have hindered its potential in MMM development. Since MOF, in general, is relatively new class of materials, the availability of the materials is very limited. Up to author knowledge, only Sigma Aldrich has commercialized the materials. However, the available ZIF-8 (Basolite Z1200) possesses large particle sizes (bulk size 5μm, particle size of ~500nm) and this would rise as challenges to incorporate the particles within the thin-selective layer of membrane. In addition, Basolite Z1200 is considerably expensive and would certainly increase the cost of polymer/ZIF-8 membrane. Hence, research to produce smaller ZIF-8 particle with economically feasible would be of special interest to the material development. For example, previous studies (Pan *et al.*, 2011a, Yamamoto *et al.*, 2013) have shown that synthesizing ZIF-8 in aqueous system in diluted system is a rapid reaction. The formation of pure phase of ZIF-8 is obtained almost instantly while eliminating the usage of organic solvent. This approach offers huge advantages over conventional methods and plausible to minimize the production cost. Utilizing base-type additives in ZIF-8 production has been reported to benefit ZIF-8 formation in various ways such as reduce their particle size (Perez *et al.*, 2009, Ordoñez *et al.*, 2010) and induce the crystal formed (Loiseau *et al.*, 2006). Such approach has been widely studied in solvothermal and microwave-assisted solvothermal while triethylamine (TEA) is the most common additive used in ZIF-8 synthesis. Till date, there is still a lack of study on the influence of base-type additives on ZIF-8 formation in aqueous system. In work by Gross *et al.* (2012), the exertion of TEA in aqueous system does provide positive impact on ZIF-8 formation by minimizing the usage of the organic ligands. Although the requirement of high solvent ratio is still in effect, the role of TEA in aqueous system is undeniably crucial factor and further investigation on this subject matter is warranted.

In MMM developments, the aims are to enhance polymeric membrane performance by incorporating inorganic phase. The inorganic phases are suggested to have superior separation performance in order to push the membrane performance beyond Robeson Upperbound. Although ZIF-8 is compatible with various polymer matrices, their intrinsic separation factor is fairly discouraging. The intrinsic CO_2/CH_4 selectivity of ZIF-8 is less than 7, significantly lower compared to zeolite

(CO_2/CH_4 = 80 (Yeo *et al.*, 2014a)) and carbon membrane (CO_2/CH_4 = 80 (Salleh and Ismail, 2011)). Moreover, the flexibility of ZIF-8 ligand allows larger molecule to access its pores (3.4Å). Consequently, the absence of molecular sieving mechanism leads to low intrinsic CO_2/CH_4 selectivity. For example, Song *et al.* (2012) has investigated the influence of ZIF-8 loadings on separation properties of Matrimid® and compared with Maxwell's model. Due to low intrinsic gas pair selectivity of ZIF-8, high filler loading would unlikely to discriminate larger molecules from permeating and resulting highly permeable with low selective membrane. The result presented having good agreement with Maxwell's model hence further highlight the selective issue of the ZIF-8.

In short, the future development of asymmetric ZIF-8-based MMM is hindered by the availability of the materials (i.e. large particle size and economically discouraging), membrane fabrication issue, and poor intrinsic CO_2/CH_4 selectivity of ZIF-8. These factors can be regarded as the main obstacles to the potential application of ZIF-8 in the MMM fabrication. Unless these limitations are addressed, the advantages offered by ZIF-8 as fillers are likely to be neglected.

1.3   Objectives of Study

The main objective of this study is to develop MMM that superior in gas separation performance, chemical and thermal stability as well as high mechanical properties compared to its polymeric counterpart. The main concerns in the fabrication of asymmetric MMM are the influence of incorporated filler on the properties of the membrane. Hence, the objectives of the study are as follows:

i.   To synthesize and study the influence of base-type additive on ZIF-8 formation.

ii.   To study influence of heat-treated ZIF-8 with different particle sizes on prepared membrane properties.

iii. To investigate the influence of ZIF-8 loading on the prepared membranes properties.

iv. To enhance PSf/ZIF-8 separation performance using amine modified ZIF-8.

1.4 Scopes and limitations of Study

In order to achieve the objectives stated above, the following scopes of study are identified:

i. Investigating the effect of TEA loading ranging from 0 to 0.007 of TEA/total reactants on ZIF-8 formation.

ii. Evaluating the particle size and morphology of prepared ZIF-8 particles using transmission electron microscopy (TEM).

iii. Fabricating the flatsheet asymmetric MMM via dry/wet phase inversion using 25wt% of PSf concentration

iv. Investigating the effect of heat treatment at 100°C and particle size of ZIF-8 ranging from 100 to 500 nm on the prepared membrane properties.

v. Identifying ideal ZIF-8 loading ranging from 0.25-10wt% (total solids) on the prepared membrane properties.

vi. Modifying the synthesized ZIF-8 using ammonia solution at different temperature up to 60°C and volume of ammonia solution ranging from 25 to 50 mL.

vii. Evaluating the properties of modified ZIF-8 using gas adsorption analyzer, and Fourier transmission infrared (FTIR)

viii. Identifying prepared ZIF-8 phase purity and change in ZIF-8 purity in mixed-matrix membrane using x-ray diffraction (XRD) at 2θ from 5 to 40°.

ix. Investigating the morphology of the prepared membranes using field emission scanning electron microscopy (FESEM).

x. Investigating thermal properties of prepared ZIF-8 crystal structure and prepared membranes using thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC)

xi. Evaluating the mechanical stability of prepared membranes using tensile strength and percentage strain at break.

xii. Evaluating the ideal gas separation performance of the prepared membranes using pure CO_2 and CH_4.

1.5 Significance of Study

Recent development of ZIF-8 synthesized via aqueous system synthesis method has highlights the advantages of this process. Most notably, this method offers rapid reaction between metal source and organic ligand. Hence, formation of pure phase ZIF-8 obtained through this method is almost instantly (Pan *et al.*, 2011a), while other methods would requires up to 24 hours (Park *et al.*, 2006). In addition, rapid reaction occurred in the synthesis system would result nano-range particle and has been highlighted in several studies (Gascon *et al.*, 2008, Pan *et al.*, 2011a). In this study, TEA as deprotonation agent is utilized to assist the formation of ZIF-8. Till date, aqueous system method requires high metal to solvent ratio (up to 1:2255) and utilizing TEA would induce deprotonation of the organic ligand; consequently minimize the excessive solvent usage. This alternative approach proposed in this study is surely more feasible compared to other conventional methods and commercially available ZIF-8 since it is environmental friendlier and economical approach by eliminating the organic solvent usage, while relatively faster and smaller particle size of ZIF-8 can be obtained.

Removal of carbon dioxide from the process is very crucial in natural gas processing to avoid pipeline corrosion, increasing heating value and comply with pipeline-quality gas. Membrane separation is a high performance separation where separation is based on molecular size, with modest energy requirement, thus low operating cost compared to the conventional methods. Since MMM is the most

promising membrane to surpass the trade-off limit, this study will develop MMM with ZIF-8 as dispersed phase and the membrane performances are evaluated. The impact of this study will be significant since MMM offers the prospect of higher productivity and selectivity as well as a safer and more environmentally friendly unit operation than the conventional method.

The development of ZIF-8-based MMM has been widely reported using variety of polymer matrix. Among them, PI-based polymer attracts the most attention due to its high CO_2 permeability and CO_2/CH_4 selectivity. In addition, the imide functional group possess by the polymer class has reported to have high affinity towards organic ligand possess by ZIF-8. Hence, the compatibility issues between ZIF-8 and the polymer class is reported as positive remarks. Notably, high ZIF-8 loading up to 50wt% was used in Matrimid® 5218 has resulted high CO_2/CH_4 selectivity (125) (Ordoñez *et al.*, 2010). Although particle agglomeration was observed at 60wt% ZIF-8 loading, the resulted membrane were able to sustain its highly selective feature (CO_2/CH_4 selectivity = 80.77, 85% better that it neat membrane counterpart). Aside from PI-based polymeric phase, the embodiment of ZIF-8 into other class of polymer also demonstrated to have good compatibility such as poly(1,4-phenylene ether-ether-sulfone) (PPEES) (Díaz *et al.*, 2011) and polymethylphenylsiloxane (PMPS) (Diestel *et al.*, 2014). In this study, PSf was chosen as polymeric phase due to good balance between permeability and selectivity, high plasticization resistance and economically feasible. Good compatibility of PSf with ZIF-8 can be expected since embodied ZIF-8 up to 30wt% into PPEES matrix provides no agglomeration issue were reported (Díaz *et al.*, 2010, Díaz *et al.*, 2011). Hence, asymmetric PSf/ZIF-8 MMM can be promising candidate for gas separation process due to good characteristic of both polymer and filler and economical approach compared to other ZIF-8-based MMM while high CO_2 separation performance can be expected.

The flexibility of MOF structure, in general, allows for ease modifications to improves specific properties of the materials. The modifications can either focused on organic ligand or metal ion during synthesis or as post-synthetic modification. In case of ZIF-8, the high chemical stability of ZIF-8 in polar and nonpolar solvent,

basic and acidic condition in wide range of temperature has allowed more intensive modifications procedure. At present, numerous modifications have been implemented on the ZIF-8 and shows promising result with ammonia-based post-synthetic modification has reported to improve ZIF-8 affinity towards CO_2 (Zhijuan. Zhang *et al.*, 2011, Zhijuan. Zhang *et al.*, 2013). Despite the positive remarks on ZIF-8 modifications, the attempt to utilize it as dispersed phase in MMM was, up to our knowledge, never been reported. In this study, amine modification is subjected to the synthesized ZIF-8 under various conditions is strictly studied to identify the ideal modification parameters before being dispersed into PSf matrix. The knowledge presented on this study will encourage the future research on materials development to further optimize and provide suitable applications.

1.6 Thesis Organization

This dissertation consists of eight (8) chapters including this introduction and is organized in line with research objectives. Chapter 2 describes the background of CO_2 separation systems that leads to membrane technology, as well as pros and cons of each technology. Additionally, a brief review regarding MMM with various polymer-filler types is covered. The advantages and limitations of our interest filler, ZIF-8, is also described and strategies to overcome the limitations is discussed. Chapter 3 discusses the experimental procedure used in this study including material synthesis, modification, membrane preparation and samples characterization techniques.

Chapter 4 describes the synthesis of ZIF-8 using triethylamine (TEA) as deprotonation agent. The chapter highlights the influences of TEA on ZIF-8 formation, particle size control agent, and surface properties. Chapter 5 focuses on the development of PSf/ZIF-8 under different particle size and heat treatment of ZIF-8. The chapter includes the ZIF-8 properties before and after heat treatment and its roles as filler in MMM. Chapter 6 presents the asymmetric membrane performances under wide range of ZIF-8 loading in order to identify the ideal loading. ZIF-8

modification is implemented in Chapter 7 and its influences as filler is also described. Chapter 7 also focused on different modified ZIF-8 loading on the prepared membrane. The prepared PSf/ZIF-8 is then compared with MOF-based MMMs to highlight the current progress on this subject. General conclusion of this research is drawn in Chapter 8. Some recommendations for future research are also included in the chapter.

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