

**POLYSULFONE (PSF) MEMBRANE INCORPORATED
WITH POLYAMIDE-TETHERED POLYHEDRAL
OLIGOMERIC SILSEQUIOXANE (POSS) FOR
CARBON DIOXIDE SEPARATION**

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CARBON DIOXIDE SEPARATION**

by

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**Thesis submitted in partial fulfilment of the requirement
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LIST OF SYMBOL

	Symbol	Unit
<i>P</i>	Permeability	GPU
<i>l</i>	Membrane layer thickness	cm
<i>Q</i>	Volumetric flow rate	cm ³ /s
<i>A</i>	Effective membrane area	cm ²
ΔP	Pressure difference	cmHg
α	Selectivity	-

LIST OF ABBREVIATIONS

MMM	Mixed matrix membrane
PSf	Polysulfone
POSS	Polyhedral Oligomeric Silsequioxane
IL	Ionic liquid
CO ₂	Carbon dioxide
N ₂	Nitrogen gas
CH ₄	Methane gas
PDMS	Polydimethylsiloxane
SEM	Scanning electron microscopy
EDX	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared

**POLYSULFONE (PSF) MEMBRAN DIGABUNGAN DENGAN
POLIAMIDA-TERIKAT POLYHEDRAL OLIGOMERIC SILSEQUIOXANE
(POSS) UNTUK PEMISAHAN KARBON DIOKSIDA**

ABSTRAK

Karbon dioksida (CO₂) adalah penyumbang utama kepada kesan rumah hijau sejak revolusi perindustrian. Matriks campuran membran (MMM) telah diperkenalkan untuk meningkatkan usaha dalam CO₂ penyingkiran. Penyebaran pengisi poros dalam matriks polimer boleh menawarkan peningkatan dramatik untuk mengatasi had di antara kebolehtelapan dan pemilihan membran polimer. Dalam kajian ini, polysulfone MMM digabungkan dengan polyhedral silsesquioxane oligomerik (POSS) telah dicadangkan untuk meningkatkan kebolehtelapan CO₂. Membran simetri telah disediakan dengan menggunakan kaedah penyongsangan fasa untuk rintangan pemindahan minimum jisim. Kesan jumlah POSS (2,5-5% berat) pada ciri membran dan prestasi telah dikaji. Tambahan pula, MMMs telah diubah suai menggunakan cecair ionik (IL) [Emim] [TF₂N] dengan 0.4 M kepekatan dan polydimethylsiloxane (PDMS) untuk meningkatkan pemilihan gas di MMMs ini. Morfologi pengubahsuaian dengan IL dengan menggunakan mikroskop elektron pengimbas membuktikan penyebaran perigi POSS tertakluk kepada meningkatkan polimer antara muka / pengisi dan EDX analisis telah dijalankan untuk mengesan taburan unsur permukaan membran. Sementara itu FTIR juga telah direkodkan untuk menyemak bon kewujudan dalam sampel. Sifat-sifat pengangkutan gas semua membran direka disiasat menggunakan ujian gas penyerapan tulen N₂, CO₂ dan CH₄ dan juga mendedahkan membran dengan 5% berat jumlah POSS, diubah suai oleh

lapisan IL dan PDMS yang mempamerkan memuaskan CO_2/N_2 (24) dan CO_2/CH_4 (9).

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ABSTRACT

Carbon dioxide (CO₂) is the main contributor to greenhouse effect since industrial revolution. Mixed matrix membrane (MMM) has been introduced to improve the efforts in CO₂ removal. Dispersing the porous filler in polymeric matrix can offer dramatic improvement to overcome the tradeoff limitation in between permeability and selectivity of polymeric membrane. In this study, polysulfone MMM incorporated with polyhedral oligomeric silsesquioxane (POSS) were proposed to improve the permeability of CO₂. The asymmetric membrane was prepared using phase inversion method for minimum mass transfer resistance. The effects of POSS loading (2.5-5 wt%) on the membrane characteristic and performance were studied. Furthermore, the MMMs were modified using ionic liquid (IL) [emim][TF₂N] with 0.4 M concentration and polydimethylsiloxane (PDMS) to improve the gas selectivity of these MMMs. The morphology of the modification with IL by using scanning electron microscopy (SEM) proved the well dispersion of POSS subjected to improve polymer/filler interface and Energy Dispersive X-ray Spectroscopy (EDX) was conducted to detect elemental distributions of membrane surface. Meanwhile Fourier Transform Infrared (FTIR) were also recorded to check the existence bond in the sample. The gas transport properties of all fabricated membranes were investigated using pure gas permeation tests of N₂, CO₂ and CH₄ and further revealed the membrane with 5 wt% of POSS loading, modified by IL and PDMS coating which exhibit satisfactory of CO₂/N₂ (24) and CO₂/CH₄ (9).

CHAPTER 1

INTRODUCTION

1.1 Introduction on CO₂ Separation from Methane

Natural gas is one of the fastest growing fossil fuels sources and it plays a vital role in today's energy production. It has been generally utilised as the energy source for domestic appliances, manufacturing of metals and chemicals, electricity generation as well as the natural gas powered vehicles (Li et al., 2010). Due to the augmentation of oil price and civic awareness in green fuel, natural gas is a massively requested vitality source (Junaidi et al., 2013). In the recent years, biogas and landfill gas are also captured to substitute the natural gas. The biogas and landfill gas contain biomethane which are more sustainable than the methane separated from natural gas. This is because biomethane can be generated using different types of waste. However, the carbon dioxide (CO₂) content in biogas and landfill gas is considerably high (30 % to 60 %). Besides reducing the calorific value of biogas and landfill gas, CO₂ is a key factor of greenhouse effect and global warming (Li et al., 2010). Therefore, the separation and utilization of carbon dioxide from natural gas, biogas and landfill gas are required to mitigate the global warming (Rahman et al., 2015).

The conventional gas separation process such as absorption, adsorption and cryogenic distillation are lack of economic benefits and they involve very high energy costs. Membrane technology has been proven to be technically and economically superior in view of the versatile properties of membrane separation systems. Membrane systems allows the natural gas refining to be efficiently

accomplished as it offers less energy usage, less environmental effect and ease of operation (Chung et al., 2007). In addition, the low pressure and temperature of biogas as well as landfill gas are not the major limits for the application of membrane separation. Membrane separation technology offers number of advantages including low capital and operating cost and lower energy requirements. At present, most of the commercial modules use polymers as the membrane material on account of the simplicity of processibility. Nevertheless, polymeric membranes possess a trade-off between permeability and selectivity (Junaidi et al., 2015; Li, Y. & Chung, T.-S., 2010). To fully exploit the growing opportunities in the field of gas separation, strong interest exists in the identification of new membrane materials that can comply with current requirements (Zhao et al., 2015). Mixed matrix membranes (MMMs), containing dispersed inorganic fillers in polymer matrix, has recently been extensively explored to achieve the required separation performance. MMMs have shown to be a promising new generation of membrane materials for the various gas separations and purifications.

1.2 Introduction on Mixed Matrix Membrane (MMMs)

Gas separation by the selective transport through polymeric membranes is one of the fastest developing branches of membrane technology. However, the current polymeric membrane materials are deficient to fully exploit the application opportunities at the industrial scale. The improvement in permeability is at the expense of selectivity and vice versa (Dasgupta et al., 2010; Junaidi et al., 2015; Junaidi et al., 2013; Li et al., 2010; Rahman et al., 2015). A new type of membrane material emerging with the potential for future applications is MMM composed of homogeneously interpenetrating polymeric and inorganic particle matrices. MMM

presents an interesting approach for improving the separation properties of polymeric membranes (Cao et al., 2016). In contrasted to the polymeric membranes, significant improvement in separation properties with trivial loss in membrane flexibility is expected for the resultant MMMs. MMMs or polymer nanocomposite membranes are normally defined as the incorporation of a solid (disperse) phase into a continuous polymer matrix (Zhao et al., 2015). MMMs have the potential to achieve higher selectivity, permeability, or both relative to the existing polymeric membranes, resulting from the addition of the inorganic particles with their inherent superior separation characteristics. At the same time, the fragility inherent in the inorganic membranes may be avoided by using a flexible polymer as the continuous matrix. MMM containing rigid permeable or impermeable particles, such as zeolites, carbon molecular sieves, silica and carbon nanotubes, dispersed in a continuous polymeric matrix presents an interesting approach for enhancing the separation properties.(Ge et al., 2017). Currently, researchers have investigated the possibility of utilizing organic–inorganic hybrid materials for various applications due to their extraordinary properties emerging from the synergizing effect of both components. It has been demonstrated that octafunctionalized POSS (polyhedral oligomeric silsesquioxanes) offers an efficient route for the development of novel hybrid nanocomposites. The influence of two novel structural features of the synthesized inorganic nanofillers, POSS on the gas separation performance of nanocomposite membranes, polysulfone (PSf) are studied on the of CO₂/N₂ and CO₂/CH₄ gas pairs in this research.

POSS is a nanoscale inorganic cage structure having a silicon–oxygen–silicon framework attached by organic substituents connected to silicon atoms (Bandyopadhyay and Banerjee, 2014). It consists of a rigid, hollow

silica core with a nanopore diameter of about 0.3–0.4nm (Dasgupta et al., 2010). The corner organic groups provide the POSS molecules with desired reactivity and solubility and help to disperse POSS molecules in hybrid polymers by physical/chemical interaction with the polymer matrix. POSS can be used as monofunctional or graftable monomers, difunctional comonomers, surface modifiers, or polyfunctional cross-linkers for the preparation of POSS modified polymers. POSS molecules can be incorporated into the polymeric matrixes easily using chemical coupling, copolymerization, cross-linking or physical blending. The unique combination of an inorganic core and an organic periphery in POSS molecules and its versatile nature has offered the opportunity to prepare high performance hybrid polymeric materials that unite many desirable properties of conventional organic and inorganic components such as high thermal and mechanical properties, nonflammability, solubility and oxidative resistances with excellent dielectric properties. POSS containing hybrid polymers have several unique applications, such as in the field of biomedicine, electronic, optical, magnetic nanodevices, sensors and catalysts. POSS is a building block of zeolite; therefore, it can produce same sieving ability as that of zeolites (Bandyopadhyay and Banerjee, S., 2014)

Moreover, smaller size and tailorable organic groups make POSS molecules more attractive and promising materials for gas separation study (Dasgupta et al., 2010). The nanoscopic size of POSS substituted with organic functionalities makes them highly soluble in most organic solvents. The cubic silsesquioxane unit possesses a well-defined nanometer-sized structure with high surface area, controlled porosity, and various functionalities (Li et al., 2010).

1.3 Problem Statement

Natural gas that is recognising as profitable alternative energy resource to replace crude oil usually contains a considerable amount of impurities like carbon dioxide since it is uncovered from underground reservoirs and need to be removed. The attractiveness and ability of membrane in gas separation has attracted attention among researchers continue to develop the advanced membrane materials for the separation. For the requirement for effective CO₂ separation, PSf membrane has been incorporated with the POSS in this research since POSS showed interesting characteristics for gas permeability improvement.

The incorporation of some fillers can cause interfacial voids due to stresses which arise during membrane formation due to solvent evaporation or removing. Rigidified polymer layer formation near the particle was related to uniform stress around the particles. If the stress directions are not uniform around the inorganic particles, interface voids will be formed in the particle–polymer interface. To reduce the interfacial voids and improve the performance of CO₂ separation membranes, Ionic liquids (ILs) can be incorporated into the porous structure of POSS. IL has drawn a great attention in the separation of CO₂ due to its high CO₂ solubility, high thermal stability, low vapour pressure and tunable physicochemical character.

There are several types of inorganic filler that widely used to form MMMs such as zeolite, titanium oxide (TiO₂), silica, alumina and metal oxide. Among these types of inorganic fillers, POSS has been chosen in this study and its effect on the performance of membrane also been observed because the incorporation of POSS can enhance the gas permeability and the modification of gas selective POSS using IL can improve the selectivity.

1.4 Research Objectives

The main objectives of this study are:

1. To fabricate the PSf membrane incorporated with POSS nanoparticles.
2. To characterize and understanding the effect of POSS and modification by using IL on membrane characteristics.
3. To study the effect of POSS nanoparticles and IL modification on the permeability and selectivity of carbon dioxide separation.

1.5 Research Scope

To improve the performance of carbon dioxide separation, fabrication of mixed matrix membrane has been studied. In this work, POSS nanocomposite was chosen as inorganic filler to be incorporated with the PSf membrane. POSS nanocomposite which can produce same sieving ability as that as zeolites offer opportunity to prepare high performance hybrid polymeric materials and can enhance CO₂ separation. The effects of POSS loading (2.5 – 5 wt%) on the membrane characteristics and modification of MMM by IL and PDMS coating were studied and have been characterized using scanning electron microscope, (SEM) with energy dispersive X-ray (EDX), Fourier Transform Infrared, (FTIR) and contact angle while gas transport properties were investigated using pure gas permeation tests of N₂, CH₄, and CO₂.

CHAPTER 2

LITERATURE REVIEW

2.1 Mixed Matrix Membranes (MMMs)

MMMs was introduced to overcome the disadvantages of conventional membrane materials by catering the limitations of polymeric and inorganic membranes in a continuous polymeric matrix with disperse inorganic particles for CO₂ separation. MMMs were commonly prepared by blending inorganic filler into polymer matrix. The inappropriate selection of material pair for MMMs could result in agglomeration, interfacial voids and more membrane defects. Thus, the selection of inorganic filler and polymer is very important to ensure the improvement of separation performance was achieved without creating defects on MMMs (Jusoh et al., 2016).

2.2 Inorganic Fillers for MMM fabrication

Over the past decades, various types of inorganic particles have been used as fillers in the fabrication of MMMs. The membrane filters included zeolite, carbon molecular sieves, silica, metal-organic framework (MOF), carbon nanotubes, TiO₂, MgO, layered and delaminated materials (Vu et al., 2003). Zeolites and MOFs are the popular fillers which had been extensively reported by researchers in the fabrication of CO₂ selective membranes, mainly due to their excellent porous structure and promising performance in the separation of gaseous molecules.

2.2.1 Zeolites

Zeolite is one of the common used inorganic filler in MMMs fabrication and these MMMs are mostly used for CO₂/CH₄ separation. Zeolite is microporous crystal, comprising elements of Si and Al with cations such as Na, K, Ca and Mg in a tetrahedral structure. Zeolites also possess a range of uniform pores that permit them to act as sieves by discriminating molecules selectively according to size and shape within the narrow pore distribution.

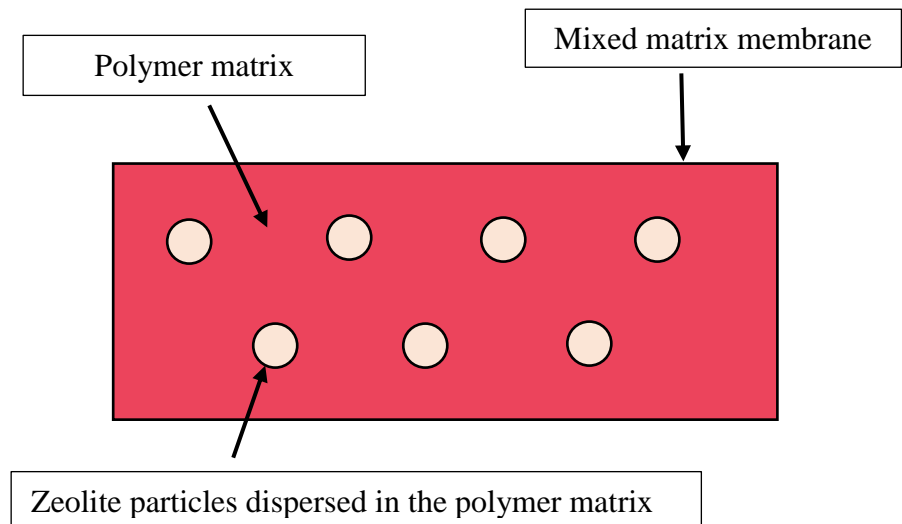


Figure 2.1 Schematic of MMM.

Gas permeates through zeolite membranes by first adsorbing in the pores, then diffusing along the pore surface, and finally desorbing into the permeate (Hong, 2007). Both adsorption and diffusion affect gas permeation through zeolite membranes. Gases usually physically adsorb in zeolite, and this process is a non-activated, exothermic as well as reversible (Hong, 2007). Molecules was adsorbed into the zeolite pores because of intermolecular attractive forces between the adsorbent and adsorbate. When all other properties being equal, the adsorption heats of adsorption are higher for molecules with larger dipole moments (F. Eder, M. Stockenhuber, 1995). Therefore, CO₂ adsorbs stronger on zeolites than other light gases such as H₂, CH₄, and N₂ because CO₂ has a higher electrostatic quadrupole moment and a higher molecular weight. The higher adsorption heat of CO₂ on LTA, FAU, CHA, and MOR zeolites was observed (Bastani et al., 2013).

Once molecules adsorb into the zeolite pores, a chemical potential gradient in the membrane drives surface diffusion. Surface diffusion takes place in any pore size, but its contribution is smaller in pores large enough to allow molecules to escape from the influence of the potential field of the lattice. Diffusion rates of different sized molecules in zeolite pores can differ by orders of magnitude, especially when one molecule is approximately the same size as or larger than the pores. If a mixture contains some molecules that fit into zeolite pores and other molecules that cannot, the membrane separates the mixture by molecular sieving (Hong, 2007).

Zeolite molecular sieves are excellent materials with significantly higher diffusivity and selectivity than polymeric materials. The accurate size and shape discrimination resulting from the narrow pore distribution ensures superior selectivity. Nevertheless, zeolite membranes have expensive cost and difficulties in forming continuous and defect-free membranes of practical meaning (Hong, 2007). Zeolites can be classified into 85 different structures but only 11 of them are used commercially; linde type A (LTA) is one of it. A-type zeolite (LTA) such as zeolite 4A and 5A are common zeolites that have been used during the early stage of development of zeolite-MMM (Goh et al., 2011).

In 1973, Paul and Kemp started to incorporate zeolite 5A in silicone rubber matrix and conveyed that although the diffusion time lag of CO₂ and CH₄ in zeolite 5A-silicon rubber MMM was improved, the steady state of permeation was slightly pretentious. This was also reported by Duval et al. al that the incorporation of zeolite 5A into PDMS matrix leads to the reduction in CO₂ permeability and insignificant changes in CO₂/CH₄ selectivity (Duval J M Mulder M H V, 1993).

Failure in improving separation properties of membrane when embedding zeolite 5A in polymer phase has led towards the utilization of other type of zeolite, LTA. Sen et al. (2007) stated the improvement of CO₂/CH₄ selectivity from 23.6 to 37.6 by incorporation of 30% of zeolite 4A into polycarbonate polymer matrix. Nevertheless, CO₂ permeability was found to slightly reduced from 8.8 to 7.0 Barrer compared to pure polycarbonate membrane. Other than that, Adams et al. (2011) also testified

that an impressive increment in CO₂/CH₄ selectivity up to 63% was perceived using 50% loaded zeolite 4A-PVAc MMM under high CO₂ partial pressure.

The properties of zeolite 4A, such as open crystal structure and pore aperture size of 3.8Å, emboldens its utilization as inorganic filler until present. In recent times, the enhancement of CO₂ permeability was reported by Surya Murali et al. from 71.4 to 155.7 Barrer and increment of CO₂/CH₄ selectivity from 26.4 to 41.3 after incorporated 30% of zeolite 4A in Pebax-1657 membrane (Surya Murali et al., 2014). Furthermore, Kusworo et al. found that by adding 25% of zeolite 13X in PI/PES membrane, CO₂ permeability was improved from 6.54 to 15.04 Barrer and CO₂/CH₄ selectivity was enhanced from 33.6 to 38.7 as compared to pristine membrane (Kusworo et al., 2008). In the Musselman et al. (2008) work, incorporation of 10% of Y-type zeolite in Matrimid phase, a thermoplastic polyimide soluble in a variety of solvents, resulted in the increment of CO₂/CH₄ selectivity from 34.7 to 57.4 as compared to neat membrane.

Zeolite Socony Mobil-5 (ZSM-5) is another type of zeolite that established significant attention in the development of MMM. Musselman and co-workers reported the improvement of CO₂ permeability from 7.3 to 14.6 Barrer and increment of CO₂/CH₄ selectivity from 34.7 to 56.4 by incorporation of 30 % of ZSM-5 into Matrimid polymer matrix (Musselman et al., 2008). Other than that, Zhang et al. found that incorporation of ZSM-5 in Matrimid phase enhanced CO₂/CH₄ ideal selectivity to 67.2, associated to pure Matrimid, with CO₂/CH₄ selectivity of only 34.7. In addition, higher CO₂/CH₄ selectivity of 67.4 was obtained for this membrane in binary gas separation (75% CO₂, 25% CH₄).

The widespread study on zeolite-MMMs for CO₂/CH₄ separation was conducted with the incorporation of SAPO-34 into polymer matrix (Junaidi et al., 2014; Peydayesh et al., 2013). SAPO-34 zeolite is a silico-alumino-phosphate molecular sieve with the chemical formula of (SixAlyPz)O₂, where $x = 0.01-0.98$, $y = 0.01-0.60$ and $z = 0.01-0.52$. SAPO-34 with 0.38 nm pore size displays remarkable separation properties even at high feed pressures (Li, S. and Fan, 2010). Jha and Way (2008) obtained an increase of CO₂/CH₄ selectivity from 42 to 53 when 25% of SAPO-34 was added into polyphosphazane (PPZ) phase. Kataray et al. (2010) and Peydayesh et al. (2013) found that CO₂ permeability was significantly enhanced after incorporating 20 wt% of SAPO-34 into polyethersulfone (PES) and Matrimid 5218 phases, respectively. Zhao et al. also reported an increment of CO₂ permeability from 111 to 338 Barrer by incorporation of 50 wt% of SAPO-34 into PEBAX 1657 phase. Meshkat et al. reported 15% enhancement of CO₂ permeability and 100% increment of CO₂/CH₄ selectivity as compared to neat membrane after incorporation of 30% SAPO-34 into polycarbonate membranes.

Recently, SAPO-34 has been incorporated in Pebax 1074 by Rabiee et al. (2015). They reported impressive improvement of CO₂/CH₄ selectivity (70%) when incorporated 20 wt% of SAPO-34 in Pebax 1074 phase. The next research which has been done by Junaidi et al. (2014) which PSf incorporated with highly selective and porous SAPO-34 zeolite. In this work, the effects of the zeolite loading on the physical and separation characteristics of asymmetric PSf membrane has been studied.

Separation performance of the fabricated membranes were summarized and tabulated in Table 2.1.

Table 2.1 Gas permeance and ideal selectivities of MMMs at different SAPO-34 loadings at ambient temperature and 3.48 bar.

SAPO-34 loading (%) (% w/w)	Permeance (GPU) ^a			Ideal selectivity	
	CO ₂	N ₂	CH ₄	α (CO ₂ /N ₂)	α (CO ₂ /CH ₄)
0	22.01 ± 3.42	1.33 ± 0.59	1.26 ± 0.44	16.5	17.3
5	205.92 ± 7.26	9.63 ± 0.56	9.12 ± 0.65	21.4	22.5
10	314.02 ± 4.65	12.03 ± 1.83	11.16 ± 0.92	26.1	28.2
20	281.18 ± 6.92	26.28 ± 1.49	25.73 ± 2.06	10.7	10.9
30	232.35 ± 3.21	78.10 ± 3.42	77.36 ± 5.28	2.9	3.0

The PSf/SAPO-34 membrane with 10 wt.% SAPO-34 loading (PSf-10) exhibited the highest separation performance enhancement on CO₂/N₂ and CO₂/CH₄ ideal gas pair properties compared to the pure PSf membrane (PSf-00). For the higher zeolite loadings (20 wt.% and above), the gas permeation properties of the MMMs were severely bothered by the enormous formation of large interfacial voids across the membrane surface due to the particle agglomeration. For zeolite loading less than 10 wt.%, well dispersion of SAPO-34 particles in the polymer matrix was observed. The maximum CO₂ permeance (314.02 GPU) was attained by incorporating 10 wt.% of SAPO-34 into asymmetric PSf membrane. Even without strong binding between PSf and SAPO-34, CO₂/N₂ and CO₂/CH₄ selectivities up to 26.1 and 28.2 respectively were perceived (Junaidi et al., 2014).

The enhancement of CO₂ permeability and CO₂/CH₄ selectivity via the incorporation of zeolites in polymer phase cannot be denied. Though, poor compatibility and poor adhesion between the zeolite and polymer, as well as phase separation are the critical issues found in development of zeolite/MMM, which limit their application. Furthermore, the fabrication of defect free zeolite MMM is very challenging and costly since modification of fillers is often required to enhance the adhesion and compatibility of zeolite to polymer phases. In addition, insufficient number of available zeolite structures and composition for specific applications also makes a demand for new filler materials for MMM (Breck, 1973). Consequently, due to these afore- mentioned drawbacks, new type of materials, metal organic frameworks (MOF) has been introduced to overcome the obstacle of zeolite in MMM fabrication.

2.2.2 Metal-Organic Frameworks (MOFs)

Metal-organic framework (MOF) has extensively developed in the recent years. It contains a metal ion as a coordination centre for various organic linkers that linked by covalent coordination bonds to form a different type of dimensional structure. As a coordination network, MOFs are mechanically less brittle and less stiff compared to zeolites. Besides, the existence of organic linkers in MOF leads to the greater compatibility with polymer matrix and consents higher loading of inorganic filler in MMM (Goh et al., 2011). Furthermore, MOFs show higher adsorption capacities, specific surface areas and pore volume compared to zeolites and other inorganic fillers. Different types of MOF were blended into PSf membranes to form MMM for CO₂/CH₄ separation as summarized in Table 2.2.

Poly(3-acetoxyethylthiophene) (PAET) incorporated with copper (II) biphenyl dicarboxylate-triethylenediamine (Cu(II) BPDC-TED) was one of the earliest MOF based MMM developed for CO₂ separation. The incorporation of 20 and 30 wt% of Cu(II) BPDC-TED into PAET increased the CH₄ permeability, while reducing permeability and CO₂/CH₄ selectivity.

Table 2.2 CO₂/CH₄ separation of MOF based mixed matrix membrane reported by various researches.

MMM materials			Membrane performance		
Polymer	MOF	Filler content (%)	CO ₂ permeability (Barrer) ^a	Ideal CO ₂ /CH ₄ selectivity	Reference
Polysulfone	Cu ₃ (BTC) ₂	10	3044.00	3.36	(Car et al., 2006)
Polysulfone	Mn(HCOO) ₂	10	6.83	9.16	(Car et al., 2006)
Polysulfone	MIL-101	19	32	23.5	(Tanh Jeazet et al., 2013)
Polysulfone	ZIF-8	16	12.10 ^b	19.80 ^b	(Zornoza et al., 2011)
Polysulfone	HKUST-1	16	8.80 ^b	16.20 ^b	(Zornoza et al., 2011)

Refer to the Table 2.2 stated previously, MIL-101, another type of MOF has shown a good adhesion and excellent dispersion in PSf matrix (Tanh Jeazet et al., 2013). Permeation test of CO₂ and CH₄ gas demonstrated a significant rise of gas permeabilities without compromising the selectivity. However, the CO₂/CH₄ separation performance of PSf/MIL-101 membrane still laid below the Robeson's upper bound line because it is highly porous with less selective pores. On the other hand, Keskin and Scholl (Luque, 2010) projected the performance of different pairs of MOF-MMM using a combination of atomistic and continuum modeling methods and they reported that the combination of Cu(hfipbb)(H₂hfipbb)_{0.5} in Matrimid phase can lead to higher separation performance surpassed Robeson's upper bound due to the dissimilarity of molecular diffusivities of CO₂ and CH₄ inside the MOF.

Zeolitic imidazolate frameworks (ZIFs), comprise a subset of metal-organic frameworks (MOFs) with exceptional thermal and chemical stability (Zhang, C. et al., 2012). The framework structure of ZIFs are comprised of transition metal (e.g. Zn, Co) cations bridged by anionic imidazolate linkers. The pore size as well as adsorption properties of ZIFs can be tailored by changing or chemically modifying the anionic imidazolate linker (Phan et al., 2010). Several studies indicated that ZIFs have similar molecular sieving properties with zeolites, signifying that they are better candidates for MMMs compared to the previously mentioned MOFs. Different from other MOFs, ZIFs are synthesized by linking meta atoms like Zn, Co or Cu through N atoms by ditopicimidazolate (1m) or functionalized 1m links to form neural frameworks and tunable nanosize pores. Thus far, there are 25 types of ZIF

crystals had been synthesized from 9600 micro-reactions of zinc (II)/cobalt (II) or imidazolate/imidazolate-type linkers (Banerjee, R. et al., 2008).

Bae et al. (2010) reported that enhancement in CO₂ permeability was achieved by ZIF-90/Ultem and ZIF-90/Matrimid MMMs, but the CO₂/CH₄ selectivity remained unaffected. However, ZIF-90/ 6FDA-DAM membrane demonstrated a higher CO₂ permeability (720 Barrer) and CO₂/CH₄ selectivity which surpassed Robeson's upper bound in comparison to the neat membrane (Li, S. et al., 2006). In other cases, nanosized ZIF-7 has been embedded in poly (amide-b-ethylene oxide) (Pebax 1657) and the resulted MMM was coated on a porous polyacrylonitrile (PAN) support with the assistance of poly(1-(trimethylsilyl)- 1-propyne) (PTMSP). Excellent adhesion with almost ideal morphology MMM was formed. Li et al. (Li, T. et al., 2013) measured a CO₂ permeability up to 145 Barrer and a CO₂/CH₄ selectivity up to 30 at low loading of ZIF-7. The incorporation of 34 wt% ZIF-7 gave a CO₂/CH₄ selectivity of 44, but the CO₂ permeability was reduced compared to the untreated membrane. This can be explained by a polymer chain rigidification that occurred at higher loading of ZIF-7. Japip et al. (Japip et al., 2014) found that the addition of 20 wt% ZIF-71 into 6FDA-durene polymer phase increased the CO₂ permeability by 3-fold and CO₂ induced plasticization pressure increased from 16 to 30 atm as compared to the neat membrane.

2.2.3 Silica

Another conventional class of inorganic filler that has acknowledged significant attention throughout the development of MMM is silica nanoparticles which can be further categorized into ordered mesoporous silica and non-porous silica. Ordered mesoporous silica with variety of particles size, shape and pore diameter is another form of silica that has been potentially used for the development of new generation of MMM. Mesoporous molecular sieves possess pores large enough (2–50 nm) to readily allow the penetration of polymer chains, resulting in better wetting and dispersion of particles. Ordered mesoporous silica materials have properties such as high mechanic and thermal stability, facility of chemical functionalization, high specific surface areas ($>500 \text{ m}^2/\text{g}$) (Chung et al., 2007). The most common ordered mesoporous silica fillers are MCM-41, MCM-48, and SBA-15 (Goh et al., 2011).

In spite of the good adhesion to the polymer matrix, ordered mesoporous materials would offer some limitations concerning gas separation performance due to the gas transport through the inorganic mesoporous membranes commonly follows the Knudsen diffusion model where the permeance is inversely proportional to the square root of molecular weight of the penetrants. The large pores of this material maybe easily blocked by the polymer chains leaving the inner pores inaccessible (Chung et al., 2007). Also, the pores of mesoporous materials are too large to achieve size selectivity. Consequently, the pores need to be chemically modified to facilitate selective adsorption.

The intensive research in silica/polymer MMM system have shown that the addition of non-porous nanosized fumed silica, which has opposed properties with porous inorganic fillers is of great potential to affect polymer chain packing in glassy and high- free-volume polymers consequently bring about alteration in the gas separation properties. Due to the non-permeability of the nonporous silica particles, the addition of this filler into the polymer matrix does not directly contribute to the change of transport property, but it alters the molecular packing of the polymer chains, resulting in an improvement of the permeation as well as the selectivity.

Ahn et al. (2008) showed that with addition of 20 vol.% nonporous silica particles into the polysulfone matrix, the void volume increases from nearly 0.2% to 2.8%. This small increase in void volume along with the insufficient polymer chain packing causes an increase in the total free volume. The increase in free volume increases the diffusion and solubility coefficients of the silica filled polymer and causes an increase in the permeability of the penetrants, as proved by Ahn et al. for all test gases (H₂, He, O₂, CO₂, N₂ and CH₄). For example, they reported that with addition of 20vol.% silica to the polysulfone matrix, the CO₂ and CH₄ permeabilities increase by 212% (from 6.3 to 19.7 Barrer) and 400% (from 0.22 to 1.10 Barrer), respectively.

2.2.4 Carbon Nanotubes

Carbon nanotubes are fundamentally new nano-porous material having the potential for overcoming Robeson's upper bound (Kim et al., 2007). The properties of polymer nanocomposites containing carbon nanotubes depend on several factors in addition to the polymer: synthetic process used to produce nanotubes; nanotube purification process (if any); amount and type of impurities in the nanotubes; diameter, length, and aspect ratio of the nanotubes objects in the composite (isolated, ropes, and/or bundles); nanotubes orientation in the polymer matrix. However, it should be noted that carbon nanotubes are still very expensive and may have hazardous health effect due to their fast migration speed.

2.3 MMMs with ILs

IL which is known by its unique properties have been highlighted as solvents for liquid membrane separation. The ionic liquid membranes (ILMs) and its separation technology have been developed rapidly to further expand its application in separation field. ILMs exhibited great advantages for the separation of gaseous mixtures because it showed the high solubility capacity of different gaseous species and was hardly lost through volatilization. In addition, the interaction between the quadrupole moment of CO₂ and the electrical charge of IL provides and enhancement in the solubility over other gases and have been proved to be very promising for the selective separation of CO₂ from gas mixture (Bara et al., 2009). Some researchers have extensively investigated the effect of type and concentration of components on the CO₂ separation performance of ILMs (Close et al., 2012;

Neves et al., 2010). ILs can be classified into two categories: room-temperature ionic liquids (RTILs) and task-specific ionic liquids (TSILs, also called functionalized ILs).

Li et al. was investigated the effects of IL anions and ZIF-8 content on gas permeability and selectivity to achieve high separation performance. The IL used was 1-butyl-3-methyl imidazolium ([Bmim]) cation based on different anions of bis(trifluoromethylsulfonyl)imide ([NTf₂]) and the result showed the CO₂ permeability of the Pebax/ZIF-8(15%)/ IL(80%) membrane was 4.3 times that of the pure Pebax membrane without sacrificing the CO₂/N₂ selectivity (Li, M. et al., 2017). Hao et al. (Hao et al., 2013) observed a great enhancement of CO₂ permeability which more than 46.0 % and a slight reduction in gas selectivity by increasing ZIF loading in the synthesis poly(RTIL)/ZIF-8 membranes via UV polymerization. Casado-Coterillo et al. incorporate the acetate based IL as the third component in chitosan/ZIF-8 MMMs containing 5 wt.% ZIF loading achieved satisfactory separation of CO₂ from N₂ and CH₄ which is near to the upper bound of Robeson plot.

Supported ionic liquid membrane (SILM) with [BMIM][NTf₂] immobilized in the hydrophobic PVDF support exhibited best performance for both separations of CO₂/N₂ and CO₂/CH₄, mainly due to the best affinity between the IL and the support. Hanioka and coworkers (Hanioka et al., 2008) reported that the SILMs prepared with IL based on amino-functionalized imidazolium cation ([C₃NH₂MIM] [NTf₂]) exhibited higher CO₂ permeability and lower CH₄ permeability in comparison with the SILM composing of a conventional imidazolium-based IL ([BMIM][NTf₂]). This was mainly attributed to the complex interaction between amines and CO₂.

The effect of confinement on gas sorption of CO₂ and H₂ was studied by confining [HMIM][NTf₂] into carbon nanotubes (CNTs) (Shi and Sorescu, 2010). The IL molecules in the CNT exhibited self-diffusivity coefficients about 1-2 orders of magnitude larger than the corresponding bulk IL molecules. Sorption of CO₂ and H₂ gases in the composite material consisting of CNT and IL indicates that H₂ molecules diffuse about 1.5 times faster than the CO₂. In addition, to investigate the effect of IL content on the permeability of different gas species (i.e. CO₂, N₂, CH₄, H₂ and O₂), the quasi-solidified ionic liquid membranes (QSILMs) containing from 20 wt.% to 80 wt.% of [EMIM][TFSI] in p(VDF-HFP) were prepared (Jansen et al., 2011). The experimental results showed that the gas permeability strongly increased with an increase in IL concentration and the transport of larger and more condensable species was favoured over that of the smaller molecules. For this reason, selectivities slightly decreased for the gas pairs of CO₂/N₂, CO₂/CH₄, and O₂/N₂ as the IL content increased, whereas CO₂/H₂ selectivity increased greatly with higher IL loadings.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

PSf pellets (MW35 000), dimethylacetamide (DMAc), tetraethylammoniumhydroxide (TEAOH, 35 wt.%) was obtained from Sigma Aldrich. Tetrahydrofuran (THF), ethanol, methanol, [emim][TF2N] IL were purchased from Merck, aminopropylisobutyl POSS (C31H71NSi8O12) was acquired from Hybrid Plastic, Inc.

3.2 Synthesis of asymmetric PSf mixed matrix membrane

The asymmetric membranes were prepared based on the formulation of 30 wt.% PSf, 35 wt.% DMAc, 30 wt.% THF, and 5 wt.% ethanol. The amount of POSS nanoparticles incorporated into PSf matrix was fixed at 5 wt.% from the total polymer. Firstly, all the solvents and co-solvents, DMAc, THF and ethanol were stirred at room temperature for 10 min. Then, POSS nanoparticles were added to the mixture and subjected to sonication for 90 min at 50 °C under operating frequency of 35 kHz. Subsequently, the mixture was primed with 10 wt.% of the total PSf pellets for 4 hours in order to ensure optimum wetting of POSS nanoparticles. After that, the solution was sonicated again for 30 min before being added with the remaining PSf and stirred for 24 hr. Pristine PSf dope solution was prepared with similar procedure to the preparation of MMM solution explained earlier, but with the exception of the filler dispersion–sonication step (Ahmad et al., 2016).