PERFORMANCE ENHANCEMENT OF PES/ZIF-L MIXED MATRIX MEMBRANE USING IONIC LIQUID FOR CO_2/N_2 SEPARATION

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By

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LIST OF SYMBOLS

A	Membrane effective area
$\propto$	Selectivity
Δp	Pressure difference
P	Permeability

LIST OF ABBREVIATIONS

MMM	Mixed Matrix Membrane
PES	Polyethersulfone
ZIF	Zeolitic Imidazolate Framework
MOF	Metal Organic Framework
PES/ZIF-L	PES-based membrane with ZIF-L as its filler
TIPS	Thermal Induced Phase Separation
NMP	N-Methyl-2-pyrrolidone
rpm	Round per minute
SEM	Scanning electron microscopy
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared
IR	Infrared
USM	Universiti Sains Malaysia

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PERFORMANCE ENHANCEMENT OF PES/ZIF-L MIXED MATRIX MEMBRANE USING IONIC LIQUID FOR CO_2/N_2 SEPARATION

ABSTRAK

Populariti membran matriks campuran (MMM) telah meningkat dalam bidang kajian kebelakangan ini kerana ciri prestasi pemisahan gas yang baik ditawarkan oleh pengisi tak organik dan ketahanlasakan kepada haba, kimia dan mekanik yang diwarisis dari membran polimer. Walaubagaimanapun, masalah yang dihadapi MMM ialah keserasian buruk antara zarah tak organik dan polimer yang menyebabkan kecacatan antara muka yang menganggu proses pemisahan gas. Semasa kajian ini, MMM yang terdiri dari ZIF-L sebagai pengisi tak organik dan polietersulfon (PES) dibikin melalui kaedah pemisahan fasa haba teraruh (TIPS). Pemuatan ZIF-L diubah dari 0.25 kepada 1.0 wt.% untuk mengkaji kesan pemuatan ZIF-L terhadap ciri MMMs dan prestasi pemisahan gas. Meningkatkan pemuatan ZIF-L telah menambahbaik ketelapan CO_2 namun ia mengurangkan kemilihan CO_2/N_2 dibandingkan dengan sifat hakiki PES. Pemerbadanan ZIF-L telah mengakibatkan lompang antara muka diantara polimer dan pengisi seperti yang ditunjukkan oleh bayangan kemiskropan elektron imbasan. Cecair ion (IL) yang mana memilih kepada CO_2 digunakan dalam kajian ini untuk mengubahsuai MMM dengan pengedapan lompang antara muka diantara membran dan juga pengisi. Dua cara pengubahsuaian telah diuji. Cara tersebut adalah pra-pengubahsuaian ZIF-L dan pasca-pengubahsuaian PES/ZIF-L MMM. Keputusan menunjukkan pra-pengubahsuaian telah berjaya mengisi lompamg antara muka dibandingkan dengan pasca-pengubahsuaian. Perbandingan telah menunjukkan pra-pengubahsuaian telah berjaya menambahbaik PES/ZIF-L membran setelah membran tersebut menunjukkan ciri yang terdekat dengan lengkung batasan atas Robeson 2008 dibandingkan dengan membran lain yang turut dibikin dalam kajuan ini. Ketelapan CO_2 dan kemilihan CO_2/N_2 PES/ZIF-L dengan pengisi 0.75 wt.% telah ditambahbaik kepada 0.721 GPU dan 37.283 masing-masing setelah pra-pengubahsuaian.

PERFORMANCE ENHANCEMENT OF PES/ZIF-L MIXED MATRIX MEMBRANE USING IONIC LIQUID FOR CO_2/N_2 SEPARATION

ABSTRACT

Mixed matrix membrane (MMM) popularity has been increasing in research field recently due to promising gas separation performance that offered by the characteristic of inorganic filler and the durability to heat, chemical and mechanical that inherited from polymeric membrane. However, the issue that has been encountered by MMM is the poor compatibility between the organic particles and the polymer that causing interfacial defects that disrupt the gas separation process. In this study, MMM that consist of ZIF-L as the inorganic filler and polyethersulfone (PES) was fabricated via thermal induced phase separation (TIPS) method. The loading of ZIF-L was varied from 0.25 to 1.0 wt.% to study the effect of ZIF-L loading on the characteristic of the MMMs and its gas separation performance. Increasing the ZIF-L loading has enhanced the CO_2 permeance but it reduced the CO_2/N_2 selectivity as it compared to intrinsic attributes of PES. The ZIF-L incorporation has resulting in voids formation between the polymer and filler as shown by the electron microscopy images. Ionic liquid (IL) which selective towards CO_2 was used in this study to modify the MMM by sealing the interfacial void between the membrane and the filler. Two methods of modification were tested. They are pre-modification of ZIF-L and post-modification of PES/ZIF-L MMM. Results obtained shows that pre-modification has successfully sealed the polymer/filler interfacial void compared to post-modification. The comparison study revealed that the pre-modification has successfully enhanced PES/ZIF-L membrane's performance as the membrane shown a promising attribute that is closest one to the Robeson upperbound curved 2008 compared to other membranes that are also fabricated in this study. PES/ZIF-L with 0.75 wt.% ZIF-L loading, CO_2 permeance and CO_2/N_2 selectivity has been enhanced up to 0.721 GPU and 37.283 respectively after pre-modification.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The global climate change issue or global warming is the implication of greenhouse gas emission and the major contributor to this issue is carbon dioxide (Hussain and Hägg, 2010). The carbon dioxide emission has no sign of slowing down in the future, even with the recent global event Covid-19 has caused the dip in year 2020, it has been forecast to increase from 34 Gt up to 36 Gt. As world population increase there will be emerging market and developing economies that will caused grow in energy demand. The majority of carbon dioxide emission will come from electricity sector followed by industry, transport and building (IEA, 2021). The effort to control greenhouse gas emission include reduced energy consumption in industrialized nation, improve energy generation efficiencies, development of renewable, capture and storage CO_2 from flue gas (Hussain and Hägg, 2010). Carbon capture and storage has become the main option for sustainable environment and combating global warming as a complete shift from non-renewable resources is currently impossible due to the major share in energy generation (Anwar *et al.*, 2018). Among all of the carbon capture and storage, membrane gas separation offers great potential for CO_2 capture for their low capital investment, small footprint, ease of scale-up, low energy requirement, environmental friendly and easy to incorporate modular up-scaling in the existing membrane process (Hussain and Hägg, 2010). Gas separation membrane has attracted a lot of researcher to invest their time in this field.

Membrane has a lot of application from industrial scale to daily consumption. Membrane has a lot of useful characteristic that makes it able to be used in several industries such as water treatment for domestic and industrial water supply, pharmaceutical, biotechnological, beverages, food and metallurgy and other separation processes (Saleh and Gupta, 2016). Membrane is defined as selective barrier between two phases, the ‘selective’ is inherent to a membrane or membrane process. The acceleration in membrane research is triggered by the development and refinement of synthetic membrane during 1980s (Basu *et al.*, 2004). Economically, there are huge advantage of membrane separation technology as it has no moving part and require less energy to operate which makes it much greener technology compared to others (Rezakazemi *et al.*, 2014).

Polymeric membrane can be classified as rubbery and glassy membranes. The difference between two of these type is the former operate above polymer glass transition temperature while the latter operates below the polymer glass transition temperature. The biggest disadvantages of polymeric membrane are swelling and plasticization. Plasticization will cause a significant drop in selectivity. The other type of membrane is inorganic membrane. While polymeric membrane has limit in term of temperature, inorganic type of membrane is able to operate at even higher temperature which is 773 K up to 1173 K for carbon and ceramic membrane. When choosing for inorganic membrane the price will be significantly expensive and have a better chemical and thermal stability. Even when inorganic membrane able to offer a good performance at laboratory scale, scaling-up inorganic membrane will have a lot of challenges. Continuous synthesis and defect-free polycrystalline membrane is not straightforward, especially in controlling the microstructure and also suppressing crack and boundary defect (Hamid and Jeong, 2018).

Polymeric membrane has advantage in term of economic and processing advantages while the performance is limited by the polymer upper-bounds. Inorganic membrane has outstanding performance in both permeability and selectivity and limited due to processing cost and mechanical stability. The middle point of both membrane type is mixed matrix membrane (MMMs) which offering a breakthrough to limitation of both membranes. MMMs is a composite membranes comprised of nano/micro-sized filter which are more selective in continuous polymer phase. MMMs offering high permeability and selectivity at much cheaper cost compared to inorganic membrane (Hamid and Jeong, 2018). In a defect-free MMMs, the polymer matric determines minimum membrane performance while the presence of the dispersed phase improved selectivity. Most of MMMs separation especially for CO_2 are based on the sieve mechanism where the smaller molecular size preferentially passes through the sieve pore (Rezakazemi *et al.*, 2014).

1.2 Problem statement

Global warming serve as an indicator that our environment suffers from uncontrollable air pollution. The reason of global warming occurred is because of the increase of greenhouse gases in the atmosphere mainly from human activities such as industrial activities, transport or energy generation. According to John M. Reilly non-CO_2 gasses only account for 17 percent of total greenhouse gasses emissions in the United States and the remaining would be CO_2 (Reilly, Jacoby and Prinn, 2003). This alarming situation urged us to approach environmentally friendly and cost-effective solution. Various technology has been deployed to fight CO_2 emission issue from feed stream such as amine absorption, adsorption, membrane and cryogenic separation. Amine absorption is the most used carbon capture and storage (CCS) technology. These conventional options have a lot of drawbacks such as high energy consumption, corrosion and low thermal stability. Among all of the option available, membrane based separation is the most promising alternatives. Membrane provide simplicity, high product recovery and low capital cost (Ahmad *et al.*, 2021).

Mixed-Matrix Membrane (MMM) have potential to be a great CO_2 separation technology. However, fabrication of MMM could be very challenging as the inorganic phase dispersion in the polymer introduce interfacial defect. Few of the defect that have been mentioned are agglomeration and interfacial void (Shimekit *et al.*, 2014). Poor adhesion of filler to polymer can causes the formation of void around the filler. Stress on the membrane during the drying phase causing detachment of the filler (Bakhtiari and Sadeghi, 2014).

1.3 Objective

1. To fabricate, characterize and evaluate the CO_2 separation properties of PES/ZIF-L MMM at different ZIF-L loading.
2. To identify the ideal ZIF-L loading in both post and pre-modification using [Bmim][BF4] for maximum permeability and selectivity for CO_2/N_2 separation.
3. To compare the performance between pre-modified and post-modified PES/ZIF-L.

1.4 Organization of Thesis

There is five chapters in this thesis. General description of each chapter is describe as below:

Chapter one is based on the issues that happened around the globe related to emission of CO_2 gases. Focus of this chapter is mainly on gas separation. Polymeric membrane and mixed matrix membrane are explained in this chapter. Ionic liquid as a promising solution to polymer/filler issue is also described. The problems of the studies are being explained in the problem statement. Lastly, the objectives are also being listed, then the scope of thesis is explained.

Chapter two is literature review which covering the related topic to mixed matric membrane for CO_2 separation. Relation between membrane and inorganic filler in mixed matrix membrane is reviewed. Issues regarding mixed matrix membrane fabrication including poor compatibility in polymer filler interface is also discussed. Later in the chapter, pre-modification and post-modification of the MMMs also will be explained.

Chapter three describing on the material that used in the experiment. The experimental procedure for the synthesis of the PES/ZIF-L including pre and post-modification of MMM will be explained. Other than that, the characterization methods of the samples and procedure for the gas permeation test are explained.

Chapter four shows the data that obtained from the experiment that related to the objectives that has been highlighted before. The experimental data are discussed in detailed along with the characterization, gas separation properties and functional group analysis. The gas transport parameters such as diffusivity and selectivity are discussed. Additionally, the data will be also compared with the data reported in the current literature and discussed.

Chapter five conclude all of the data that related to the objectives in this research. Any improvement for the future works will be described in the recommendation.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane as CO_2 Separation

Membrane popularity has risen recently as it has offer a lot of advantages in term of sustainability and low-operating cost. Hence, the number of research in this field has increase throughout the decades. Membrane basically is an interphase film that located between two adjacent phase that acting as a selective barrier that control the transport of gases between gas mixture. The component that pass through the membrane is known as permeate, while the one that remains is called retentates. In gas separation membrane, separate the gases from the gas mixture when gas particle sizes are different (Shindo and Nagai, 2020). As shown in Figure 2.1, pressure or concentration gradient becomes the driving force in membrane gas separation. Other than that, productivity, durability and mechanical integrity at the operating conditions must be cost efficient. To compare the performance between membrane, the common factor that is considered are permeability and selectivity (Ismail *et al.*, 2009). Permeability is the measure of the ease of passage of liquid or gases or specific chemicals through the material and it is also used to determine the amount of liquid or gas pass through sample (Fidjestol and Lewis, 2003). Selectivity is the ratio of permeability coefficients of two gases, it indicates that one of the gas is permeable compared to the other one in binary gas pair (Freeman, 1999). In membrane development, enhancement of both selectivity and permeability of membrane is desired. High permeability will result in faster gas separation, while high selectivity will result in higher of the desired gas purity.

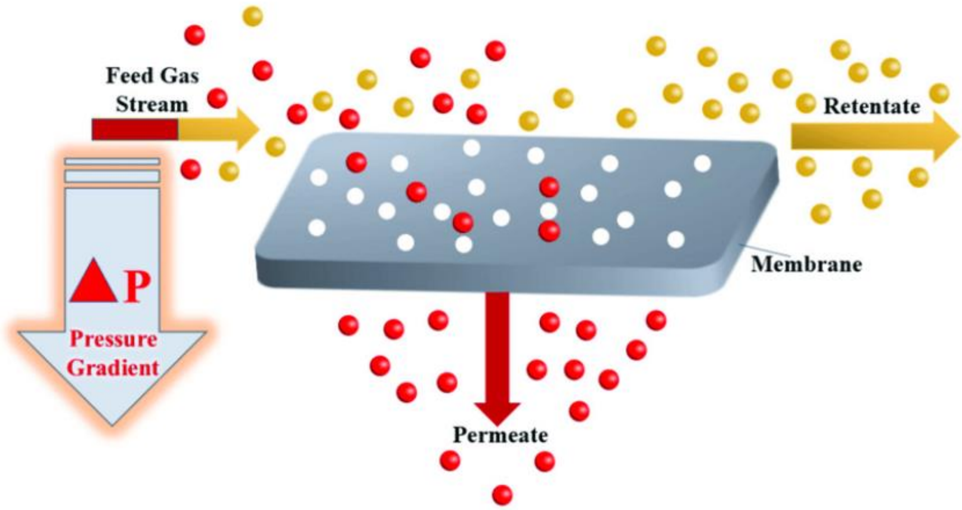

Figure 2.1 Gas separation mechanism (Elhenawy *et al.*, 2020)

2.2 Type of membrane

Polymeric membrane is the first generation membrane technology that has been develop in 1980s for gas separation purposes. Thanks to low production cost and the simplicity of the fabrication process, polymeric membrane applications grow quickly. Polymeric membrane is divided to two type depend on the operating temperature of the membrane which are rubbery and glassy (Ahmad *et al.*, 2021; Farnam, bin Mukhtar and bin Mohd Shariff, 2021). The polymer that operate below their glass transition temperature is known as glassy polymer which is rigid and hard. These type of membrane exhibit high selectivity and low permeability as the dense pack polymer chain in the structure give less room to the molecule to pass through the membrane. Table 2.1 showed various glassy and rubbery polymer that has been used as membrane. In both research and industrial, polyethersulfone (PES) has been widely used in biomedical, water purification and protein separation as PES is consider to have an excellent mechanical and thermal stability. Rubbery polymers are very soft and flexible which operate above glass transition temperature (T_g). The polymer basically fully amorphous with no crystalline segments. The membrane that made out of rubbery polymer are typically has a high permeability and low selectivity (Farnam, bin Mukhtar and bin Mohd Shariff, 2021).

Currently, gas separation using polymeric membrane has to compete with other technology such as cryogenic distillation, pressure swing absorption and chemical absorption technology. Despite its advantages in ease of production and simplicity, membrane technology has a few drawbacks which putting its place behind other carbon capture technology. The bad side of polymeric membrane technology are the permeability/selectivity trade off, physical aging of the polymer and plasticization. Trade-off relationship is observed between permeability and selectivity. The high permeability is obtained in the cost of lower selectivity. The relationship can be represented by the double logarithmic plot, where log-log plots of selectivity versus permeability of the more permeable gas demonstrated that virtually all the data points were below a well-defined line (Du *et al.*, 2012) as shown Figure 2.2.

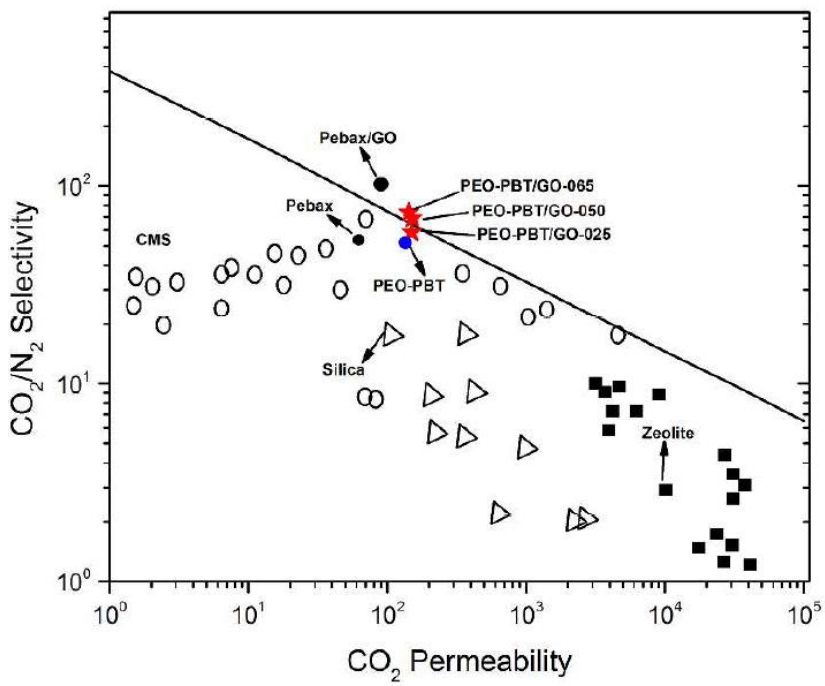

Figure 2.2 Relationship between CO2 permeability and CO2/N2 selectivity (Robeson plot) (Karunakaran *et al.*, 2015)

The other membrane class that are in development for gas separation is inorganic membrane. Inorganic membrane comes with higher cost for production which providing a better selectivity and permeability. It is also come with better chemical and thermal stability compared to polymeric membrane. Inorganic membrane has a few disadvantages which makes it impractical in industry which are high capital cost, embrittlement phenomenon, low membrane surface per module and difficulty in achieving high selectivity in large-scale microporous membrane (Ladewig and Al-Shaeli, 2017). Zeolite is one of the example of inorganic membrane are thermally stable to over 773 K and chemically stable in alkaline or acidic condition. Recent research, metal-organic framework, a hybrid between inorganic and also organic porous materials has received significant attention in gas separation field (Hamid and Jeong, 2018)

Table 2.1 Polymer membrane and respective gas separation performance

Polymer	Type	μ_{CO_2} [Barrer]	$\propto_{CO_2/N_2}$	Reference
Polyethersulfone (PES)	Glassy	570	1.01	(Lestari *et al.*, 2021)
Polyimide (PI)	Glassy	-	25.6	(Farnam, bin Mukhtar and bin Mohd Shariff, 2021)
Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO_{dm})	Glassy	48.4	14.7	(Farnam, bin Mukhtar and bin Mohd Shariff, 2021)
Polydimethyl siloxane (PDMS)	Rubbery	3628	4.1	(Farnam, bin Mukhtar and bin Mohd Shariff, 2021)
Polyurethane (PU)	Rubbery	26.5	19.5	(Sodeifian *et al.*, 2019)

2.3 Structure of the membrane

Membrane structure can be described in two types, which is isotropic or symmetric membrane and anisotropic or asymmetric membrane. Isotropic membrane is rigid with interconnected pore and void structure with pore that randomly distributed (Ho, Su and Cheng, 2021). Gas separation is affected by the pore size distribution of microporous membrane and hydrodynamic conditions. To synthesized microporous membrane, phase inversion, track etching stretching and electrospinning can be used (Mohammad *et al.*, 2018). Phased inversion is the common method of producing isotropic microporous membrane. The other type of membrane would be anisotropic, which made of layered structure varying the porosity and pore across the cross section of the membrane. Commonly, the dense layer of anisotropic membrane would be very thin while being supported by thick microporous layer. The isotropic and anisotropic membrane is shown in Figure 2.3.

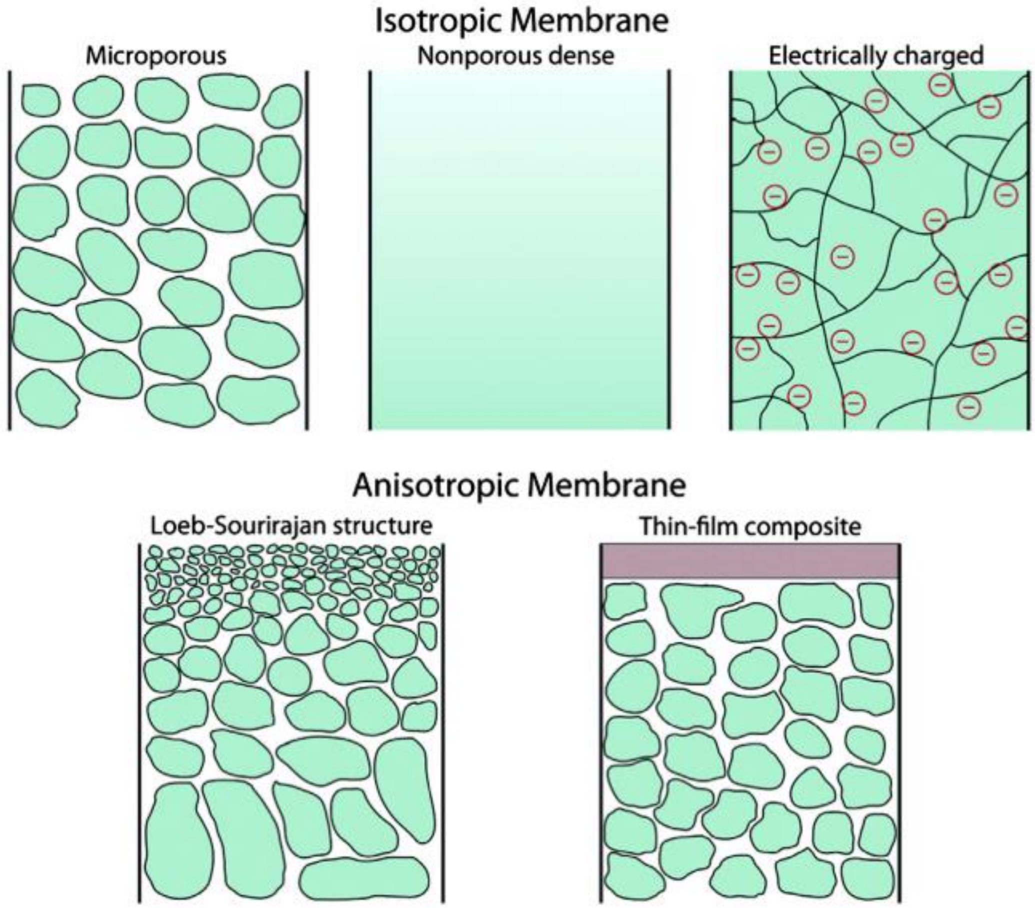

Figure 2.3 Isotropic and anisotropic membrane (Abdullah *et al.*, 2018a)

2.4 Mixed Matrix Membrane as Carbon Dioxide Gas Separation

Efficiency of a polymeric membrane decreases with time due to fouling, compaction, chemical degradation, and thermal instability. While, inorganic membranes have issue regarding its mechanical stability and processing cost. In 1991, Robeson showed that in a selectivity versus permeability plot, the data for many polymeric membranes lie below a straight line which is also known as upper bound tradeoff curve. Due to the same factor as inorganic membrane, it becomes a huge limitation to be used in industry. Mixed Matrix Membrane start to emerge as an alternative approach in membrane technology (Aroon *et al.*, 2010). Research shows that mixed matrix membrane (MMM) have potential to overcome both polymeric and inorganic membrane limitations. Nano/micro-sized inorganic particles homogeneously dispersed in a continuous organic polymer has merged both desirable properties of organic and inorganic phases (Hamid and Jeong, 2018).

Inorganic filler into polymer phase can significantly alter the transport properties of one or several gases through MMM compared to that of neat polymeric matrix. Inorganic particle could determine the path to be pass through by one of the gases over the other. These inorganic particles usually exhibit great affinity towards specific gas molecules due to surface interaction that will facilitated transport for the gas separation. Conventionally, there are various organic materials have been explored to be used as filler in membrane application such as zeolite, carbon molecular sieve, silica and metal oxide (Goh *et al.*, 2011). Data on MMM CO_2/N_2 separation capabilities from various report has been taken and tabulated in Table 2.2. MMM inorganic filler playing a sieving role with sorption capacity and the gas transport through it is solution-diffusion. One of the inorganic particles that can be used as a filler is Metal organic frameworks (MOFs). MOFs and its subclass Zeolitic Imidazolate framework (ZIF-L) are promising class of nanoporous material that can be used to create one, two or three dimensional porous structure (Abhang, 2017). ZIF-L which is 2D nanosheet providing a greater aspect ratio is hypothesized to have greater selectivity even at lower filler loading compared to its parent ZIF-8.

Table 2.2 MMMs and their gas separation properties

Mixed Matrix Membrane (MMM)	Inorganic filler	μ_{CO_2} [Barrer]	$\propto_{CO_2/N_2}$	Reference
Pebax	Cu-BTC	119	55.13	(Ge *et al.*, 2018)
polyvinyl acetate (PVAc)	Titanium dioxide (TiO2) (10wt.%)	-	78	(Farnam, bin Mukhtar and bin Mohd Shariff, 2021)
Polyurethane (PU)	Silica nanoparticles (20 wt %)	-	41.26	(Farnam, bin Mukhtar and bin Mohd Shariff, 2021)