FABRICATION OF ANISOTROPIC POLY(4-METHYL-1-PENTENE) MEMBRANE FOR CO_2 AND N_2 GAS SEPARATION

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by

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LIST OF SYMBOLS

Symbol	**Description**	**Unit**
T	Operating temperature	℃
ΔP	Transmembrane pressure	Bar
P	Gas permeability	Barrer
l	Membrane thickness	cm
A	Membrane's effective surface area	m^2
V	Volume displaced by the bubbles	cm^3
t	Time taken for gas permeation test	s

Greek letter

α	Gas selectivity

Subscripts

i,j	Gas components

LIST OF ABBREVIATIONS

CA	Cellulose acetate with acetyl content
CH_4	Methane
CO_2	Carbon dioxide
DI	Deionized water
EVAL	Poly(ethylene-co-vinyl alcohol)
GPU	Gas Permeance Unit
H_2	Hydrogen
HF	Hollow fibre
MMM	Mixed matrix membrane
N_2	Nitrogen
NIPS	Nonsolvent induced phase separation
NMP	N-methyl-2-pyrrolidone
PEI	Polyetherimide
PES	Polyethersulfone
PMP	Poly(4-methyl-1-pentene)
PVDF	Polyvinylidene difluoride
SEM	Scanning electron microscopy
SF_6	Sulphur hexafluoride
SO	Sulphur oxide
TFC	Thin film composite
T_g	Glass transition temperature
TIPS	Thermal induced phase separation
VIPS	Vapor induced phase separation

FABRIKASI MEMBRAN POLI(4-METIL-1-PENTENA) ANISOTROPIK UNTUK TUJUAN PEMISAHAN GAS CO_2 DAN N_2

ABSTRAK

Pemisahan karbon dioksida (CO_2) daripada gas serombong menggunakan teknologi membran telah menjadi fokus para penyelidik sejak beberapa dekad lalu kerana penggunaan tenaga yang rendah dan alternatif yang lebih murah. Dalam tesis ini, poli(4-metil-1-pentena) (PMP) anisotropik telah dikaji untuk memastikan kebolehlaksanaan penggunaan PMP untuk memisahkan gas CO_2 dan nitrogen (N_2). PMP membran yang padat secara penuh dibuat dengan pelbagai PMP wt% pada 20 dan 70 ℃ untuk mengkaji kesan suhu keatas struktur lapisan padat membran tersebut. Sudut kontak air dan FTIR-ATR dilakukan bagi mencirikan membran PMP yang telah dibuat. Sudut kontak air yang diperoleh untuk permukaan PMP membran tanpa modifikasi di permukaan seperti rawatan plasma atau salutan adalah antara 105^0 dan 116^0 menyebabkan membran ini diklasifikasikan sebagai hidrofobik. Imej SEM keatas keratan rentas PMP membran padat penuh menunjukkan tiada perbezaan yang ketara dari segi struktur padat membran tersebut bagi membran yang menjalani penyongsangan semasa fasa kering pada 20 ℃ dan 70 ℃. Perbezaan rembesan CO_2 dan N_2 dan selektivitnya juga tidak begitu ketara dengan perbezaan suhu fabrikasi. 5 wt% PMP yang difabrikasi pada suhu 20 ℃ menunjukkan kondisi yang terbaik bagi membuat membrane PMP anisotropic berdasarkan keputusan test rembesan gas. Untuk 5 wt% yang dibuat pada 20 ℃, rembesan CO_2 dan N_2 masing-masing direkodkan sebagai 5.91 ± 0.29 GPU dan 0.51 ± 0.03 GPU dengan selektiviti CO_2/N_2 sebanyak 11.57 ± 0.10. Kondisi tersebut kemudian digunakan untuk membuat PMP anisotropik dengan mempelbagaikan waktu untuk penyongsangan semasa fasa kering daripada 10 saat sehingga 60 saat. Rembesan CO_2 didapati naik sebanyak 10 kali ganda manakala rembesan N_2 didapati naik sebanyak 5 kali ganda secara purata menyebabkan selektiviti CO_2/N_2 jatuh sebanyak separuh daripada PMP membran yang padat secara penuh. Imej SEM digunakan untuk memerhatikan kesan tempoh penyongsangan semasa fasa kering ke atas lapisan padat membran PMP anisotropik. Penyongsangan semasa fasa kering selama 40 saat menunjukkan tempoh yang terbaik bagi membuat PMP membran anisotropik. Rembesan CO_2 dan N_2 masing-masing direkodkan sebanyak 51.49 ± 1.56 GPU dan 9.90 ± 0.58 GPU dengan selektiviti gas CO_2/N_2 sebanyak 5.21 ± 0.15 dengan penyelewangan yang paling sedikit. Campuran air-etanol tidak sesuai untuk dijadikan perantara sebagai mandi pembekuan kerana air dan sikloheksana tidak mampu bercampur. Menggunakan alkohol dengan rantaian yang lebih tinggi akan mengurangkan parameter kelarutan antara sikloheksana dan alkohol yang akan menyebabkan keliangan pada PMP anisotropic membran akan berkurang pada kawasan yang poros. Dalam hal ini, kami mendapati bahawa penggunaan air sebagai campuran kepada mandian pembekuan adalah tidak sesuai bagi memfabrikasi membran PMP dengan sikloheksana sebagai larutan kerana air dan sikloheksana adalah tidak sebati dan akan membentuk sistem dua fasa.

FABRICATION OF ANISOTROPIC POLY(4-METHYL-1-PENTENE) MEMBRANE FOR CO_2 AND N_2 GAS SEPARATION

ABSTRACT

Carbon dioxide (CO_2) separation from flue gas with the use of membrane technology has become the focus of researchers over the past decades due to its lower energy consumption and cheaper alternative. In this thesis, anisotropic poly(4-methyl-1-pentene) (PMP) was studied to determine the feasibility of using PMP to separate CO_2 from nitrogen (N_2) gas. A full dense PMP membrane with various PMP wt% was fabricated at both 20 and 70 ℃ to determine the effect of temperature on dense layer of the membrane. Water contact angle and FTIR-ATR was used to characterize the fabricated PMP membrane. The water contact angle of PMP membrane surface without modification such as plasma treatment or coating that have been obtained ranged between 105° and 116° which makes the membrane to be classified as hydrophobic membrane. The SEM image on the cross section of the full dense PMP membrane also showed no significant difference of the dense layer between the membrane that undergo dry phase inversion at 20 ℃ and 70 ℃. CO_2 and N_2 gas permeance as well as the selectivity does not differ greatly with fabrication temperature. 5 wt% PMP fabricated at 20 ℃ seems to be the best condition to fabricate anisotropic PMP membrane based on the gas permeance test. The CO_2 and N_2 permeance is 5.91 ± 0.29 GPU and 0.51 ± 0.03 GPU respectively, and with CO_2/N_2 selectivity as 11.57 ± 0.10. The parameter was then used to fabricate anisotropic PMP membrane with varying dry phase inversion time from 10 to 60 seconds. The CO_2 permeance increased by 10 times while the N_2 permeance increased by 5 times on average which makes the CO_2/N_2 selectivity dropped by half from the full dense PMP membrane. SEM imaging is used to observe the effect of dry phase inversion time on the thickness of the dense layer of the fabricated anisotropic PMP membrane. With 40 second dry phase inversion time, it appears to be the best duration to fabricate the anisotropic PMP membrane. The CO_2 and N_2 permeance is recorded to be 51.49 ± 1.56 GPU and 9.90 ± 0.58 GPU respectively with selectivity of CO_2/N_2 gas as 5.21 ± 0.15 with the least deviation. Water-ethanol mixture is not suitable as coagulation bath due to the immiscibility between cyclohexane and water. Using higher alcohol chain will reduce the solubility parameter between cyclohexane and the alcohol which will cause the reduction in porosity of the PMP membrane in the porous section. In our case, we conclude that introducing water component as a mixture to the coagulation bath is not suitable for the production of PMP membrane with cyclohexane as its solvent as water and cyclohexane is immiscible and will form two-phase system.

CHAPTER 1

INTRODUCTION

1.1 Carbon Dioxide Gas Separation

Carbon dioxide (CO_2) emission increased from year to year due to urbanization and advancement of industrial sector (Zhang et al., 2017). The emission of CO_2 gas to the atmosphere will contribute the global warming. In 2018, the concentration of CO_2 in the atmosphere is at its highest peak (Page, 2019). It shows global increase of 1.7% CO_2 emission in 2018. Most CO_2 emission accounts from the usage of fossil fuels and burning of coal (IEA, 2019). In an effort to combat climate change in line with Sustainable Development Goals (SDG) which is Goal 13, researchers around the world have been working to figure out the most eco-friendly and cheapest way in reducing the carbon emission to the atmosphere. Conventionally, CO_2 is treated by removing it from the atmosphere and storing it under the seabed or soil that is surrounded by roots of plants. CO_2 gas commonly comes from combustion of natural gas, fuel or coal in industry. To capture CO_2 from the flue gas, the flue gas is passed through a series of membrane to separate it from nitrogen (N_2) or sulphur oxide (SO) (Zuwairi & Rahman, 2017). Gas separation membrane has been one of the interest research field in membrane.

Membrane has found its various application in many fields ranging from industrial application to daily consumption. Those fields includes pharmaceutical, biorefinery, waste-water treatment, desalination plant as well as gas separation application. Membrane act as a selective barrier to allow the desired component to pass through the membrane while retaining the unwanted components or impurities. Employment of membrane as an alternative to the conventional separation process will eliminate the need of energy driven process that requires high heat energy, which in turn will reduce the capital cost as well as operating cost of the separation operation, thus making the process to be more economical (Dharupaneedi et al., 2019).

Polymeric membrane is more favourable in gas separation due to its easy processability and fabrication method. It is also easier to be shaped and assembled for its application process compared to the inorganic membrane. However, polymeric membrane is not heat resistant, making it not suitable for a very high temperature application. Typically, the gas inside a plant stream would be at several hundred degrees Celsius. Cooling the gases for membrane separation process would be impractical from economic point of view. Uses of carbocyclic and heterocyclic aromatic polymer is a promising alternative to overcome the limitation of polymeric membrane, but preparing membrane from carbocyclic and heterocyclic aromatic membrane would still be a huge challenge as the solubility of the polymer in solvent is lower (Rezakazemi et al., 2018).

Inorganic membrane is another alternative for gas separation process and the main advantage of inorganic membrane over polymeric membrane is that inorganic membrane can withstand high temperature. However, the main problem with inorganic membrane is that it is harder to be synthesized and much more expensive compared to polymeric membrane. The incorporation of inorganic filler into the polymeric membrane to produce mixed membrane matrix (MMM) is one of the promising ways to overcome the limitation of performance for polymeric and inorganic membrane. The main barrier for this process would be the compatibility of the polymeric membrane and the inorganic filler as well as scalability (Jusoh et al., 2016).

Gas separation membrane to separate CO_2 from flue gas or syngas produced industrially has been actively studied by researchers in other to improve the practicability of the membrane. The study would commonly investigate the separation of CO_2 from N_2, CO_2 from methane (CH_4) or CO_2 from sulphur hexafluoride (SF_6) in order to reduce carbon emission to the atmosphere. Carbon dioxide also have its own usage. Some of its usage is for foaming rubber and plastics, blasting coal, carbonated beverages and refrigerant in fire extinguisher (The Editors of Encyclopaedia Britannica, 2020). Carbon dioxide extinguisher is used to extinguish Class B and Class C flames. Apart from that, another important application is supercritical CO_2 extraction. The solubility and selectivity of the supercritical CO_2 is heavily affected by the temperature and pressure of the supercritical CO_2 fluid. For instance, according to a study conducted by Pérez wt al. (2015) the yield of extracted oil is the highest at 40 ℃ and 300 bar or 60 ℃ and 250 bar. However, myristic acid which is one of the components from free fatty acid is only extracted at 40 ℃ and 300 bar while linolenic acid is only extracted at 60 ℃ and 200 bar. Therefore, separating CO_2 from the flue gas or syngas produced in the industry would be beneficial as we can use the CO_2 for other purpose as listed in the example above instead of releasing it to the atmosphere which will contribute to air pollution and greenhouse gas effect. CO_2 separation with the use of membrane is being actively studied to improve the practically of its application.

1.2 Problem Statement

To reduce the CO_2 global emission to reduce the greenhouse effect on global warming, removal of CO_2 from flue gas is essential. Cryogenic distillation is one of the conventional technologies that is utilized for CO_2 removal from the flue gas. Under high pressure and low temperature, CO_2 gas will condense and collected from the bottom of the distillation tower while the N_2 will remained as gas and collected from the top outlet of the tower (Aaron & Tsouris, 2005). Pressure swing adsorption technology is also used for CO_2 removal from flue gas in which it requires two chamber for adsorption and desorption of the CO_2 gas (Ho et al., 2008). The main problem with all these conventional technologies is the operational cost and energy intensive.

Membrane technology is an interesting application for CO_2 removal. Membranes such as polyvinylidene difluoride (PVDF), polyethersulfone (PES), and cellulose acetate is studied for CO_2 and N_2 gas separation. Poly(4-methyl-1-pentene) (PMP) membrane is a glassy polymer that is also a potential candidate to be studied for CO_2 and N_2 gas separation. To ensure that gas separation by using membrane to be viable, the membrane need to exhibit anisotropic structure with dense skin for effective separation with high flux. Even though PMP membrane exhibit dense skin layer upon fabrication, the main problem with PMP membrane is its low glass transition temperature (T_g) that is only about 35 °C, which is very near to ambient temperature and PMP membrane has limited solubility with most solvents (Kim, 2020).

Various parameters may also affect the performance of the gas separation using membrane. Increasing the thickness of membrane will reduce the permeance of gases as it introduces more resistance to the gases, hence thinner membrane is preferable for gas separation. But under high pressure application, thin membrane will prone to mechanical failure and rupture. This is the reason why anisotropic membrane with dense skin layer is favourable as it can provide high selectivity with great mechanical strength. The morphology of PMP membrane can be affected by several parameter such as polymer concentration, drying time and the ratio of water-ethanol as the nonsolvent. The dry phase inversion is a slow process and is crucial in developing a dense skin layer, while the wet phase inversion with water-ethanol as nonsolvent is a faster process that will give microporous structure to the membrane. The duration of the dry phase inversion is necessary to be controlled in order to control the thickness of the skin layer formed for the anisotropic PMP membrane. Water is used to control the rate of liquid-liquid demixing between ethanol and cyclohexane to create a spongelike structure to provide mechanical strength with minimal resistance to the gases. These parameters will determine the feasibility on the study to produce anisotropic PMP membrane with dense skin layer for CO_2 and N_2 gas separation by conducting gas permeance test for both CO_2 and N_2 individually and determine the selectivity by calculating the ratio of permeance between CO_2 and N_2.

1.3 Research Objectives

1. To fabricate flat sheet poly(4-methyl-1-pentene) membrane with varying polymer concentration through phase inversion method.
2. To investigate the factors affecting the morphology of the membrane formed through phase inversion by varying the drying time and water-ethanol coagulation bath composition.
3. To calculate and determine the selectivity of CO_2/N_2 of the fabricated poly(4-methyl-1-pentene) membrane.

1.4 Scope of Thesis

Application of polymeric membrane has been widely studied due to its ability to cut operating expenses and eliminate the need for energy intensive process. Thus, understanding the parameter that affect the structure and performance of the membrane is crucial. The scope of this project is to determine the optimum parameter such as the polymer concentration, dry phase inversion temperature, dry phase inversion time and composition of coagulation bath to fabricate anisotropic PMP membrane. In order to determine the best polymer concentration and dry phase inversion temperature, a full dense PMP membrane is first produced and subjected to individual gas permeance test to determine the selectivity of PMP membrane towards CO_2/N_2 gas. The test is run three times and the membrane that has the least deviation on selectivity is taken as the best parameter for polymer concentration and drying temperature to produce anisotropic PMP membrane. SEM micrograph is also conducted on the dense PMP membrane to study the cross-sectional structure.

After the best polymer concentration and drying temperature is determined, the parameter is then chosen to fabricate anisotropic PMP membrane by only manipulating drying time from 10 to 60 seconds with pure ethanol as coagulation bath. The fabricated anisotropic PMP membrane is similarly subjected to gas permeation test individually and the ideal selectivity is calculated. The test is run three times and the membrane that has the least deviation on selectivity is taken as the best drying time to produce anisotropic PMP membrane. Lastly, coagulation bath composition is manipulated by introducing water component to the ethanol as the coagulation bath.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane for Gas Separation

The first anisotropic membrane is made from cellulose acetate by Loeb and Sourirajan in the 1960s from cellulose acetate. It have been a big breakthrough for the membrane field which opened the possibility of using membrane for separation process in the industry. The membrane have a dense top skin layer that acts as the selective barrier with a more porous support layer at the bottom side that makes the membrane able to exhibits high flux and high mechanical strength which makes it suitable for high pressure operation (Baker, 2012). Anisotropic membrane has been the subject of interest for gas separation application since that it can withstand high operating pressure while maintaining the flux without easily breaking down. Various polymers have been studied to produce a membrane for gas separation application.

Generally, polymeric membrane is commonly used for gas separation, and it can be divided into two categories that is glassy polymers and rubbery polymers. The classification of these two polymers depend on the temperature of formation of the polymer relative to their glass transition temperature (T_g). For a polymer that is formed above the T_g are called rubbery polymers, while the polymer formed below their T_g are called glassy polymer. Glassy polymers generally have good mechanical strength, reproducibility, and relatively better economical processing capability while rubbery polymer has lower mechanical strength. Glassy polymers are also commonly used for (MMM) fabrication. Compared to rubbery polymer, glassy polymer have higher selectivity but lower permeability due to the rigid chains which becomes an obstacle for gas molecule to pass through, whereas in rubbery membrane, the chain is more flexible that allows the gas molecule to pass more easily with lower selectivity (Farnam et al., 2014).

Polymeric membrane has a general trade-off between the permeability of a gas component and the selectivity between the gas pair which is characterize by a curve known as Robeson's upper bound limit which is illustrated in Figure 2.1. Robeson's upper bound limit shows the relationship between permeability and selectivity of a polymeric membrane for a given gas pair. In general, when the permeability is too high, the selectivity is low but at lower permeability, the selectivity will increase. Glassy polymer is closer to the upper limit curve compared to rubbery polymer due to its owing higher diffusivity coefficient (Robeson et al., 2015).

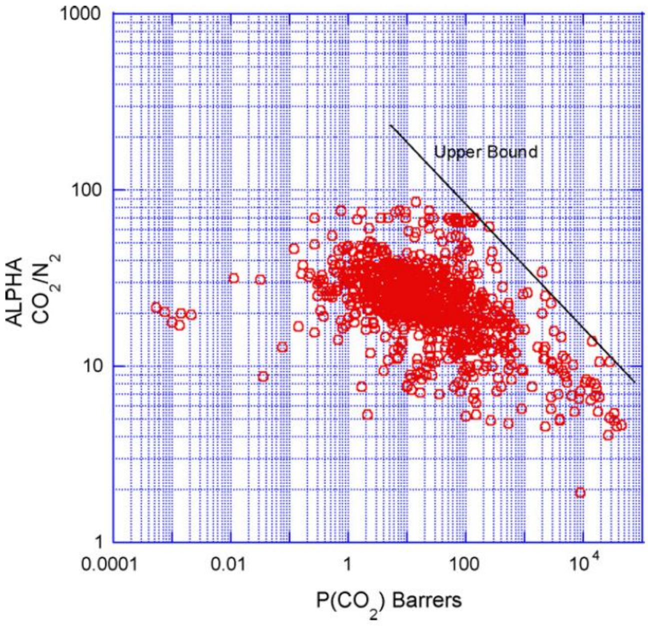

Figure 2.1: Robeson's upper bound curve for CO_2/N_2 gas separation (Robeson, 2008).

2.2 Polymeric Membrane for Carbon Dioxide Gas Separation

As of now, many polymers has been studied to be used to fabricate the membrane for gas separation study. Polyetherimide (PEI) is one of the derivatives of a broad class mineral known as polyimides. In a study conducted by Ahmad et al.

(2017a), PEI membrane with constant 25 wt.% PEI with varying casting thickness from 150 to 300 µm is produced to study the effect of thickness on the membrane. Their study shows that PEI with 150 µm has the highest CO_2 and N_2 permeability which is 10.365 barrer for CO_2 and 5.956 barrer for N_2. The selectivity obtained however is the lowest for PEI with 150 µm which is only 1.740. For PEI with 300 µm, the permeability of CO_2 and N_2 is the lowest which is 2.588 barrer for CO_2 and 1.012 barrer for N_2. However, the selectivity of CO_2/N_2 for PEI with 300 µm is determined to be the highest which is 2.559 compared to the rest of the PEI membrane. It is also observed that with thicker casting thickness of the membrane, it will prone to the formation of macrovoid which will weaken the integrity of the structure of the membrane and will not be suitable for high pressure operation as the membrane is susceptible to collapse. The same group of researchers also conducted the studies to determine the effect of polymer wt.% on the separation of CO_2 and N_2 gases. Polymer concentration of 20, 25 and 30 wt.% PEI is studied to determine the effect of the polymer concentration to the separation of CO_2 and N_2 gases. It is reported that the optimal yield for selectivity is achieved at 30 wt.% of polymer concentration. The selectivity of the CO_2/N_2 is determined to be 10.7 (Ahmad et al., 2017b).

Another type of membrane studied on CO_2/N_2 membrane is polyethersulfone (PES) membrane for a pure PES membrane without any coating or additives. The reported CO_2 permeability for pure PES is 2.77 barrer while for N_2 permeability for pure PES is 0.07 barrer at room temperature and operating pressure of 2 bar. The selectivity of CO_2/N_2 is reported to be 39.57. When the operating pressure is increased to 7 bar, the permeability of CO_2 increase to 3.82 barrer while permeance of N_2 slightly increase to 0.35. The selectivity of CO_2/N_2 however dropped to 10.91 (Mazinani et al., 2018). In another work, it is observed that the permeability of CO_2 and N_2 dropped once the operating pressure exceed the plasticizing pressure of PES during the gas permeance test on PES membrane. However, for methane (CH_4) it is completely opposite as the permeability increases with pressure. According to them, PES is a glassy polymer, hence it exhibits lower permeability against condensing gas such as CO_2. When the operating pressure is higher than plasticizing pressure, the volume of inter chain in the glassy polymer increase faster than the adsorption rate of CO_2 which causes the permeability of CO_2 to decrease with increasing pressure (Kamble et al., 2020b). The plasticizing pressure of PES is 27.58 bar (Ahmad et al., 2015). In this case, pure PES membrane will not be suitable for higher operating pressure to separate CO_2 and N_2 gases as it reduces their permeability and subsequently the selectivity of CO_2/N_2 gases. Certain modification can be done to the PES membrane such as adding a filler to enhance the performance of PES membrane.

Cellulose acetate is one of the extensively studied membrane for gas separation application. Cellulose acetate with acetyl content blend of 39 wt.% acetyl (CA-39) and 56 wt.% acetyl (CA-56) with polymer ratio of CA-39/CA-56 at 4:6 shows the best CO_2 permeance. The CO_2 permeance is reported to be 99.26 GPU while N_2 permeance is 87.12 GPU with a CO_2/N_2 selectivity of 1.139. The reported selectivity is rather low. In their work, acetic acid is used as the solvent for membrane fabrication (Jin et al., 2020). However, according to Mubashir et al. (2018), cellulose acetate fabricated with methyl-2-pyrrolidone (NMP) shows high CO_2 and N_2 permeance with relatively higher CO_2/N_2 selectivity. In their reported work, the CO_2 permeability is determined to be 15.56 barrer while N_2 selectivity is 1.77 barrer with CO_2/N_2 selectivity of 8.80. In another study by Jami’An et al. (2016), they varied the solvent evaporation time during the fabrication of cellulose acetate membrane. It is found that, with longer solvent evaporation time, the permeability of the gases reduced dramatically.

However, it is also evident that the selectivity of the gases increase with increasing solvent evaporation time. With increasing solvent evaporation time, dense structure is formed on the skin layer of the membrane which resulting in reduced permeability, but increased selectivity compared to fast solvent evaporation time. The dense layer formed on the surface of the membrane act as the selective layer to separate the gas.

PMP is a potential glassy polymer to create the membrane used for selective separation of CO_2 and N_2 gases. In a study that is conducted by Nematollahi et al. (2016), at the condition of 25 °C and 4 bar, the permeability of CO_2 for pure PMP membrane is recorded to be 129.1 barrer while the permeability of N_2 is 3.40. The reported selectivity of CO_2/N_2 for pure PMP in their work is 38.18. Another reported study on PMP membrane with a thickness 60 μm with operating pressure of 2 bar and 35 °C shows the permeability of CO_2 to be 76.1 barrer while the permeability of N_2 is 3.7 barrer. The selectivity of CO_2/N_2 is calculated to be 20.5 (Abedini et al., 2018). In another work by Markova et al. (2020), at 25 °C for pure PMP membrane, the reported permeability of CO_2 is 84 barrer while the permeability of N_2 is 7.6. Table 2.1 shows the permeability of permeance of CO_2 and their selectivity with various gas pair for a typical polymeric membrane that is commonly studied.

Table 2.1: Summary on the selectivity of gas separation membrane.

Membrane	**Gas pair**	**Condition**	**CO_2 permeability / permeance**	**Selectivity**	**Reference**
Polyetherimide (PEI)	CO_2/N_2	25 ℃ 1 bar	2.588 barrer	2.559	(Ahmad et al., 2017a)
			6.35 GPU	10.76	(Ahmad et al., 2017b)
		40 psi	-	1.09	(Kamble et al., 2020a)
	CO_2/CH_4	25 ℃ 1 atm	0.74 barrer	17.5	(Vega et al., 2019)
Polyimide (PI)	CO_2/N_2	-	2.31 barrer	15.4	(Sun et al., 2017)
	CO_2/CH_4	-		10.04	
Polyethersulfone (PES)	CO_2/N_2	25 ℃ 2 bar	2.77 barrer	39.57	(Mazinani et al., 2018)
		25 ℃ 7 bar	3.82 barrer	10.91	
	CO_2/CH_4	10 bar	-	9.13	(Abdul Mannan et al., 2016)
Polysulfone (PSf)	CO_2/N_2	-	5.55 barrer	29.23	(Waheed et al., 2016)
	CO_2/CH_4	-		27.77	
		35 ℃	29.08 barrer	23.12	(Adewole et al., 2015)
		10 bar	-	4.80	(Abdul Mannan et al., 2016)
Cellulose acetate (CA)	CO_2/N_2	25 ℃ 2.5 bar	2.48 GPU	1.139	(Jin et al., 2020)
		25 ℃ 3 bar	15.56 barrer	8.80	(Mubashir et al., 2018)
	CO_2/CH_4	25 ℃	0.449 GPU	21.48	(Jami’An et al., 2016)

Poly(4-methyl-1-pentene) (PMP)	CO_2/ N_2	25 °C 3 bar	129.1 barrer	38.18	(Nematollahi et al., 2016)
		35 °C 2 bar	97.2 barrer	16.4	(Abedini et al., 2018)
		25 °C	84 barrer	11.05	(Markova, Zhmakin, et al., 2020)
6FDA-durene	CO_2/ N_2	2 bar	1468.3 barrer	25.4	(Nafisi & Hägg, 2014)
		30 °C 2 atm		12.1	(Hossain et al., 2019)
	CO_2/ CH_4	2 bar	1468.3 barrer	22.6	(Nafisi & Hägg, 2014)
		30 °C 3.5 bar	468 barrer	7.03	(Jusoh et al., 2017)
		30 °C 2 atm		13.2	(Hossain et al., 2019)

Despite various polymers have been studied for gas membrane separation and various available literatures, application of membranes on industrial level for CO_2 separation are still limited to only a few types of polymer. High pressure operation for gas separation in industry demand the membrane used to exhibit high mechanical strength while maintaining high flux. On top of that, at high pressure, CO_2 tend to condense which may cause plasticization of membrane. Polymeric membrane also aged over time which will cause the reduction of their performance in term of the selectivity of the gases.

2.3 Fabrication Design for Gas Separation Membrane

2.3.1 Dense Membrane

For gas separation membrane to be viable, the pore needs to be very small to allow the separation to occur. Generally, microporous membrane is not ideal for gas separation as the pore of the membrane is still too large for gas separation to occur. In this light, dense membrane is always preferred for gas separation. With dense membrane, the selectivity of the gas pair to be separated is very high. However, the main limitation with dense membrane is its low flux. Despite of its effectiveness in separating gas, the thick dense layer of the membrane will cause the flux to be very low which is not practical for industrial application. Low flux and thick dense layer will give rise to the need of long operating time with high transmembrane pressure, which will incur high operating cost. However, dense membrane are still used in laboratory work for characterization of the membrane's property (Baker, 2012).

For dense membrane separation, the most widely accepted mechanism to describe the transport across the dense membrane layer is solution-diffusion mechanism. The working principle of solution-diffusion mechanism model is that the permeant will dissolve in the membrane material which is followed by the diffusion of the permeant through the membrane material down a concentration gradient. The separation between the feed permeants is achieved due to the different amount of material dissolved in the membrane and the rate of diffusion of the material through the membrane. There are three postulated steps for solution-diffusion mechanism. The first is the dissolution of gas permeant into the high-pressure upstream surface of the membrane. The second step is the diffusion of the gas permeant through the dense layer of the membrane. The third step is the desorption of gas permeant into the low-pressure downstream surface of the polymer (Fauzi et al., 2005). The flux of dense membrane is governed by the following equation:

$$Q = \frac{P_i A}{l} dP \tag{1}$$

Where Q is the flux of the gas in cm^3/s, P is the permeability coefficient of the gas species *i* in Barrer (1 Barrer = 1×10^{-10} (cm^3 @ STP·cm)/(cm^2·s·cmHg)), A is the area of the permeation site for the membrane, *l* is the thickness of the membrane in cm, and dP is the differential pressure between the feed and permeate side. The permeability constant is determined by the following equation:

$$P = D \cdot S \tag{2}$$

Where P is defined as the permeability constant of the gas for a given membrane in Barrer (1 Barrer = 1×10^{-10} (cm^3 @ STP·cm)/(cm^2·s·cmHg)), D is the diffusivity of the permeant through the membrane, and S is the solubility of the permeant through the membrane. Figure 2.2 shows the schematic representation of a solution-diffusion mechanism model.

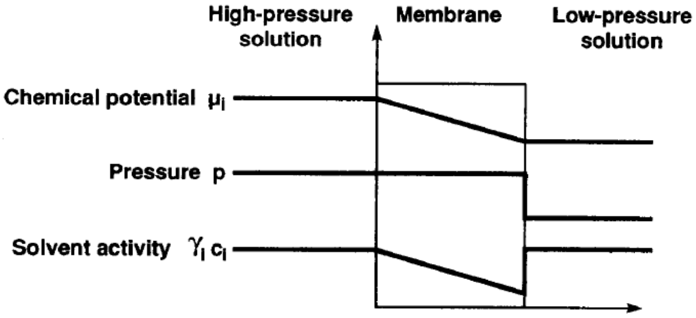

Figure 2.2: Schematic diagram of solution-diffusion mechanism model (Wijmans & Baker, 1995).

Based on the equation, we can control several factors to increase the flux. Permeability is the intrinsic property of the polymer. Therefore, the permeability constant varied from one polymer to other polymers and will not change for the same polymer material. Pressure difference is the parameter defined by the operating condition of the process. Increasing the pressure will increase the flux, however from economical perspective, increasing the pressure will also increase the operating cost. Reducing the thickness of the membrane and increasing the effective surface area will increase the flux. Nevertheless, thin dense membrane is still susceptible to collapse at higher operating pressure and requires a support to make it fully functional as intended. Hence, anisotropic is a more favoured option for gas separation membrane application. Figure 2.3 shows the isotropic structure of the membrane which is for porous and dense membrane.

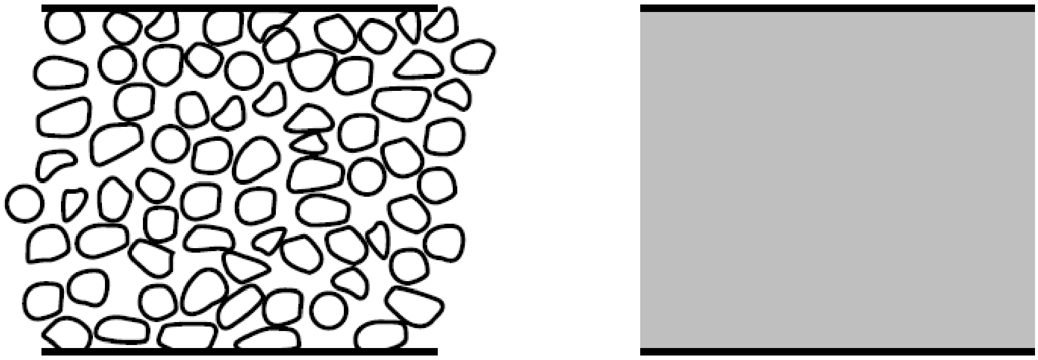

Figure 2.3: Isotropic microporous and non-porous dense membrane structure (Baker, 2012).

2.3.2 Anisotropic Membrane

Anisotropic membrane is a membrane that has different pore size throughout the membrane structure. Anisotropic membrane can either be a membrane in which the dense skin layer and microporous structure consists of the same polymer or thin film composite (TFC) in which the dense skin layer is made from one polymer while the microporous support is made from a different polymer as illustrated in Figure 2.4. These configurations have their own benefit and advantage.

Anisotropic membrane can be fabricated by phase inversion method in which it has four technique namely thermal induced phase separation (TIPS), non-solvent induced phase separation (NIPS), vapor induced phase separation (VIPS) and immersion precipitation. The first two is the most applied method in fabricating membrane. The structure of the membrane depends on the liquid-liquid demixing step which is usually explained by a ternary diagram. For a delayed liquid-liquid demixing, usually a sponge-like structure can be observed formed by the polymers during membrane formation because more time taken for the membrane formation as the solvent evaporation process is slower which result a dense structure to be formed. For instantaneous liquid-liquid demixing process, usually a finger-like structure will be observed in the membrane structure due to fast evaporation of solvent in which the polymer does not have enough time to arrange themselves in order, which resulted the elongated finger-like structure in the membrane formation (Idris et al., 2017). Fast liquid-liquid demixing may also cause the formation of macrovoids in the membrane structure (Singh et al., 2020). Macrovoids is not favourable in membrane separation process as it will weaken the mechanical strength of the membrane (Ahmad et al., 2017a).

TFC is basically one thin dense layer that is normally coupled with another microporous membrane structure as a support. So, it consist of two separate polymer material. Thin film composite membrane is easier to be fabricated compared to anisotropic membrane which require precise control of demixing process to obtain a dense skin layer followed by a microporous structure support. There are several common methods to fabricate TFC such as dip coating, chemical reactions, interfacial polymerization and plasma treatment including three methods that are not so common which include chemical vapor deposition, sputtering and spray pyrolysis (Khulbe & Matsuura, 2018). Even though TFC displays advantage in term of the composite design, however TFC still have its own disadvantages. The first problem that may arise is the lateral diffusion of gas permeant at the composite interface. Another problem may arise is the impregnation of the selective layer solution onto the surface of the microporous support which will increase the gas permeation resistance across the membrane. For TFC to function as intended, the suitability of the solvent used as the selective layers with the underlying support also plays an important role (Mohd Shafie et al., 2019).

All membranes with a dense selective layer are governed by solution-diffusion mechanism model which is the most accepted model. Porous membrane is possible to be used for gas separation application, but only inorganic membrane able to accomplish such feat since inorganic membrane able to maintain same precise pore size throughout the membrane. Polymeric membrane has a fluid backbone which cause it to have range of pore sizes. When the pore size is greater than the mean free path of the gas molecule, the diffusion is separated by Knudsen diffusion mechanism in which the selectivity of the gas pair is low which is not favourable to achieve high separation factor. Known example of application on Knudsen diffusion is the separation of uranium isotope (Keizer et al., 1988). Table 2.2 shows the summary of advantage and disadvantage of anisotropic membrane and TFC membrane.

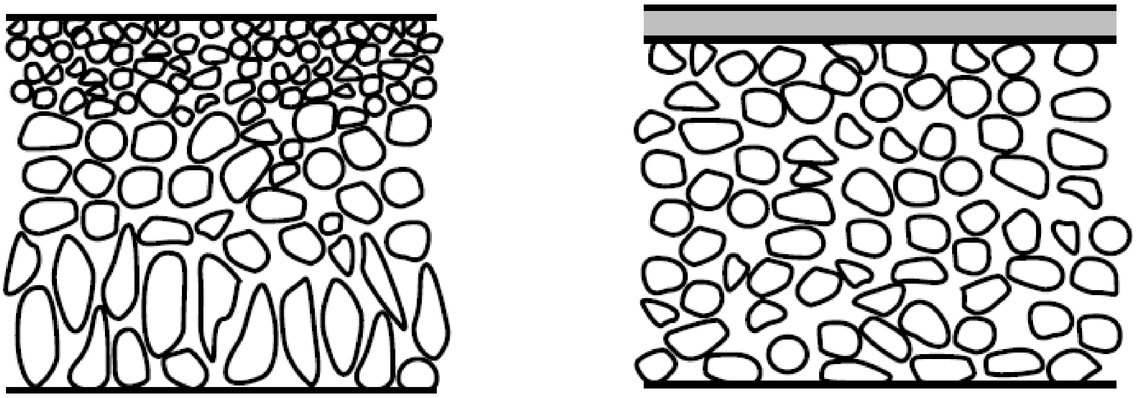

Figure 2.4: Loeb-Sourirajan anisotropic membrane and thin film composite membrane structure (Baker, 2012)

Table 2.2: Summary on advantage and disadvantage of anisotropic membrane and TFC.

Type	Advantage	Disadvantage
Anisotropic membrane	- High mechanical strength with high flux - Consist of one single polymer material	- Need precise control during demixing process to fabricate dense skin layer with microporous support - Possible formation of macrovoid during fast demixing process for thick membrane
Thin film composite (TFC)	- Easier to assemble - Can use different material between TFC and its support layer	- Occurrence of lateral diffusion and impregnation of microporous support with its selective layer solution - Suitability of solvent as selective layer.

2.4 Poly(4-methyl-1-pentene) (PMP) membrane fabrication

Phase inversion method is normally employed to produce anisotropic PMP membrane with dense skin layer. Dry phase inversion is deployed by Mohr & Paul (1991) to study the effect of casting solvent on the selectivity of gases. They found that different casting solvent used affects the permeability and selectivity of the gases. In their study they dried the solvent at room temperature. It is observed that the casting film used to fabricate the PMP membrane affect the crystalline structure and the spatial arrangement of the film. Their results shows that the permeability of CO_2 and N_2 is 83 and 6.5 respectively which makes the selectivity to be 12.769 for PMP fabricated with cyclohexane as the casting solvent. The highest permeability of CO_2 and N_2 recorded in their report is for PMP membrane fabricated with cyclopentane where the permeability for CO_2 is 93.8 and permeability for N_2 is 7.4 which makes the selectivity of CO_2/N_2 to be 12.676. For PMP with chloroform as the casting solvent, the permeability for CO_2 and N_2 is much lower which is only 15 and 1.1 respectively but it has the highest selectivity of CO_2/N_2 which is 13.636.

Wet phase inversion involved the use of non-solvent to induce the liquid-liquid demixing process. Another group of researchers which used chloroform as the solvent, their fabricated PMP membrane exhibits a more porous structure than the PMP membrane fabricated with different solvent with methanol as the coagulation bath. They postulated that for the system of methanol/chloroform/PMP, the solubility difference between solvent (chloroform) and polymer (PMP) is higher than the solubility difference compared to other solvent and polymer that are used in their experiment. Meanwhile the solubility difference between solvent (chloroform) and coagulant bath (methanol) is the lowest compared to solubility difference of other solvent and methanol coagulation bath system in their experiment. Large solubility difference between solvent and polymer means that chloroform is a poor solvent for PMP membrane which makes the demixing gap between chloroform and PMP to be larger compared to other system that used different solvent. Furthermore, the low solubility difference between methanol and chloroform compared to other system that used different solvent, it indicates that chloroform as a solvent has stronger interaction with methanol compared to interaction between other solvent and methanol, which results in fast exchange rate between the solvent and coagulant that caused the microporous structure of PMP for methanol/chloroform/PMP system compared to other system studied in their experiment (Lin et al., 1996). From this we can understand that the solubility of solvent used between polymer and coagulation bath also affect the rate of solvent evaporation that affects the structure of the membrane formed with phase inversion method.

Another method to fabricate PMP membrane is by melt spinning method to produce a hollowfibre (HF) PMP. The polymer granulate will be melted in the extruder by heat induced heating element and dissipation of mechanical energy. Processing temperature and pressure control of the extruder is set according to the suitability of the polymer. To achieve faster cooling rate of the fibres, air stream with a determined velocity is blown onto it. The property of HF PMP membrane produced by this method mainly is determined by the process temperature. When PMP is processed at 270 ℃, the fibre cross section does not have a very round shape which makes it less reproducible. As for PMP processed at higher temperature which are 280 ℃ and 290 ℃, closed HF can be obtained with a more regular structure. At higher temperature, the PMP has lower viscosity which makes the melts flow easier out of the spinneret. Another reason is higher temperature takes longer time to cool down and solidify. PMP need to be processed at 60 ℃ higher than its melt temperature to obtain the desired closed HF. This temperature is much higher compared to polyester or polyamide processed with melt spun method (Pelzer et al., 2020).

2.4.1 Current usage of Poly(4-methyl-1-pentene) membrane

Currently PMP membrane is being used in various fields. For example, PMP is studied for its potential use as dielectric for the capacitor. Dielectric refers to the material that is in between the two capacitor plates. The purpose of dielectric is to prevent the two capacitor plates of coming into contact while allowing very small plate separation and to increase effective capacitance by reducing the field strength. PMP is suitable as dielectric as it can be melt processed at temperature of lower than 270 ℃ without degrading and can be operated at a temperature of 160 – 190 ℃. PMP offers high flexibility towards thin film manufacture solution by processing due to favourable solubility characteristics that provides an advantage over other polymers (Gupta et al., 2017).

In medical field, oxygenator is used to enhance exchanging of oxygen and carbon dioxide in blood of a patient during a surgical procedure. HF is commonly used as oxygenator, but it is prone to plasma leakage that leads to complication. With PMP as oxygenator, it is observed that there is less pressure drop in the PMP oxygenator with better gas exchange (Formica et al., 2008). PMP oxygenators also have reported to have last longer and lower rate of thrombus formation and haemolysis. However, PMP oxygenator may still fails after a few days in which the deposition of red blood cells and platelet on the surface of the membrane increase the resistance to blood flow and lowered the gas diffusion (Sidebotham et al., 2012).

Another common example of the usage of PMP is food packaging. Plastic food packaging is important in current time as it provides a mean of simplicity to transport the food source to far places without it polluting the food inside or for temporary storage before being transported to another place. Because of this, it is important to ensure that the plastic food packaging is reusable and recyclable. There are several polymers used that is listed for the use as food packaging and PMP is one of them (Raheem, 2013). Food that is packed by PMP material can be heated by microwave or radiation ovens (Coles et al., 2003). Despite being one of the common polymers used as food packaging, PMP has low surface energy which is only 21.5 mJ/m^2. Good adhesion is important to seal areas at polymer-polymer interface or polymer-metal interface to prevent the food from being contaminated with food-borne organism or foreign material. Surface treatment such as plasma treatment is effective in increasing the surface energy of polymers with low surface energy. The adhesion between metal and polymer is observed to increase by using plasma treatment (Han, 2005).

2.5 Gaps in Knowledge

PMP membrane with its high permeability towards CO_2 and high mechanical strength as it is a glassy polymer is suitable to be processed into the anisotropic Loeb-Sourirajan membrane. However, its nature that lacks compatibility with other materials reduce interest for research on fabrication of mixed matrix membrane with PMP polymer. However, its high permeability towards CO_2 with capability to be self-supporting since it is glassy polymer means it is suitable to be used as a gutter layer as noted by Mohd Shafie et al. (2019). Gutter layer is normally used in thin film composite to overcome the limitation on lateral diffusion and pore penetration by the selective layers. It is important to ensure that the gutter layer can enhance the overall performance of the membrane such as having high permeability and selectivity. Gutter layer can increase the permeability of the gases but at the cost of reduced selectivity between the gas pair especially when the porous support has low porosity (Kattula et al., 2015; Yoo et al., 2018). Understanding in anisotropic design of PMP membrane is crucial to create a thin dense layer with controllable dense skin thickness and porous substructure with minimal resistance as this will open the possibility of PMP research on its own anisotropic Loeb-Sourirajan membrane and as co-gutter substrate layer in TFC membrane for CO_2 separation.

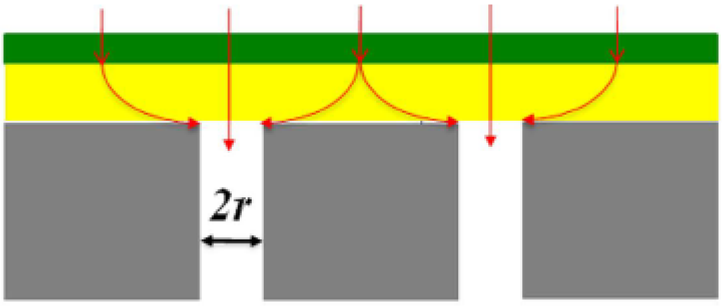

Figure 2.5: Schematic diagram of typical gutter layer as selective layer on TFC membrane (Kattula et al., 2015).