POLY(4-METHYL-1-PENTENE) MIXED-MATRIX MEMBRANE FABRICATION WITH SILICA NANOPARTICLE FILLER FOR CO_2/N_2 GAS SEPARATION APPLICATION

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by

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Reasmyraj A/P R Subramaniam

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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

6FPAI	fluorinated poly(amide-imide)
BPPO	Brominated poly(2,6-diphenyl-1,4-phenylene oxide)
C60	Fullerence
CA	Contact angle
CCP	Climate change power
CFC	Chlorofluorocarbons
CH_4	Methane
CHA	Chabazite
CMS	Carbon Molecular Seive
CNT	Carbon nanotubes
CO_2	Carbon dioxide
CSM	Carbon silica nanocomposite
DDR	Deca-Dodecasil 3 Rhombohedral
DI	Deionized water
EO	Ethylene oxide
FAU	Faujasite
FER	Ferrierite
GHG	Greenhouse gases
GO	Graphene oxide
GPU	Gas permeance unit
H_2SO_4	Sulphuric acid
HFM	Hollow Fiber Membrane
LTA	Linde type A
MFI	Mobil Five
MI	Matrimid
MMM	Mixed Matrix Membrane
MMT	montmorillonite
MOF	Metal Organic Framework
MOR	Mordenite
MWCNT	Multi-walled carbon nanotubes
N_2	Nitrogen

NP	nanoparticles
PAA	Polyamid acid
PDMS	Polydimethylsiloxane
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PEOPBT	Poly(ethylene oxide)-poly(butylene terephthalate)
PES	Polyether sulphone
PI	Phosphoinositides
PMP	Poly(4-methyl-1-pentene)
PSF	Polysulfone
PU	Polyurethane
PVA	Polyvinyl alcohol-titanium
SEM	Scanning Electron Microscopy
SF_6	Sulphur hexafluoride
SiO_2	Silica nanoparticles
SWCNT	Single-walled carbon nanotubes
TEOS	Tetraethoxysilane
TFC	Thin Film Composite
T_g	Glass transition temperature
TiO_2	Titanium Dioxide
ZnO	Zinc oxide
6FPAI	Fluorinated poly(amide-imide)

FABRIKASI MEMBRAN MATRIKS CAMPURAN POLI(4-METIL-1-PENTENA) DENGAN PEMUAT NANOPARTIKEL SILIKA UNTUK APLIKASI PEMISAHAN GAS CO_2/N_2

ABSTRAK

Pemisahan karbon dioksida (CO_2) dari gas serombong dengan penggunaan teknologi membran telah menjadi tumpuan para penyelidik sejak beberapa dekad yang lalu kerana penggunaan tenaga yang lebih rendah dan alternatif yang lebih murah. Dalam tesis ini, membran matriks campuran (MMM) poli (4 -metil- 1 -pentena) (PMP) dengan pemuat nanopartikel silika dikaji untuk menentukan kemungkinan menggunakan MMM untuk memisahkan CO_2 dari gas nitrogen (N_2). Kelikatan larutan dengan pelbagai PMP wt. % diukur untuk mencari kepekatan polimer kritikal. Untuk mengesahkannya, membran PMP dengan pelbagai PMP wt.% difabrik pada suhu bilik dan diuji menggunakan pelbagai tekanan untuk menentukan kesan tekanan dan kepekatan polimer pada lapisan membran yang padat. Sudut kontak air dan FTIR-ATR dilakukan untuk mencirikan membran PMP dan membran MMM yang telah dibuat. Sudut kontak air dari kedua-dua permukaan membran tanpa pengubahsuaian seperti rawatan plasma atau sautan adalah antara 111° dan 114° yang menyebabkan membran diklasifikasikan sebagai membrane hidrofobik. Imej SEM di permukaan membran PMP tidak menunjukkan perbezaan yang signifikan antara pelbagai kepekatan PMP manakala imej SEM keatas keratan rentas membran PMP menunjukkan bahawa apabila PMP wt. % meningkat, ketebalan PMP turut meningkat. Tren rembesan gas CO_2 dan N_2 serta selektivitinya tidak banyak berbeza dengan tekanan yang berbeza. 7 wt.% PMP yang dibuat pada suhu bilik merupakan kondusi terbaik untuk membuat MMM berdasarkan keputusan test rembesan gas. Rembesan CO_2 dan N_2 masing-

masing adalah 3.51 ± 0.15 GPU dan 0.29 ± 0.02 GPU dengan selektivitinya CO_2/N_2 sebagai 12.04 ± 0.26. Kondusi tersebut kemudian digunakan untuk membuat MMM dengan pemuatan pengisi yang berbeza-beza. Rembesan CO_2 dan N_2 meningkat serta selektiviti CO_2/N_2 meningkat berbanding membrane PMP. Pengimejan SEM digunakan untuk memerhatikan kesan kepekatan nanopartikel silika pada ketebalan MMM dan juga aglomerasi. Apabila kepekatan pengisi (wt. %) meningkat, ketebalan membran hampir serupa tetapi aglomerasi meningkat. Dengan pemuatan 7.5 wt. % silika pada tekanan 1 bar, MMM memberikan keputusan penyerapan gas yang terbaik. Rembesan CO_2 adalah 13.88 ± 0.45 GPU dan rembesan N_2 adalah 0.59 ± 0.01 GPU yang menjadikan selektiviti ideal tertinggi menjadi 23.34 ± 0.34 dengan sedikit penyelewangan. Dalam penyelidikan kami, kami menyimpulkan bahawa MMM lebih sesuai dibandingkan dengan membran PMP untuk aplikasi pemisahan gas CO_2/N_2.

POLY(4-METHYL-1-PENTENE) MIXED-MATRIX MEMBRANE FABRICATION WITH SILICA NANOPARTICLE FILLER FOR CO_2/N_2 GAS SEPARATION APPLICATION

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, mixed matrix membrane (MMM) of poly(4-methyl-1-pentene) (PMP) with silica nanoparticles was studied to determine the feasibility of using MMM to separate CO_2 from nitrogen (N_2) gas. Viscosity of solution with various PMP wt.% was measured to find the critical concentration of polymer. To confirm that, a full dense PMP membrane with various PMP wt.% was fabricated at room temperature and tested using various feed pressure to determine the effect of pressure and polymer concentration on dense layer of the membrane. Water contact angle and FTIR-ATR was used to characterize the fabricated PMP membrane and MMM membrane. The water contact angle of both membrane surface without modification such as plasma treatment or coating that have been obtained ranged between 111° and 114° which makes the membrane to be classified as hydrophobic membrane. The SEM image on the surface of pristine PMP membrane showed no significant difference between various PMP concentrations. The SEM images on the cross section of the pristine PMP membrane showed that when PMP wt.% increases, the thickness of the pristine PMP increases as well. The trendline of gas permeance of CO_2 and N_2 as well as the selectivity does not differ greatly with feed pressure. 7 wt.% PMP fabricated at room temperature seems to be the best condition to fabricate MMM based on the gas permeance test. The CO_2 and N_2 permeance is 3.51 ± 0.15 GPU and

0.29 ± 0.02 GPU respectively, and with CO_2/N_2 selectivity as 12.04 ± 0.26. The parameter was then used to fabricate MMM with varying filler loading. The CO_2 permeance and the N_2 permeance increased as well as the CO_2/N_2 selectivity increased compared to pristine PMP. SEM imaging is used to observe the effect of silica nanoparticles concentration on the thickness of MMM and the agglomerations as well. When filler concentration (wt.%) increases, the thickness of membranes were almost similar but the agglomerations increase. With 7.5 wt.% silica loading at 1 bar, the MMM seems to give the best gas permeance performance. The permeance of CO_2 is 13.88 ± 0.45 GPU and the permeance of N_2 is 0.59 ± 0.01 GPU which makes the highest ideal selectivity to be 23.34 ± 0.34 with less deviation. In our research, we conclude that MMM is more suitable compared to pristine PMP for CO_2/N_2 gas separation application.

CHAPTER 1

INTRODUCTION

1.1 Carbon Dioxide Gas Separation

Due to the obvious growing worry about climate change, reducing greenhouse gas emissions, which are mostly made up of CO_2, has gotten a lot of attention in recent years (Rezakazemi et al., 2018). In 2018, the global CO_2 concentration reached an all-time high which is 407.8 ppm (Lamb et al., 2021). There has been a lot of research on the enhancement of technologies for selective CO_2 capture and separation. The highest percentage of greenhouse gases, according to the pie chart in Figure 1.1, is carbon dioxide due to human activities (Nematollahi et al., 2016). According to Nematollahi et al., (2016), fossil fuels, natural gas, petrochemicals, power plants, and coal resources may all be considered important emitters of harmful greenhouse gases into the environment. To extract CO_2 from flue gas, it is passed through a succession of membranes to separate it from nitrogen (N_2) or sulphur oxide (SO) (Zuwairi & Rahman, 2017).

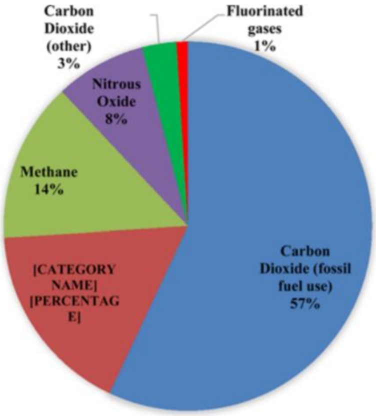

Figure 1.1 Composition of greenhouse gas emissions due to human activity (Nematollahi et al., 2016).

Membrane is a thin film that acts as a selective barrier to allow the desired molecule to pass through the membrane while retaining unwanted molecules on the surface of the membrane. Membranes are used to separate solute–solvent, solute–solute, particle–solute, and particle–solvents in a variety of applications ranging from industrial to everyday life, including water treatment for domestic and industrial water supplies, chemical, pharmaceutical, biotechnological, beverages, food, metallurgy, and other separation processes (Saleh & Gupta, 2016). Membrane separation has a broader industrial and environmental applicability because of its advantages as smaller operating units, less technical complexity, minimal fire or explosion concerns, efficient process design, as well as effective and uniform separation (Mazinani et al., 2018). Other benefits include reduced footprint, easier to scale-up, no moving components, minimal energy, and simple to handle (Sainath et al., 2021). In addition, the technique may be used in conjunction with other separation methods to create hybrid processes. Concentration polarization and membrane fouling, as well as short membrane lifespan, selectivity, and flow, are some of the challenges that this technology faces (Saleh & Gupta, 2016).

Polymeric membrane technology is gaining popularity because of its variety of applications as they are low-cost and easy to produce in large-scale modules. Polymeric membranes have been created for use in a wide range of industrial applications, including microfiltration, ultrafiltration, reverse osmosis, and gas separation (Carreon, 2017). The use of polymeric membranes to treat gas streams for gas separation has become commonplace in various sectors due to their great efficiency (Vinoba et al., 2017). However, one of the biggest drawbacks of today's polymeric materials is their low endurance for high temperatures. During the gas separation process, many hot gas streams in all chemical industries are at a high temperature. Membrane-based separation methods are ineffective for many of these streams. In certain cases, the process streams are just chilled to permit a membrane gas separation process before being heated again. This chilling followed by re-heating causes the waste of a large amount of energy and expenses (Rezakazemi et al., 2018). Fouling, compaction, chemical degradation, and thermal instability reduce the effectiveness of polymeric membranes over time. Polymeric membranes have not found usage in separation procedures involving hot reactive gases due to their low thermal stability and sensitivity to abrasion and chemical attack. As a result, inorganic membranes have become more popular (Carreon, 2017).

Separating gas mixtures with inorganic membranes differs from that of polymeric membranes, where pores may be generated from the movement of polymer chains (PS Lee, 2017). Inorganic membranes often have substantially larger gas fluxes than polymeric membranes, besides having well-known thermal and chemical stabilities. Examples of commercial porous inorganic membranes are alumina, silica, titanium, glass, stainless steel and silver. These membranes are characterized by high permeability but low selectivity (Carreon, 2017). As for example, inorganic membrane has been applied on large scale for uranium isotope enrichment in Manhattan Project in the 1940s. The inorganic membrane acts as a porous media which separates the uranium isotope through the difference in diffusivity which is governed by Knudsen diffusion. As a result, the selectivity of the separation is not effective and it requires over 1000 stages just to get about 3%-4% enrichment (Carreon, 2017; Keizer et al., 1988; Wu, 2018). The main problem with inorganic membrane is that it’s manufacturing technique is difficult and expensive compared to polymeric membrane (Jusoh et al., 2016). Therefore, the development of mixed matrix membranes (MMMs) based on the incorporation of inorganic fillers into the polymer matrix has emerged as a viable option for overcoming the constraints of both polymeric and inorganic membranes in gas separation (Pazani & Aroujalian, 2020).

The development of mixed matrix membrane (MMM) in the gas separation process has drawn great attention for CO_2/N_2 separation due to its promising properties. MMM consists of a polymer as the continuous matrix phase, whereas the inorganic filler serves as the dispersed phase. While developing MMM, interface adhesion between polymer and inorganic filler, good dispersion, suitable particle size and appropriate loading of inorganic filler in polymer phase should also be taken into account (Jusoh et al., 2016). Various research on MMM has proven to show increased gas permeability and selectivity performance (Rosyadah Ahmad et al., 2016; Muthukumaraswamy Rangaraj et al., 2020; Julian et al., 2019). However, despite of the potential observed by incorporating inorganic filler into the polymer matrix, MMM still faced several fundamental problems such as the incompatibility between polymer and the filler, agglomeration of the filler, formation of non-selective voids, interfacial defect, leaching as well as scalability (Ahmad et al., 2018; Salahshoori et al., 2021; Sainath et al., 2021; Goh et al., 2011; Jusoh et al., 2016). Thus, in order to enhance separation performance and physical parameters of the fabricated MMM, suitable consideration of inorganic filler and polymer is critical during MMM synthesis. In this case, silica nanoparticles have been chosen as fillers because of their good physical and chemical properties, as well as potential improvement for permeability and selectivity of the membrane (Salahshoori et al., 2021; Beltran et al., 2013).

Researchers are currently studying a gas separation membrane to remove CO_2 from flue gas or syngas generated industrially in order to increase the membrane's practicability. CO_2 separation from N_2, CO_2 separation from methane (CH_4), and CO_2 separation from sulphur hexafluoride (SF_6) are all common research topics (The Editors of Encyclopaedia Britannica, 2020). Carbon dioxide is utilised in a variety of technologies such as food industry, fumigant, anti-fire, water treatment, and fluid in circuits (Aresta & Dibenedetto, 2010). In food industries, CO_2 is used for additives to carbonate beverages, food packing and dry ice (N Kaliyan et al., 2013). CO_2 is used as a fumigant instead of other medications, which have a complicated molecular structure and produce a lot of waste, or very hazardous substances such as methylbromide, cyanidric acid, methylisocyanide, formaldehyde, and sulphonylfluoride (Aresta & Dibenedetto, 2010). For anti-fire technology, carbon dioxide is used in fire extinguishers to extinguish Class B and Class C flames (The Editors of Encyclopaedia Britannica, 2020). In addition, CO_2 is used for basic water treatment, it is usually a substitute for sulphuric acid (H_2SO_4) since CO_2 has the same neutralization power as H_2SO_4 to avoid the accumulation of sulphate (Enyi & Appah, 2007). Apart from that, the other benefit of CO_2 is a substitute for other chemicals such as chlorofluorocarbons (CFC) in terms of climate change power (CCP) reduction, considering that the CCP of CFC is 8500 times higher than CO_2 (Aresta & Dibenedetto, 2010). 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 purposes as listed in the example above instead of releasing it to the atmosphere which will contribute to air pollution and greenhouse gas effect.

1.2 Problem statement

CO_2 is one of the greenhouse gases (GHGs) that contributes to climate change. An international agreement known as the Kyoto Protocol was established in 1997 that aims to reduce the concentration of CO_2 and the presence of GHGs in the atmosphere. Following this, industry has adopted various strategies to reduce CO_2 emission to the atmosphere including cryogenic distillation (Aaron & Tsouris, 2005), pressure-swing adsorption (Ho et al., 2008), solvent absorption and many more. However, these conventional processes are not very economic from an industrial point of view as it involves extreme operating conditions and the use of solvents. Hence, membrane seems as a better alternative as it eliminates the needs of energy intensive processes (Dharupaneedi et al., 2019).

Polymeric membrane is favoured for gas separation due to its processability and easy fabrication method (Vinoba et al., 2017). To obtain high flux of gas separation, the selective layer of the membrane needs to be as thin as possible while the porous layer acts as the support. Despite that, the performance of polymeric membranes is still bounded by the famous Robeson's upper bound (Robeson, 2008). Furthermore, their thermal instability and susceptibility to chemical attack cause the limitation of polymeric membrane application in the separation process involving the hot reactive gases (Pandey and Chauhan 2001, Nasir et al. 2013). Inorganic membrane has shown excellent perm selectivity property as well as thermal and chemical stability, but the major constraint is in its application because of its high production cost and difficulty in processing (Aroon et al. 2010, Yeo et al. 2012, Zhang et al. 2013). To overcome these problems, researchers have studied various inorganic and nanofillers to be incorporated into the polymeric phase to fabricate mixed matrix membrane (MMM) (Chawla et al., 2020). However, the main barrier of MMM is the compatibility between the polymer phase and the filler as well as its scalability (Jusoh et al., 2016). Hence, overcoming this issue will improve the feasibility of MMM to be used for gas separation application while improving the properties of the pristine polymeric membrane.

The dense polymeric membranes are produced mainly by dry phase inversion or solvent evaporation method which is a slow liquid-liquid demixing process. Thin dense PMP membrane is susceptible to mechanical failure and rupture at high pressure.

To overcome these boundaries, silica nanoparticles which are inorganic fillers are dispersed into PMP membrane to produce alternative membrane with better separation properties. The polymer-inorganic filler interaction enhances the gas separation performance (Vinoba et al., 2017). On the other hand, based on the nature of the fillers, these interactions also may cause reverse effects and reveal poor performances. Therefore, filler loading is necessary to be controlled in order to increase the permeability and selectivity of the membrane. These parameters will determine the feasibility of the study to produce PMP MMM for CO_2 and N_2 gas separation by conducting gas permeance tests 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 dense polymeric membrane at various PMP wt.% through dry-phase inversion method.
2. To investigate the effect of operating pressure towards the performance of the membrane.
3. To determine the optimum filler loading (wt.%) for fabrication of MMM.
4. To calculate the permeability and selectivity of the CO_2/N_2 gases for all membrane fabricated.

1.4 Scope of thesis

Application of MMM has been widely studied due to its potential to overcome the barriers cause by polymeric membrane and inorganic membrane. Thus, understanding the parameter that affect the structure and performance of the MMM is important. The scope of this project is to determine the optimum parameter such as the polymer concentration, and filler concentration to fabricate MMM and also feed pressure to get optimum performance of the membrane. In order to determine the best polymer concentration, viscosity of various PMP concentration was recorded and the critical concentration was determined. Then, a full dense PMP membrane is casted and subjected to individual gas permeance test with varying feed pressure 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 to produce MMM. SEM micrograph is also conducted on the dense PMP membrane to study the surface structure and cross-sectional structure.

After the best polymer concentration is determined, the parameter is then chosen to fabricate MMM with silica nanoparticles by manipulating fillers concentration from 2 to 15 wt.% with varying feed pressure. The fabricated MMM is similarly put through 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 filler loading concentration to produce MMM and the best feed pressure to use while gas separation process.

CHAPTER 2

LITERATURE REVIEW

2.1 Fabrication Design of Polymer

A selective barrier in the shape of a thin layer film or a thin sheet that is found between two phases regardless of whether it is in the state of vapour, gas or liquid is known as a membrane. This membrane acts as an interface between two sides which is the feed and permeate to regulate the transportation of the components between them where it only allows specific molecules or substances to pass through while holding back the remaining substances. Membranes are often utilised to separate certain gases such as CO_2, N_2 and CH_4 from the mixture of gases of flue gas, biogas upgrading process and hydrogen purification through the permeation difference of the substances in them (Carreon, 2017). There are few advantages of this specific gas separation method application such as the consumption of less energy and capital investments (Mustafa et al., 2016). Membrane separation also offers a simple operation that eases the gas separation process. Hence, this technology is vastly applied in various industries and plays a significant role considering the economic needs of an industry as gases are commonly found in various chemical industries.

When it comes to the selection of membrane for the separation of gas, the permeability and the selectivity plays a considerable role as it influences the efficiency of the gas separation process. This intrinsic property is known as Robeson upper boundary. Some membranes consist of small pores to ease the separation process between tiny particles while some contain bigger pores for bigger particles and some membranes do not contain pores (Robeson, 2008). Porous membranes show relatively high flux levels but offer a low selectivity. Thus, membranes are commonly used to separate various substances regardless of their nature such as solute-solute, particles-solvents, particle-solute and solute-solvent by considering the permeability and selectivity of the gasses (Saleh & Gupta, 2016). In addition, when it comes to the material of the membrane for the application of gas separation, it can be grouped into two classes which are inorganic membrane and polymeric membrane. Polymeric membranes are massively used in big scale applications due to its low cost (Mohammad et al., 2018). In comparison to polymeric materials, inorganic materials have better chemical, mechanical, and thermal stability (Li et al., 2016). These materials, on the other hand, have the shortcomings of being extremely brittle and being more expensive than organic materials. Moreover, when the treatment and disposal of both the polymeric and inorganic membranes are compared, the latter has significantly lesser impact on the environment as it is more durable (Wu, 2018). Table 2.1 shows the advantages and the disadvantages of polymeric and inorganic membranes.

Table 2.1 Pros and cons of inorganic and polymeric membranes (Vinoba et al., 2017)

Type of membranes	Pros	Cons
Organic	● Easy to synthesis and fabricate ● Good mechanical properties ● Low cost	● Low chemical and thermal stability ● Low resistance to high temperature ● Plasticization effect with condensable gas such as CO_2, N_2 and CH_4
Inorganic	● High temperature capability	● Costly

	● High resistance to chemicals ● Can operate at harsh conditions	● Easily breakable ● Difficult to process

2.1.1 Dense Membrane

Dense membranes consist of dense structure consisting of no detectable pore with the scanning of electron microscopy. A mixture of gases is transported across the dense membranes by diffusion under the driving force of a pressure difference, concentration of polymer difference or electrical potential gradient (Baker, 2004). Here, we are going to differentiate two type of membranes which have two types of structures which are symmetric or an asymmetric structure. The first type has a standardised arrangement and structure across the whole cross section, and the flux is established by the thickness of the membrane. This type of membrane is known as homogeneous or dense membranes. The membrane with asymmetric structure is made up of a thin and dense selective layer which is known as skin layer that is supported by a considerably thick microporous support layer to provide mechanical support (Li et al., 2016). The surface layer performs the separation, and it is the principal barrier to the flow through the membrane. (Strathmann et al. 2006). Metallic membranes, mainly palladium alloy membranes used for hydrogen separation, are among the dense inorganic membranes that have been extensively explored during the last decade (Li et al., 2016).

The phase inversion procedure and coating technique are some of the methods used to create dense polymeric membranes. A regulated conversion of a polymer from a fluid to a solid state is known as phase inversion. The transition from one liquid state to two liquids which is also known as liquid-liquid demixing is usually initiated for the solidification process. At a certain point during demixing process, either of the liquid phases, usually phase that consist higher polymer concentration, will solidify forming a solid matrix (Purkait et al., 2018). A two-step technique is required to create a dense membrane via coating (Li et al., 2016). Coating is a process to create thin and dense structures for high gas flux separation. The first step is to create an appropriate porous support using phase inversion, and the second is to create a barrier layer on the support's surface. Dip coating, spray coating, spin coating, grafting, plasma polymerization, interfacial polymerization, and in situ polymerization are some of the processes that can be utilized to create these membranes (Mulder, 1996).

The pore size of a membrane for gas separation application needs to be very small (up to the magnitude of ~10^-10 (Å)) in order for the separation to happen. In general, microporous membranes are not appropriate for gas separation application because the pore size of the membrane is still too large to allow gas separation. A dense membrane is always recommended for gas separation processes. Usually, the selectivity of the gas pair to be separated is extremely high when using a dense membrane depends on the polymer used. The fundamental disadvantage of thick dense membrane is its low gas flux. Despite its efficiency in separating gases, the thick dense layer of membrane with very low flux, making it not suitable for industrial use. This is because low flux and a thick dense layer will necessitate a long working period combined with a high transmembrane pressure, resulting in a high operating cost. However, dense membranes are still being utilised in laboratory work to study on the performance of membranes and characterise membrane properties (Amaliyyah, 2021).

Therefore, to boost the flux, several parameters can be manipulated. A few common examples of parameters that are usually being tested are the operating conditions such as pressure difference, temperature difference and concentration difference of the materials used to fabricate the dense membrane. Increasing the pressure will increase the flux, but it will also raise the operating cost from an economic standpoint as mentioned before. In addition, the flux can be improved by reducing the thickness of the membrane and increasing the effective surface area. The thickness of membrane can be controlled by the concentration of materials used to fabricate the membrane. Nonetheless, at greater working pressures and thin dense membranes are prone to collapsing which leads to necessitating the use of a support such as fillers to ensure that they function properly. Consequently, anisotropic membranes are preferred over dense membranes in some cases for gas separation applications (Gugliuzza & Basile, 2013).

2.1.2 Anisotropic Membrane

Anisotropic membrane is one with pore sizes that vary throughout the membrane structure. Anisotropic membranes have a number of layers that are often made up of one or different polymer material, each of which can be adjusted separately and with different structures and also permeability. The membrane typically has a moderately dense, extremely thin surface layer also known as the permselective layer built on an open, considerably thicker, porous substructure. The top layer controls all separation features and permeation rates, whereas the substructure serves mostly as a mechanical support with little separating function. The thin surface layer influences the resistance to mass transfer. It is possible to make the membrane thick enough to resist the compressive forces employed in separation. The thin film is always on the high-pressure side of the membrane, which is the feed side, because this makes the most use of the support layer to stabilise the thin film.

Phase inversion method are the most commonly used in the fabrication of the anisotropic membrane too. The liquid-liquid demixing stage, which is commonly explained using a ternary diagram, determines the membrane structure. When a delayed liquid-liquid demixing occurs, the polymers typically form a sponge-like shape during membrane development. The membrane formation takes longer since the solvent evaporation process is slower, which result in a dense structure. Fast liquid-liquid demixing will cause the polymers to have less time to arrange themselves in a more orderly manner, often resulting in a finger-like structure in the membrane (Idris et al., 2017). The advantage of applying anisotropic membrane is that it has a high mechanical strength with a high flux which will be very advantageous for the separation process. Conversely, the disadvantages are that it requires an accurate control throughout the demixing process in order to fabricate the dense skin layer with the support of the microporous. Thick membranes usually lead to the formation of the macrovoid during the demixing process (Conesa et al., 2007).

Thin Film Composite (TFC) is essentially a single thin dense layer that is usually supported by another microporous membrane structure. Therefore, it is made up of two different polymer materials. TFC can be made in a variety of ways, which includes chemical reactions, interfacial polymerization, dip coating and plasma treatment, as well as three less prevalent methods such as chemical vapor deposition, sputtering, and spray pyrolysis (Khulbe & Matsuura, 2018). Even while TFC has a competitive edge in terms of composite design, it still has drawbacks. The lateral gas permeant diffusion at the composite interface is the first issue that may develop. The implantation of the selective layer solution on the surface of the microporous support, which would reduce the permeation of gas flux across the membrane, is another issue that could occur. The compatibility of the solvent employed as the specific layers with the fundamental support is also critical for TFC to work as intended (Idris et al., 2017). Figure 2.1 shows the schematic diagram of dense membrane and anisotropic membranes.

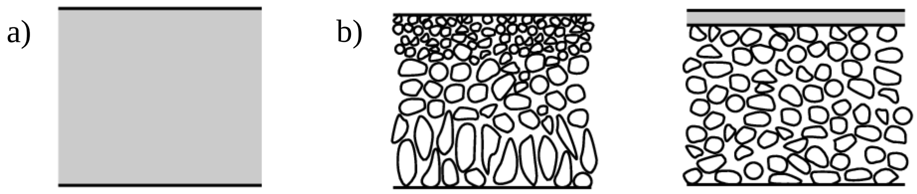

Figure 2.1 a) dense membrane, b) anisotropic membranes (Afzali et al., 2015)

2.1.3 Flat Sheet Membrane vs Hollow Fiber Membrane

Flat sheet are the most common geometries for asymmetric membranes. These membranes are made from casting a thin coating of a polymer dope solution over a substrate. The thin film membrane is subsequently submerged in a non-solvent which is typically water or a solvent/nonsolvent mixture bath. The final geometry of the membrane is determined by both the dope content and the immersion bath composition. Some of the advantages of flat sheet membranes are that they are easy to fabricate, can be fabricated as dense membrane as asymmetric membrane and easy to study the demixing process. However, the drawbacks of flat sheet membranes are limited permeation area, cannot assemble in stack module and does not allow larger flux separation (Wan et al., 2017). Flat sheet asymmetric membranes have become a significant step forward in membrane technology because they allowed significantly larger fluxes to be achieved than typical dense film membranes without sacrificing structural integrity. Flat sheet membranes are combined into spiral wound modules for most practical, large-scale operations, where the membrane is wrapped around a central perforated tube and fixed into a module housing. The feed gas mixture is then utilised to pressurise the module, where the high permeable gas is preferentially carried across the membrane towards the middle of the tube, while the less permeable gas is retentate (Brinkmann et al., 2013).

During phase inversion, one of the primary problems with this membrane is the creation of pinhole pores in the dense skin separating layer. Pinhole flaws are becoming increasingly relevant as the attempt to develop thinner dense selective layers continues (Linck & Kalika, 2018). These flaws are created by poor polymer chain packing during phase separation, and they dramatically affect the membrane's overall performance by switching the gas transport mode from solution diffusion across the dense skin to Knudsen diffusion through the pinhole pores. This is because Knudsen diffusion only gives a selectivity value that is essentially proportional to the inverse of the square root, of the constituent gases' molecular weights ratio. This shift in diffusion process results in a significant loss of selectivity (Zhu et al., 2011).

Hollow fiber (HF) is also one of the most common membranes used in industry. The HF usually has a membrane coated on the outside of a porous fiber support as shown in Figure 2.1.3. The membrane is often applied to the outside fiber by a dip-coating process in which the polymer membrane is dipped inside a solvent (McKeen, 2012). HF are made in the same way as solution spun solid fibers are made. During HF spinning, an appropriate bore fluid is metered through the center of the dope through a concentric needle, and the polymer dope solution is metered through an annular spinneret using precision syringe pumps. The nascent fiber then flows through an air gap, where solvent evaporation and phase inversion begin at the dope/air interface and the dope/bore contact, respectively. Finally, the fiber is immersed in the primary coagulation bath (typically water), which causes phase inversion on the fiber's outer wall. The fiber is removed out of the bath and wrapped onto a spindle with a water wash once phase inversion is complete. Following the conclusion of fiber spinning, the leftover solvent is removed from the fiber using the same solvent exchange and drying procedure as flat sheet membranes (Linck & Kalika, 2018).

HF membranes have a number of advantages over flat sheet membranes. HF membranes undergo the same concept as flat sheet membranes, but the main difference is presence of air gaps. HF configurations, compared to the flat sheet, are designed for higher fluxes, operated at lower concentrations, cleaned more often and protected by stricter pre-treatment (Chen & Xu, 2019). Moreover, we can stack multiple HF membranes in one module. The fiber has a hollow core membrane shape allowing for a higher surface area to volume ratio, resulting in a larger effective membrane area for a given membrane module size (Li et al., 2021). Therefore, membrane modules become more productive and efficient. Hollow fiber membranes also have a self-supporting structure, making them easier to handle during the manufacturing process (Wan et al., 2017). Since hollow fiber membranes have a modular character, the operation process is flexible and scale-up operation is simple (Bazhenov et al., 2018).

HF on the other hand, have a variety of drawbacks too. One of the most prominent drawbacks is that membrane fouling happens more frequently than with other methods due to the membrane design. Additionally, if the feedstream that goes through the fibre is contaminated in any way, the fouling level will rise much more, especially in HF. Defects such as holes and scratches can frequently happen to HF membranes too. Therefore, coatings are required to cover those defects. For HF membrane, fully dense H membrane is impossible be fabricated. In addition, the capital cost of HF is usually higher than that of other membranes due to its fabrication method where we need high polymer concentration to get a skin layer and reduce macrovoid formation (Demeuse, 2009, Hung et al., 2016). Figure 2.2 shows the cross section of a HF membrane.

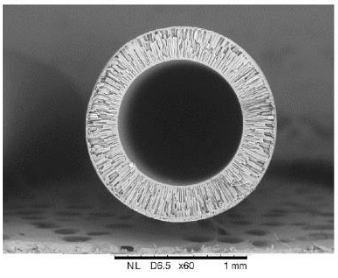

Figure 2.2 Cross section of a HF membrane (Bazhenov et al., 2018)

2.2 Type of Polymer for CO_2 Gas Separation

Membrane gas separation has several advantages over other technologies, including compactness, simplicity, flexible operation and interaction with existing systems, low capital costs, and decreased energy use. It also eliminates the need for potentially costly and difficult-to-handle chemicals. Progress in membrane post-combustion CO_2 capture has been extensively examined from a variety of angles, including advances in membrane material design, process engineering, and engineering economics.

Lately, dense polymeric membranes dominate existing gas separation membrane technology. This is due to polymer materials' appealing combination of low costs, ease of processing, and innovation, as well as their good mechanical stability, ability to form thin films and hollow fibers, and simple scalability. Polymeric membranes can be classified into two classes for practical purposes which are rubbery and glassy. The temperature of the polymer glass transition (T_g) determines the difference between them. A rubbery membrane is an amorphous polymeric material that operates above its T_g under conditions of thermodynamic equilibrium whereas glassy polymeric membranes operate below their T_g. Gas permeability across polymers from both types can vary by several orders of magnitude, and there is a general principle that rubbery membranes are often more permeable than glassy membranes, but membrane overall selectivity shows the opposite trend. Robeson demonstrated this trade-off phenomenon, which he described as an upper bound connection between the log of selectivity versus the log of permeability for a quicker penetrating gas (Robeson, 1991, Robeson, 2008).

Polysulfone, cellulose acetate, polyamides, polyimides, polyacetylenes, polycarbonates, poly(phenylene oxide), poly(ethylene oxides), and polyaniline are some of the polymer membranes that are often used. However, because of their poor performance and scalability, only a handful of them have been investigated for industrial use as commercial membranes. Therefore, the aforementioned barriers must be overcome in order to promote the commercialization of polymer membranes in industrial gas separation processes (Karunakaran et al., 2017).

Segmented copolymers, which are made up of overlapping flexible and rigid segments, are one of the most fascinating types of materials. The segments' microphase separate is due to their incompatibility, resulting in a two-phase system with glassy or semi-crystalline hard segment domains acting as virtual crosslinks and strengthening filler for the rubbery matrix. The properties of these materials can be significantly altered by changing the molecular structure, length, and composition of the segments. Among the segmented copolymers, those with soft segments based on poly(ethylene oxide) (PEO) have piqued interest as potential CO_2 post-combustion collection materials. According to the findings of a study, PEO-based copolymers have strong CO_2 permeability and selectivity for CO_2/N_2. It's also worth noting that membrane gas selectivity is less affected by copolymer structural variation than permeability, which was discovered to be substantially influenced by copolymer morphology. Poly(ether imide)s have drawn particular attention in this group of membrane materials due to the anticipated benefits associated with the presence of polyimide units, as aromatic polyimides have excellent gas transport properties as well as a number of other outstanding properties, including excellent thermal stability, chemical resistance, film forming ability, and mechanical durability (Jankowski et al., 2021).

Another material with good CO_2 separation performance is poly(ethylene oxide)-poly(butylene terephthalate) (PEOPBT) known as polyactive. Polymeric membranes were customized by adding poly(ethylene glycol) (PEG) to PEO-PBT in a controlled manner. The developed membranes have a high CO_2 permeability as well as a good selectivity over H_2 and N_2. Following these two studies, Yave et al., (2010) we discovered that increasing permeability and selectivity using PEG had a limit. The hydroxyl group of PEG tend to establish hydrogen bonds with the ether groups in the copolymer, resulting in a decrease in the amount of free ethylene oxide units and a maximise in CO_2 solubility. Hence, the permeability increase was limited. Other ways were examined to enhance the overall free volume, that is, the static and dynamic free volume of the polymer system, to a considerably greater extent than that seen for Pebax/PEG blends, in order to boost CO_2 permeability without reducing selectivity (Yave et al., 2010).

Polyethersulfone (PES) polymer has recently received a lot of attention in the manufacture of most polymer blend membranes. Surface structure of polyether sulphone ultra-filtration membranes combined with surface modifying macromolecules and separation performance. The porous PES membrane of the hyper thin-skin layer was coated with silicone rubber to create defect-free high performance membranes for O_2/N_2 separation. The primary fabrication parameters in determining skin layer thickness and skin integrity have been found as evaporation time and casting shear. To investigate the separation of ethylene from nitrogen gas, blended polyimide membranes containing PES were prepared and characterized. The addition of PES had no discernible effect on the produced membranes' optimum selectivity. PES with polyamic acid (PAA) blend membranes were made using various PES (25 wt%) and polyamic acid (25 wt%) blending ratios (15 wt%). The mixing ratio of PES/PAA casting solutions had a significant impact on the optimal selectivity. A spin casting approach was used to make PES, Matrimid (MI), and their mixtures, followed by a dry/wet induced phase inversion process (Reads, 2017).

In the field of gas separation polymeric membranes, resolving the upper bound interaction is the subject of significant research. Membrane performance can be increased in the application of CO_2 post-combustion capture by enhancing CO_2 solubility or diffusivity in the membrane. The first method involves adding polar groups to a polymer that can interact with CO_2, hence boosting its solubility in comparison to nitrogen. The second can be accomplished by blocking polymer chain packing while also impeding backbone mobility, allowing smaller CO_2 molecules to diffuse. Various combinations of these technologies have led to a wide range of polymeric membranes with great carbon capture potential (Jankowski et al., 2021).

Regardless of blend composition, N_2 permeance rose as feed pressure increased. For instance, in a study by Kapantaidakis & Koops, (2002), they discovered that an increase in feed pressure, the perm selectivity of PES/MI (30/70 wt%) reduced from 5.4 to 4.9. Dry/wet spinning can be used to make polyethersulfone–polyimide hollow fibers. At room temperature, the developed blend hollow fibers have CO_2 permeances ranging from 31 to 60 GPU and CO_2/N_2 selectivity ranging from 40 to 35. The chemical cross-linking of dual-layer Polyimide/Polyethersulfone hollow-fiber membranes for gas separation was changed. Chemical cross-linking of dual-layer hollow fibers resulted in a reduction in permeance but greatly improves CO_2/N_2 and especially CO_2/CH_4 selectivity in pure gas tests (Kapantaidakis & Koops, 2002).

Generally, these polymers are limited by the Robeson upper boundary aspect. These strategies include the polymer blend, although feasible to be applied but it has its own constraints due to its miscibility (Yong & Zhang, 2021). Therefore, mixed matrix membrane is advantageous and offers simplicity along with effectiveness to overcome the Robeson upper boundary.

2.2.1 Mixed Matrix Membrane (MMM)

Mixed matrix membranes (MMMs) must be carefully constructed and regulated to achieve high efficiency in terms of the evolution of appropriate characteristics and chemical structure for exceptional productivity of gas separation by membranes. To increase industrial applicability, high-performance membranes with improved gas permeability and selectivity are required. Polymeric membranes' weaker perm selectivity and inorganic membranes' mechanical deficiencies have prompted more study into MMM. A solid-solid system constituted of an inorganic phase integrated into a polymer matrix is known as an MMM. The first report on MMM gas separation research was published in the 1970s, when a delayed diffusion time lag effect for CO_2 and CH_4 was identified in an MMM made up of the rubbery polymer polydimethylsiloxane (PDMS) and zeolite 5A. In comparison to the pure polymeric membrane, this membrane had increased permeability, selectivity, or both. This was accomplished by integrating inorganic elements, which have intrinsic greater separation qualities, into a polymer with improved mechanical properties and flexibility (Esmaeili, 2019).

In the creation of mixed-matrix membranes, selection of materials for both the polymer matrix and inorganic filler phases is critical. Inorganic materials that have been employed as fillers in MMM manufacturing include porous and non-porous materials. Palladium and its alloys, silver, nickel, and stabilized zirconia can all be used to make membranes. They are employed in the separation of gases. Dense ceramic membranes, for example, are utilized in the separation of oxygen from air and hydrogen gas from a mixture. Since their low permeability, they are limited in their industrial applications. Porous membranes, on the other hand, are used in industrial applications due to their molecular sieving capabilities, which include high permeabilities and selectivity.

Ceramic has a high chemical and thermal stability. This allows them to be expose to harsh operating condition such as high operating temperature, separation of hostile media like acids, strong solvents and corrosive substance. Porous membranes, such as silica, zeolites, and carbons, are given special attention because they appear to be promising in the separation of gases in real-world applications.

Silica-based membranes, for example, selectively separate hydrogen from other gases. Permselectivity between similar-sized molecules, such as oxygen and nitrogen, appears to be insufficient and undetectable in real-world applications. Carbon molecular sieves made from pyrolysis of thermosetting polymers like polyacrylonitrile, poly(vinylidene chloride), perfluoroalkoxy polymer, cellulose, cellulose triacetate, saran copolymer, and phenol formaldehyde resins, or from coals like coconut shell, show promise for gas separation in adsorption. The size and pore dimensions of carbon, and hence the molecular sieving effect, are influenced by a number of factors (Saleh & Gupta, 2016).

Based on the size and form of the gas molecules, the molecular sieve property of porous inorganic fillers influences the gas separation method. The adsorption and selective surface flow mechanisms are important when the filler pore size is much bigger than the gas molecule size. Porous filler materials are classified as rigid or flexible based on their structure. Metal organic frameworks (MOFs) are a type of flexible inorganic material that has recently been investigated (Bastani et al., 2013). Metal ions are linked to organic ligands to generate MOFs, which are flexible frameworks with variable pore geometries. This type of filler includes ZIF-8, ZIF-11, MIL-88, MIL-53 (Al), ZIF-L, and MIL-53 (Cr). Zeolite and carbon molecular sieves (CMS) are rigid fillers that have been employed as porous inorganic materials in the fabrication of MMMs (Esmaeili, 2019).

Non-porous inorganic materials can cause the matrix tortuous pattern to increase and the diffusion of bigger molecules to diminish. Nano-sized non-porous fillers can enhance void volume by disrupting polymer chains, resulting in a faster gas diffusion rate. Silica, titanium dioxide (TiO_2), graphene oxide (GO), and clay are the most common impermeable inorganic fillers used in MMM gas separation applications (Hashemifard et al., 2011). The interaction of organic and inorganic phases at the interface, on the other hand, is a complicated issue that has an impact on gas separation performance. Poor contact between the two phases can result in flaws, allowing gas to bypass via voids and lowering permselectivity (Bastani et al., 2013). Figure 2.3 shows a schematic diagram of a mixed matrix membrane where the green spots are fillers and the box is polymer while Figure 2.4 shows the common defect that arise from incompatibility between the fillers.

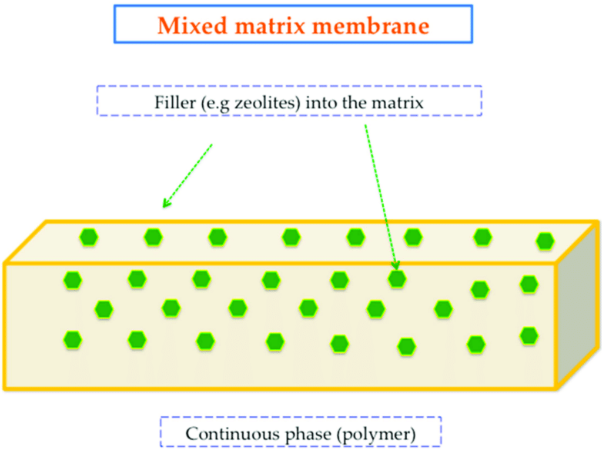

Figure 2.3 Schematic diagram of mixed matrix membrane (Castro-Muñoz & Fíla, 2018)