DEVELOPMENT OF ASYMMETRIC POLYETHERSULFONE (PES) MIXED MATRIX MEMBRANE FOR O_2/N_2 SEPARATION

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Gas Technology).

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledge. This thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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To arwah Mak and Ayah : Shobihah binti Hj. Bakar & Che Bahar bin Embong
"I will love you till the end of time"
To my beloved sibling: Fairuz, Abang Halim, Nurul, Fasihah & Adik Mat
"Thanks for your blessing"

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ABSTRACT

The latest rising of polymer-based organic-inorganic composite membrane materials known as mixed matrix membranes (MMMs), have potentially to combine the easy processability of organic polymers with the excellent gas separation properties of inorganic molecular sieve material. In this study, the development of mixed matrix membranes for oxygen/nitrogen (O_2/N_2) separation by manipulating the different types of zeolite was studied in order to identify the best composition of zeolite. Three types of zeolite were used are 4A, 5A and 13X. To enhance the adhesion of zeolite with polymer matrix and also to modify the surfaces of inorganic material, 3-aminopropyl-trimethoxysilane (APTMOS) was introduced to treat the zeolite prior to dope solution preparation. The polymer solution consists of 30 wt% of polyethersulfone (PES) as polymer, 60 wt% of n-methyl-pyrrolidone (NMP) as solvent, 5 wt% of distilled water as non solvent and 5 wt% of different types of zeolite. Asymmetric flat sheet mixed matrix membranes were fabricated using manually casting through dry/wet phase inversion process. Membrane produce was coated with polydimethylsiloxane (PDMS) to produce defects-free membrane. Then, the membrane was tested with the pure oxygen (O_2) gases and nitrogen (N_2) gases by using the permeation test unit with the feed pressure range between 1 to 5 bars. From the pure gas permeation test result, it shows that the MMMs incorporation with zeolite 4A produce the highest selectivity, which is 3.2 and the lowest selectivity can be achieved using zeolite 13X and the selectivity was 1.7 at the optimum pressure of 2 bars. The differences of selectivity value between difference zeolite are because of the pore size of the zeolite. The morphology of prepared membrane had been identified by using Scanning Electron Microscope (SEM). As a conclusion, by adding the polymer solution with difference type of zeolite will exhibit difference membrane performance. It is because of difference zeolite have difference pore size. It also proves that, by adding zeolite 4A, the selectivity of O_2/N_2 is increased.

ABSTRAK

Peningkatan terbaru dari polimer berasaskan bahan organik-bukan organik komposit membran dikenali sebagai membran campuran matrik (MMMs) mempunyai potensi untuk menggabungkan proses mudah polimer organik dengan kecemerlangan sifat pengasingan gas oleh bahan bukan organik bertapis. Dalam kajian ini, pembangunan membran campuran matrik untuk pengasingan oksigen/nitrogen (O_2/N_2) dengan cara memanipulasikan jenis zeolit dilakukan untuk mengenalpasti komposisi zeolit terbaik. Tiga jenis zeolit yang digunakan dalam kajian ini adalah 4A, 5A dan 13X. 3-aminopropil-trimetoksisilan (APTMOS) telah diperkenalkan bagi meningkatkan perekatan antara zeolit dengan matrik polimer dan juga telah mengubahsuai permukaan bahan bukan organic. Larutan polimer yang digunakan terdiri daripada 30 % jisim poliethersulfona (PES) sebagai polimer, 60 % jisim n-metil-pyrrolidona (NMP) sebagai pelarut, 5 % jisim air suling sebagai bahan tambah bukan pelarut dan 5 % jisim pelbagai jenis zeolit. Asimetrik kepingan rata membran campuran matrik dihasilkan secara manual dengan menggunakan proses fasa balikan kering/basah. Membran yang dihasilkan akan disaluti dengan polidimetilsiloxana (PDMS) untuk menghasilkan membran yang tidak mempunyai kecatatan. Selepas itu, membran tersebut akan diuji dengan gas oksigen asli (O_2) dan juga gas nitrogen (N_2) dengan menggunakan mesin penguji kadar penembusan dengan menggunakan tekanan diantara 1 hingga 5 bar. Keputusan kajian kadar penembusan gas asli menunjukkan bahawa penggabungan membran campuran matrik dengan zeolit 4A menghasilkan kadar pemilihan yang tertinggi iaitu 3.2 manakala kadar pemilihan yang paling rendah telah dicapai melalui penggabungan membran campuran matrik dengan zeolit 13X yang menghasilkan kadar pemilihan sebanyak 1.7 pada tekanan yang maksimum iaitu 2 bar. Perbezaan antara nilai kadar pemilihan antara zeolit adalah kerana saiz liang zeolit. Morfologi membran yang dihasilkan dikenalpasti dengan menggunakan Mikroskop Pengimbas Elektron (SEM). Kesimpulannya, dengan menggabungkan larutan polimer dengan jenis zeolit yang berbeza, prestasi yang dihasilkan oleh membran adalah berbeza kerana zeolit yang digunakan mempunyai saiz liang yang berbeza dan ia juga menunjukkan bahawa dengan penambahan zeolit 4A, kadar pemilihan dan kadar pengasingan adalah meningkat.

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LIST OF SYMBOLS

P_{eff}	Effective permeability
$\emptyset$	Volume fraction of the dispersed phase
α_{eff}	Effective selectivity of mixed matrix membrane
P_{rel}	Permeability ratio of continuous phase to dispersed phase
P	Pressure-normalized flux
Q_i	Volumetric flow rate of gas i
l	Membrane skin thickness
A	Effective surface area
ΔP	Pressure difference
$\alpha_{i/j}$	Selectivity

LIST OF ABBREVIATIONS

PES	Polyethersulfone
SEM	Scanning electron microscope
MMMs	Mixed matrix membrane
CMS	Carbon molecular sieve
APDMES	Aminopropyldimethyl silane
PSF	Polysulfone
O_2	Oxygen
N_2	Nitrogen
STP	Standard temperature and pressure
GPU	Gas permeation unit
APTMOS	Aminopropyltrimethoxysilane
NMP	1-methyl-2-pyrrolidone
PI	Polyimide
PDMS	Polydimethylsiloxane

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

The development of membrane has seen a rapid growth in the separation technology during a few decades. According to Mulder (1996), a general definition of a membrane could be a selective barrier between two phases of selective. Membrane can identify as an interphase between the two adjacent phases which is function as a regulating transport of substances between two compartments (Mathias, 2006).

From the point of view for gas separation, it has shown that polymeric membranes are very useful thus, it is providing the economical alternatives to conventional separation processes (Sangil and Eva, 2005). However, according to Robeson (1991), polymeric membranes have a limitation in the application of gas separation due to the transaction between permeability and selectivity as shown in upper bound curves.

To increase the gas separation membranes performance, recent work has concentrate on the fabrication of polymer membranes by doing some modifications in the physical and chemical structures of polymer films to enhance better separation quality (Spillman, 1990). According to previous researchers, the incorporation of various inorganic materials such as zeolites or carbon molecular sieve into polymer membrane has been applied (Mahajan and Koros, 2000; Mahajan and Koros, 2002; Kulprathipanja and Neuzil, 1988). The latest emerging polymer-based organic-inorganic composite membrane material may potentially surpass the “upper bound” limit (Vu *et al.*, 2003).

In recent times, many researchers have focused on novel polymer-zeolite mixed matrix membrane to overcome the limitations for the reason that the interaction of materials in the matrix membrane and structure-selective catalytic properties of zeolite can support the perselective separations (Murat *et al.*, 1994).

According to previous researcher (Duval *et al.*, 1993), a very uprising effect in the separation oxygen/nitrogen was observed. By blending the poorly selective rubbery polymers with polydimethylsiloxane (PDMS) with silicalite-1 as zeolite, it has shown an increasingly in the ideal selectivity for oxygen. From the results obtained, it has shown that there is an improvement in performance of permeability oxygen and nitrogen for PDMS membranes with zeolite. The permeability of oxygen and nitrogen for PDMS membrane with zeolite are 1370 barrer and 521 barrer while for PDMS membrane without zeolite is 606 barrer and 289 barrer. There was also having improvement in the selectivity performance of oxygen/nitrogen. For PDMS membrane with zeolite, the selectivity of oxygen/nitrogen is 26 while for PDMS membrane without zeolite is 21. Therefore, from the result obtained, it has shown that the hybrid of mixed matrix membrane have give enhancement on permeability for gas separation compared to using conventional polymer membrane.

Thus, as conclusion the suit combination of polymer membrane with adsorbent such as zeolite can give the improvement on mixed matrix membrane. Therefore, it is expected to provide the superior separation performance that suitable for gas separation application.

1.2 PROBLEM STATEMENT

The different types of zeolite used in mixed matrix membrane played an important role in morphology and separation performance. Nowadays, the challenge face by current application of gas separation membrane is to seek out for a higher selectivity and permeability. By blending the zeolite in the polymer solution, it shows that the permeability and selectivity for gas separation have higher improvement. Spillman (1990) has studied in the case pervaporation of ethanol/water mixture using silicon rubber membrane and have found that both ethanol selectivity and permeability were enhanced by the incorporating of silicalite-1 known as zeolite into the polymer membrane. However, the study is limited for one type of zeolite. Therefore, this study is focus on the development of high performance mixed matrix membranes for gas separation by using various types of zeolite to provide enhancement of selectivity and permeability of gas separation. In order to achieve higher performance of polymer membrane for gas separation, the high quality of membrane should use. Hence, it is essential to blend the polymer membrane with zeolite to ensure the permeability and selectivity of gas separation will be increased.

1.3 OBJECTIVE OF STUDY

Based on the research background and problem statement described in the previous section, the following are the objectives of this research:

1. To develop an asymmetric polyethersulfone (PES) mixed matrix membrane for oxygen/nitrogen (O_2/N_2) separation.
2. To study the effect of different types of zeolite in casting solution on the gas separation performance.

1.4 SCOPES OF RESEARCH

In order to accomplish the above mentioned objectives, the following scopes were drawn:

1. Developing new types of membrane by applying differences type of zeolite to fabricate asymmetric polyethersulfone (PES) membrane for gas separation .
2. Characterization of the developed uncoated and coated membrane using pure N_2 and O_2 gases.
3. Study the morphology of the surface layer and cross section of the developed membrane using Scanning Electron Microscopy (SEM).

1.5 RATIONALE AND SIGNIFICANT

It has been shown that, from the point of view of gas permeation, gas separation through a membrane has been hoped to be an environmentally begin and simple process. Membrane separation by polymer membrane is a proven technology and has been found in wide range of industrial applications. Gas separation processes require a membrane with high permeability and selectivity. Traditionally, there has been a trade-off between selectivity and permeability. It is because of “upper bound” limit, which a high selectivity membranes tend to exhibits less permeability and vice versa.

Thus, to improve the gas separation characteristics is to incorporate specific adsorbent such as zeolites into the polymeric matrix. A mixed matrix material with inorganic zeolites or carbon molecular sieves will cause the excellent gas separation properties embedded into the matrix of a polymer. By doing some research on the development of high performance mixed matrix membrane, with the inclusion of different types of zeolite as an adsorbent, it will have the potential to achieve the high selectivity without decrease the permeability of gas. For that reason, we can attain a better gas separation.

CHAPTER 2

LITERATURE REVIEW

2.1 MEMBRANE SEPARATION TECHNOLOGY

The process industries produce a wide variety of chemicals and components which present the manufacturer with a need for separation, concentration and purification of range materials. In the past decade, the simple concept of separation has been introduced such as a membrane to improve or replace the technique of distillation, adsorption, extraction, crystallization and so on (Baker, 2000).

Membrane separation process has attained an important position in chemical technology presently. It has emerging a rapid growth during the few past decades and also was used in a broad range of application. Generally, membrane is a permeable or semi-permeable phase, commonly a thin polymeric solid which is limited to the motion of certain species. This phase is important barrier between the feed stream for separation and one product stream. The relative transport rate of various species is controlled by membrane through itself (Baker, 1991).

There are many significant capability of membrane technology. The improvement capability of membrane appliance will give a much deeper impact on many features of lives in the future. Membranes have significantly different structures. However, they have the common characteristics of selective transports to different component in feed. Membranes may be homogenous or heterogenous, symmetrical or asymmetrical and porous or non-porous. They also can be organic or inorganic, liquid or solid (Mulder, 1996).

2.2 MEMBRANE HISTORY AND CURRENT STATUS

2.2.1 History of Membrane Technologies

The development of membrane process has become an emerging technology. It has been starting growth since early 1748 by Abbe Nolet. Then, it has seen a very rapid progress of this technology by other researchers. Table 2.1 clarify the history of membrane development.

Table 2.1: History of membrane technologies

Year	**Name of inventor**	**Inventor**
1748	Abbe Nolet	• The word 'osmosis' is coined to describe the permeation of water through diaphragm.
Membranes had no industrial or commercial uses in the 19th and early 20th centuries. It only were used as laboratory tools to develop physical and chemical theories. Traube and Pfeffer were made the measurements of solution osmotic pressure with membranes.		
1887	Van't Hoff	• Develop his limit law which the measurements of solution osmotic pressure made with membranes to give the explaination about the behavior of ideal dilute solutions. • Lead directly to Van't Hoff equation.
	Maxwell et al	• Used the concept of a perfectly selective semipermeable membrane in developing the kinetic theory of gases.
1907	Bechhold	• Develop a technique to prepare nitrocellulose membranes of graded pore size which determined by a bubble test.
1903	Elford, Zsigmondy and Bachmann and Ferry	• Microporous collodion membrane was commercially available.
During the next 20 years, the early microfiltration membrane technology was spread out to other polymers such as cellulose acetate. The first significant application of membrane is in the testing of drinking water.		
1960	Loeb-Sourirajan	• Development of membrane industrial process for making defect-free, high flux, anisotropic reverse osmosis membranes. • These membranes consist of an ultrathin, selective surface film on a much thicker but much more permeable

		microporous support which provides the mechanical strength. • The flux of the reverse osmosis membrane was 10 times higher than any of membrane.
1966	Alex-Zaffaroni	a) Found many company were used membrane in the pharmaceutical industry to improve the efficiency and safety of drug delivery.
1980	Monsanto Prism ®	b) Develop membrane for hydrogen separation.
Few years later	Dow	c) Produced systems to separate nitrogen from air.
	Cynara and Separex	d) Produced systems to separate carbon dioxide from natural gas.

Source: Baker (2000)

In the period from 1960 to 1980, the status of membrane technology has seen rapidly growth. It is begun with the original Loeb-Sourirajan technique. There were several membrane formation processes. It was include the interfacial polymerization and multilayer composite casting and coating for making high performance of membrane (Baker, 2000).

2.2.2 Current Status of Membrane Technologies

Membrane technology has more lately been applied commercially to separate individual components. The uses of membrane are varied which it can be locate in different ways. It can be used for separation of mixtures of gases and vapors, miscible liquids (organic mixture and aqueous/organic mixtures) and solid/liquid and liquid/liquid dispersion s and dissolved solids and solutes from liquids (Mulder, 1996). The current status of membrane technologies in industrial application are shown in Table 2.2.

Table 2.2: Current status of membrane technologies

Category	**Process**	**Status**
Developed industrial membrane separation	Microfiltration, ultrafiltration, reverse osmosis, electrodilysis	Well-established unit operations. No major break-throughs seem imminent.
Developing industrial membrane separation technologies	Gas separation, pervaporation	A number of plants have been installed. Market size and number of applications served expanding.
To-be-developed industrial membrane separation technologies	Carrier-facilitated transport, membrane contactors, piezodialysis	Major problems remain to be solved before industrial systems will be installed on a large scale.
Medical application of membranes	Artificial kidneys, artificial lungs, controlled drug delivery	Well-established processes. Still the focus of research to improve performance.

Source: Baker (2000)

2.3 MEMBRANE CLASSIFICATION

Membrane can be classified according to their structure and function. A comprehensive representation of the relationships between pore diameters, membrane separation process and penetrant size is shown in Figure 2.1 (Mulder, 1996).

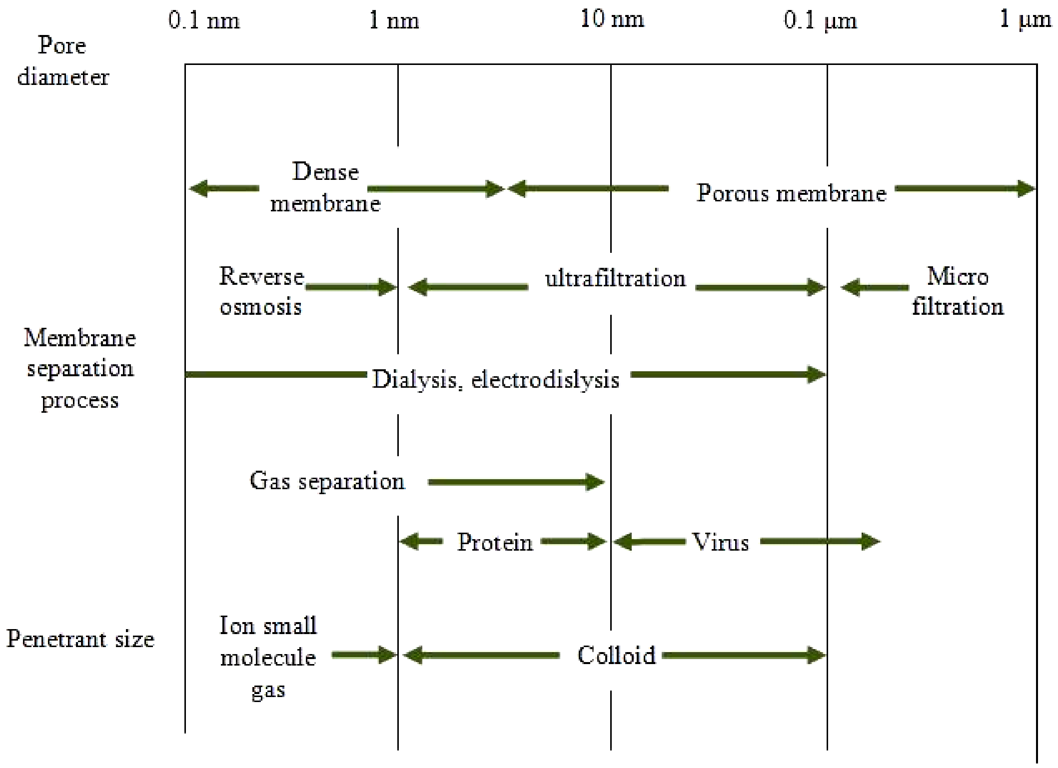


Figure 2.1: Relationship between pore diameter, membrane separation process and penetrant size

Source: Mulder (1996)

According to Mulder (1996), membranes may be homogenous or heterogenous which means the classifying homogenity of a membrane phase. The homogenous membranes specify a homogenous membrane structure parallel and perpendicular to the membrane surface while heterogenous membranes means it have a heterogenous structure. Usually, the degree of heterogenity for various types of membrane is different. Membranes may be also symmetrical or asymmetrical, porous and non porous. They also can be organic or inorganic and liquid or solid. The membrane types and its applications are shown in Table 2.3 below.

Table 2.3: Major application of membrane process

Membrane separation	**Membrane type**	**Driving force**	**Applications**
Microfiltration	Symmetric microporous	Hydrostatic pressure	Clarification, steril filtration, purification of fluids in semiconductor manufacturing industry, clarification and biological stabilization in the beverage industry, sterilization (in the food and pharmaceutical industries) analysis
Ultrafiltration	Asymmetric microporous	Hydrostatic pressure	Separation of macromolecular solutions, electrodialysis pretreatment, electrophoretic paint, cheese whey treatment, juice clarification, recovery of textile sizing agents, wine clarification, separation of oil/water emulsion, concentration of latex emulsion from wastewater, dewaxing, deasphalting, egg-white preconcentration, kaolin concentration, water treatment, affinity membranes, reverse osmosis pretreatment
Nanofiltration	Asymmetric microporous	Hydrostatic pressure	Separation of small organic compounds and selected salts from solutions, water treatment, product and chemical recovery, concentration/dewatering, fractionation of monovalent and diavalent cations, water softening
Hyperfiltration	Asymmetric, composite with homogenous skin	Hydrostatic pressure	Separation of microsolutes and salts from solutions
Gas permeation	Asymmetric or composite, homogenous porous polymer	Hydrostatic pressure, concentration gradient	Separation of gas mixture, Hydrogen recovery (Synthesis gas ratio adjustment (H2/CO), H_2 recovery from hydroprocessing purge streams, H_2 recovery from ammonia plant purge streams and other petro chemical plant streams), oxygen/nitrogen separation, helium recovery, removal of acid gases from light hydrocarbons, biogas processing, separation of organic vapors from air

Table 2.3: (Continued)

Dialysis	Symmetric microporous	Concentration gradient	Separation of microsolutes and salts from macromolecular solutions, hemofiltration and hemodiafiltration, donnan dialysis, alcohol reduction of beverages
Pervaporation	Asymmetric, composite	Concnentration gradient, vapor pressure	Separation of mixtures of volatile liquids, removal of organics from water, water removal from liquid organics, organic/organic separation
Vapour permeation	Composite	Concentration gradient	Separation of volatile vapours and gases Removal of organics from air
Membrane distillation	Microporous	Temperature	Separation of water from non-volatile solutes
Electrodialysis	Ion-exchange, homogenous or microporous polymer	Electrical potential	Separation of ions from water and non-ionic solutes, desalination of brackish water, production of table salt, waste water treatment, concentration of RO brines, applications in the chemical, food and drug industries
Electro-osmosis	Microporous charged membrane	Electrical potential	Dewatering of solutions of suspended solids, sea water and brackish water desalination, waste water treatment (industrial and municipal, pulp and paper. Textile waste water), production of boiler quality water for steam generation, petroleum industry, recovery of plating chemicals from wastewaters and process waters in the electroplating chemicals from wastewaters and metal-finishing industry
Electrophoresis	Microfiltration membranes	Electrical potential, hydrostatic pressure	Separation of water and ions from colloidal solutions
Liquid membranes	Microporous, liquid carrier	Concentration, reaction	Separation of ions and solutes from aqueous solutions

Source: Khulbe *et al.* (2008)

2.4 ADVANTAGES OF MEMBRANE TECHNOLOGY

Membranes separation process has become one of the vital technologies for industrial application. It has seen in many industrial applications since it has many benefits. Below are the following advantages of membrane technologies.

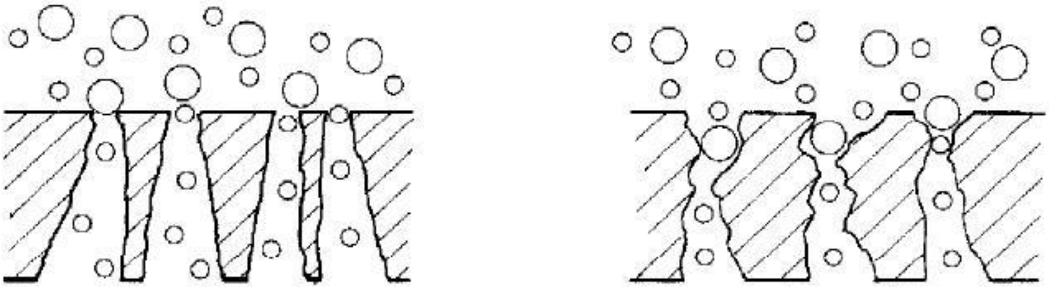
a) Membrane separation process offer the low capital cost and have cost effectiveness. It is because membrane used low operating cost and low energy consumption.
b) The operation of membrane process used low energy consumption. It is because during the separation process there is no phase change. So, the energy used is low and at the same time we can save the energy.
c) The membrane process is easy to operate. Membrane separation processes do not required a complex machine. Its only need the simple, easy to operate and compact equipment.
d) Membrane separation has space efficiency because of its shape, molecular size and also charge. The porous structure of the membrane can make the membrane will have the larger space effectiveness.
e) Keep the product quality. The membrane separation can be operate at room temperature. So, it is not required to increase and decrease the temperature during the separation process.
f) No additional waste product. Membrane is a clean technology because it is not produce the unwanted product.

2.5 TYPES OF MEMBRANES STRUCTURE

Membranes can be classified according to their morphology. Generally, the functioning of membrane will depend on its structure since this configuration determines the mechanism of separation and thus application. There have two types of structure that usually found in membrane. They are either homogenous or symmetric membrane or heterogenous or asymmetric membrane. This study is focusing only for asymmetric membrane. Table 2.4 below shown the differences between symmetric and asymmetric sructure of membrane and Figure 2.2. shows the schematic diagram of the structure of membrane.

Table 2.4: Differences of membrane structure

Asymmetric membrane (heterogenous)	**Symmetric membrane (homogenous)**
1) Have three basic structures 2) Integral skinned asymmetric membrane with a porous skin layer 3) Integral skinned asymmetric membrane with a dense skin layer 4) Thin film composite membranes	1) The structure is same across the thickness of membrane 2) Can be porous or dense uniform structure



(a) Asymmetric membrane

(b) Symmetric membrane

Figure 2.2: Schematic diagram of the membrane behavior of (a) asymmetric membrane and (b) symmetric membrane

2.6 ASYMMETRIC MEMBRANES

Most membranes that are used in industrial have an asymmetric structure. Asymmetric membrane consists of two structurally distinct layers, one of which is a thin, dense, selective skin or barrier layer and the other a thick, porous matrix layer whose chief function is to provide a physical support for the thin skin. The skin layer performs the separation with a high flux because it is thin and with a high selectivity due to its high density. The porous sublayer provides the mechanical strength that the gases permeate without resistance (Baker, 1991). Figure 2.3 shows asymmetric membranes that have developed by Loeb Sourirajan. The membranes consist of an extremely thin and dense surface layer (0.1µm to 1 µm) supported on a much thicker porous sublayer (100 µm to 200 µm of the same material). (Guang-Li, 1993; Ismail and

Lai, 2003; Srathman, 1986; Wang and Minhas, 1991; Chung *et al.*, 1997). Basically, asymmetric membrane with efficient skin layer thiknessof approximately 1000-5000 angstroms (Å) is classified as ultra thin-skinned asymmetric membrane.

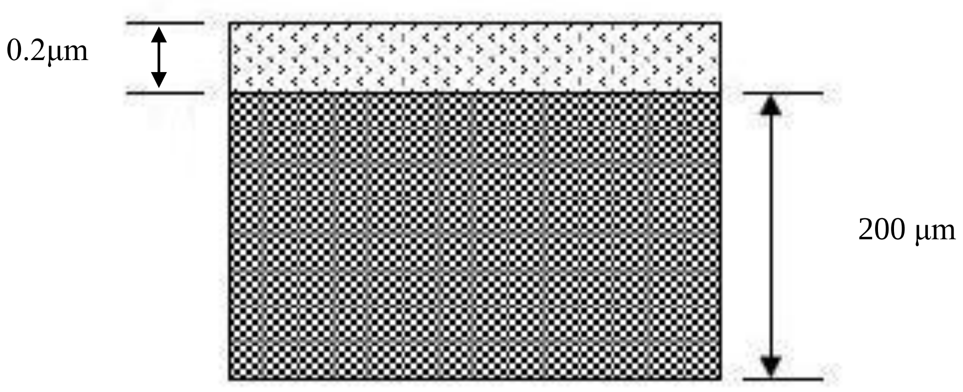


Figure 2.3: A schematic illustration of the structure of integrally-skinned asymmetric membranes

In asymmetric membrane, density and mass transfer resistance of the skin layer is somewhat greater than that of the sub layer, therefore permeability of asymmetric membranes does not depend on the entire membrane thickness but instead is inversely proportional to thickness of skin layer (Strathman, 1986; Kesting, 1993). Development of thin-skinned asymmetric membranes would result in defects or pinholes on skin surface due to irregular packing of kinked polymer chains and incomplete coalescence of polymer molecules in skin layer (Datta *et el.,* 1992; Pinnau and Koros, 1992). According to Baker (1991), the gas separation properties will decrease because of drawback with asymmetric membranes.

Ideal asymmetric membranes for gas separation must meet the following requirements (Paul and Yampol'Skii, 1994).

a) The selective layer should be defect-free so that the gas transport takes places completely solution/diffusion, not by poorly selective flow through pores.
b) The selective skin layer should be as thin as possible in order to maximize the gas fluxes.
c) The supporting substructure should not contribute any resistant to gas transport.
d) The substructure should provide sufficient mechanical strength to support the delicate selective layer in higher pressure.

2.6.1 Characteristics of Asymmetric Membranes

As mentioned in the previous section, asymmetric membrane should consist of a thin skin layer supported by an open sublayer. Table 2.5 shows the characteristics of asymmetric structure.

Table 2.5: Characteristics of asymmetric membranes

Characteristic	**Description**
Porosity of the top layer	This property largely determines the type of the process in which the membrane can be used. A pore-free toplayer gives pervaporation or gas separation properties, while an open toplayer gives an ultrafiltration or a microfiltration membrane.
Thickness of the top layer	The thickness of the top layer determines the permeation rate and for most of the separation process this permeation rate is reduced with an increasing skin thickness.
Porosity of the sublayer	The desired sublayer only serves as a mechanical support for the toplayer and does not give any additional transport resistance. This means that it should have a regular structure and a high porosity with sufficient interconnection of the pores.
Presence of macrovoids	During membrane formation by immersion precipitation, often large conical voids are formed, called macrovoids (Van't Hof, 1988). When the membranes have to be used at high pressure, microvoids may give rise to ruptures in the thin toplayer.

2.7 ASYMMETRIC MEMBRANE FORMATION BY PHASE INVERSION PROCESS

2.7.1 Dry Phase Inversion Process

Phase inversion is a process where apolymer solution is transformed in a controlled manner from a liquid to solid state. Acccording to Baker (2000), the phase inversion method is widely used to prepare a variety of polymeric membranes for gas separation. Basically, this process is based on phenomenon of liquid-liquid phase separation. It also known as solution precipitation or polymer precipitation.

In this process, a clear polymer solution is precipited into two phases which is solid that consist of polymer-rich phase that forms the matrix of the membrane and a liquid which is polymer-poor phase that forms the membrane pore. If the precipitation process is rapid, the pore-forming liquid droplets tend to be small and the membranes formed is asymmetric. If the precipitation proceeds slowly, the pore forming liquid droplets tend to agglomerate while the casting solution is still fluid (Baker, 1991). Figure 2.4 shows the schematic diagram of dry phase inversion process.

Figure 2.4: Schematic of dry phase inversion process

2.7.2 Wet Phase Inversion Process

The basic procedure of wet phase inversion method consist of two stages which is is the first stage is casting process and the second stage is quench process. First, the polymer solution is cast over a suitable substrate to form a thin film. Then, the thin polymer film is immersed in a coagulation bath where the replacement of solvent by coagulant and the precipitation of polymer take place. The wet phase separation is characterized by the demixing of a stable, homogenous polymer solution in a non solvent precipitation bath. Figure 2.5 shows the schematic on wet phase inversion process (Lai *et al.*, 1996; Lin *et al.*, 1996).

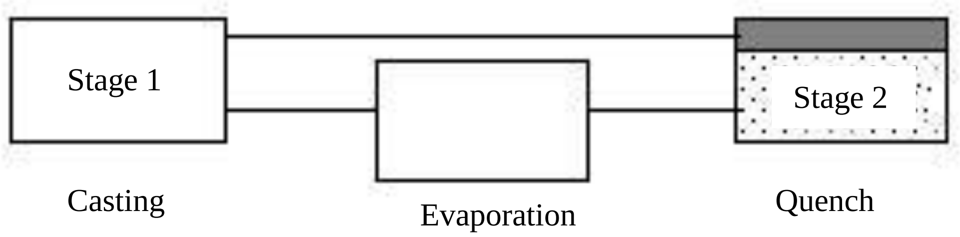


Figure 2.5: Schematic of wet phase inversion process

2.7.3 Dry/wet Phase Inversion Process

According to Khulbe (2008), dry/wet phase inversion technique is a common method that used in membrane manufacturing. This inversion technique is also known as Loeb-Sourirajan technique since it was used by Loeb and Sourirajan in their development of the first cellulose acetate membrane for seawater desalination. Figure 2.6 shows the schematic on dry/wet phase inversion process.

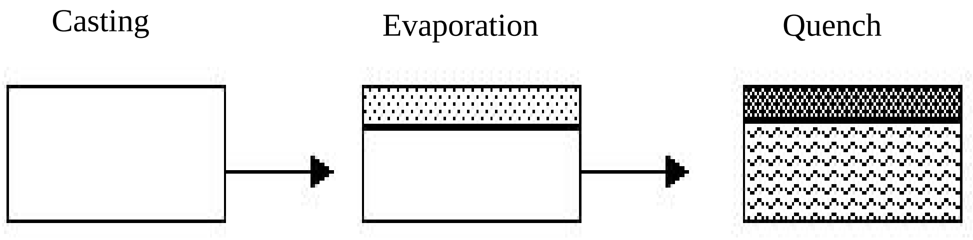


Figure 2.6: Schematic of dry/wet phase inversion process

In this method, a polymer solution is prepared by mixing polymer and solvent. Then, the solution is cast on a flat surface by a doctor blade to a precalculated thickness. The cast film subsequently is immersed in a nonsolvent medium called a gelation bath after the solvent have partial evaporation. Due to a sequence of the two desolvation steps which are evaporation of the solvent and solvent-nonsolvent exchange in the gelation bath then the solidification of the polymer film will take place. It is desirable to choose a solvent of strong dissolving power with a high votality. A thin skin layer of solid polymer is formed instantly at the top of the cast film due to the loss of solvent during the first step of desolvation by solvent evaporation. For the process of solvent-nonsolvent exchange, the nonsolvent diffuses into the polymer solution film through the thin solid layer while the solvent difuses out. Figure 2.7 below shown the composition path of changes in composition of polymer solution film during the solvent-nonsolvent exchange process.

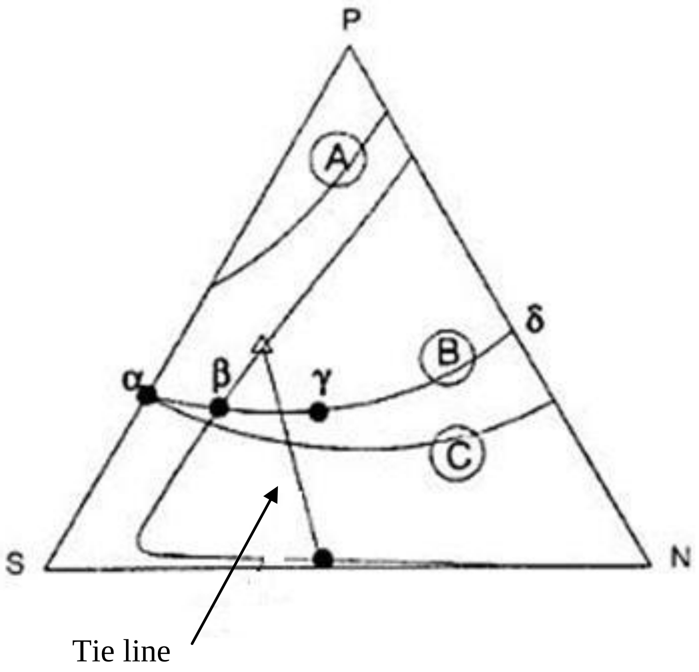


Figure 2.7: Composition path of polymer (P), solvent (S), and nonsolvent (N)

Source: Khulbe *et al. (*2008)

2.8 MEMBRANE FOR GAS SEPARATION

The concept of separating gases with polymeric membranes is more than 100 years old but the extensive use of gas separation membranes has occurred only within the last 20-30 years. The membrane process that separates components based on their relative rates of permeation distinguishes it from equilibrium processes such as distillation or extraction. The separation is accomplished because of differences in the relative transport rates of feed component. The components that diffuse more rapidly become enriched in the low pressure permeate stream while the slower components are concentrated in the retentate or residue (Khulbe *et al*., 2008). Membrane gas separation (GS) is a pressure-driven process with different industrial applications. It is represent only a small fraction of the potential applications in refineries and chemical industries (Bernado *et al*., 2009). Gas separation process requires a membrane with high permeability and selectivity that is the asymmetric membrane (Lin *et al.*, 1996). Nowadays, gas separation is widely used in variety of application. A proven technology in membrane gas separation has been found in a wide range of industrial application by using polymer membrane. Figure 2.8 below shows the diagram of basic membrane for gas separation.

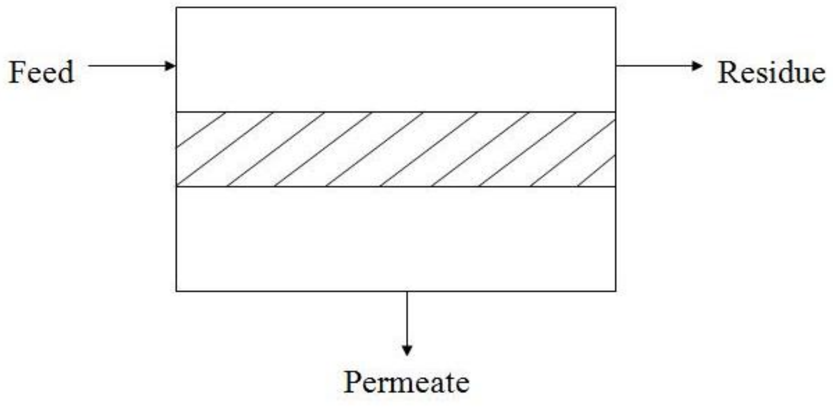


Figure 2.8: Schematic diagram of basic membrane for gas separation

According to Bernado *et al.* (2009), in the review of membrane for gas separation, there are several properties of membrane depend on:

a) The material (permeability, separation factors)
b) The membrane structure and thickness (permeance)
c) The membrane configuration (e.g., flat, hollow fiber)
d) The membrane module and system design

Nowadays, gas separation membranes are widely used in variety of application since it has many advantages as shown in Table 2.6 below.

Table 2.6: Application of gas separation membrane

Typical gas separation	**Application**
O_2/N_2	Oxygen enrichment, inert gas generation
H_2/Hydrocarbons	Refinery hydrogen recovery
H_2/N_2	Ammonia purge gas
H_2/CO	Syngas ratio adjustment
CO_2/Hydrocarbons	Acid gas treatment, landfill gas upgrading
H_2O/Hydrocarbons	Natural gas dehydration
H_2S/Hydrocarbons	Sour gas treating
He/Hydrocarbons	Helium separation
He/N_2	Helium recovery
Hydrocarbons/Air	Hydrocarbons recovery, pollution control
H_2O/Air	Air dehumidification

2.9 MECHANISM FOR GAS SEPARATION

There is various mechanisms for gas transport through membranes. Basically, it is depending on the properties of both the permeant and the membrane. These mechanisms include Knudesn diffusion, the molecular sieve effect and a solution diffusion mechanism (Baker, 1991). Figure 2.9 and Table 2.7 shows the mechanism of gas transport through membranes.

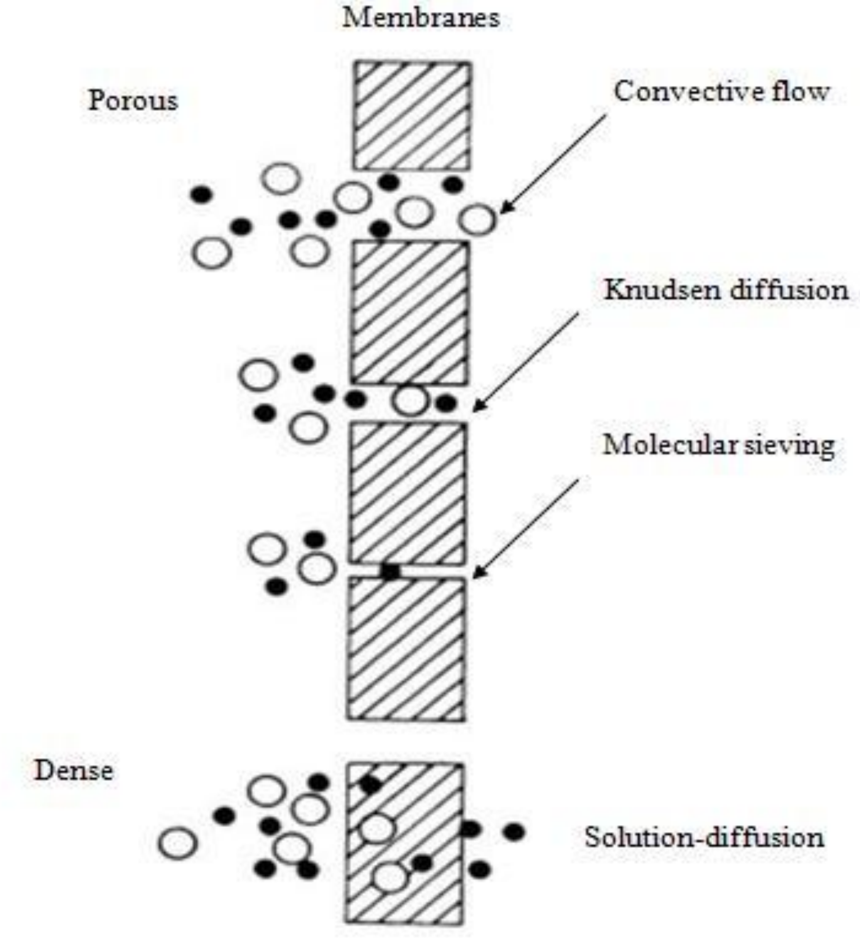


Figure 2.9: Schematic of mechanism for permeation of gases through membranes

Source: Baker (1991)

Table 2.7: Mechanism for permeation of gases through membranes

Mechanism	Description	Pore size
Convective flow	• This type of flow occurs when there are large pores on the membrane surface. • No separation occur.	>>10^2 nm
Knudsen diffusion	• Knudsen diffusion occurs through membrane when there are pores on the membrane surface. • Pores with diameter less than the mean free path of the gas molecules allow lighter molecules to preferentially diffuse through pore.	10^2 – 10^0 nm

Molecular sieving	• Large molecules are excluded from the pores by virtue of their size.	< 1nm
Solution-diffusion	• Gases dissolve into membrane material and diffuse across it. • Solution-diffusion separation is based on solubility and mobility factors in essentially all cases. • Diffusivity selectivity favors the most condensable molecule	(NA)

Source: Baker (1991)

2.10 MIXED MATRIX MEMBRANES (MMMs)

Currently, the novel of mixed matrix membranes (MMMs) is considered as a technique to overcome the limitation for gas separation (Mahajan and Koros, 2000). Mixed matrix membrane is a blend of molecular sieving particles in polymer matrix that combine the superior gas separation properties of rigid molecular sieving materials with the processability of the polymers (Duval *et al*., 1993).

It is expected that the membrane properties has improvement since the molecular sieving materials have unique crystalline microporous pore structure, surface chemistry and mechanical strength (Chandak *et al.*, 1997). According to Zimmerman *et al.* (1997), it has found the important fundamental in the development of MMM. It is need to have a proper material selection for both matrix and molecular sieving. The molecular sieving must accurately distinguish between the size and shape differences of molecules.

Molecular sieve such as zeolite and carbon molecular sieve (CMS) have been used as a molecular sieve in the development study of MMM. It shows that their permeation properties can be adapted through variation in the composition and membrane preparation process (Vu *et al.*, 2003). Zimmerman explained, the selection of polymer matrix verify the minimum membrane performance while molecular sieve addition can only improve membrane selectivity in the absence of defects (Zimmerman, 1997).

Currently, glassy polymers that control the gas separation membrane exhibits economically acceptable permeability and selectivity. Although the formation of MMM using rigid glassy polymer is more difficult due to poor polymer sieve contact but most of the researchers have focused on it. Some successes were achieved using various techniques to modify the preparation and formation protocol of the glassy polymer-sieve MMM. Figure 2.10 below shows the formation of flat sheet mixed matrix membrane in the laboratory (Wahab *et al.,* 2004).

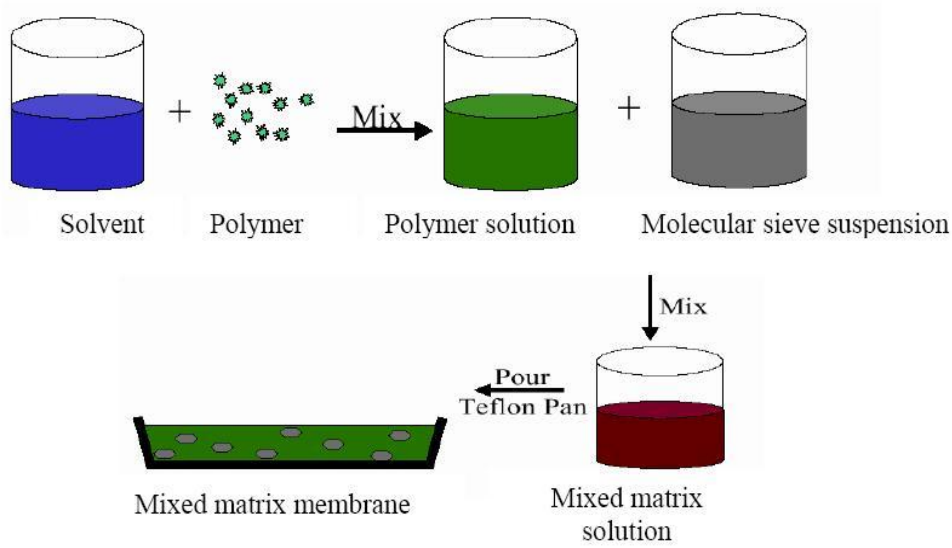


Figure 2.10: Formation of mixed matrix membrane

Source: Ismail *et al*. (2004)

2.10.1 Zeolites

Zeolites molecular sieves are crystalline structures, highly porous materials which belongs to the class of aluminosilicates that composed of AlO_4 and SiO_4 tetrahedra, which build up a network of channels and cavities (Duval *et al.*,1993). It can be represent by the chemical formula $M_{2/n}O.Al_2O_{3}.{}_ySiO_{2}.{}_wH_2O$ where y is 2 or greater, M is the charge balancing cation, such as sodium, potassium, magnesium and calcium, n is the cation valence and w represents the moles of water contained in the zeolitic voids.

According to Aizan (2006), zeolite molecular sieve have special charaxteristics since the microporous character with uniform pore dimensions, allowing certain hydrocarbon molecules to enter the crystals while rejecting others based on too large a molecular size, the ion-exchange properties which performing all sorts of ion-exchange reactions and the ability to develop internal acidity which makes the zeolits materials for catalyzing organic reactions and high thermal stability of the zeolites. Figure 2.11 and figure 2.12 shows the structure of zeolite according to their types.

Figure 2.11: Zeolite molecular sieve type A

Figure 2.12: Zeolite molecular sieve type X

In spite of this, zeolites also have their dynamic properties which is pore of uniforms size that are determined by the crystal structure of the material. All the pores will completely exclud molecules that are larger than thei diameter. Thus, the zeolite molecular sieve for a particular separation can be selected based on the pore size and the dimension of the penetrants (Yang, 1987). Table 2.8 will summarize the some common zeolite molecular sieve.

Table 2.8: Common zeolite molecular-sieve nominal pore aperture

Zeolite	Nominal Pore Apeture (Å)	Molecules Admitted	Molecules Excluded
Zeolite 3A	3	H_2O, NH_3, H_2, He, Ne (molecules with an effective diameter less than 3 Å)	CO_2, etc. (Larger than 3 Å)
Zeolite 4A	3.8	CO_2, Ar, O_2, N_2, CO, CH_4 (molecules with an effective diameter less than 3.8 Å)	C_3H_8, etc. (Larger than 3.8 Å)
Zeolite 5A	4.9	C_3H_8, n-C_4H_{10}, CF_2C_{l2}, other than n-paraffins, n-elefins (molecules with an effective diameter less than 4.9 Å)	Iso-parrafins, etc. (Larger than 4.9 Å)
Zeolite 10X	8	Iso-arrafins, iso-olefins, benzene, toluene (molecules with an effective diameter less than 8 Å)	Di-n-butylamine, etc. (Larger than 8 Å)
Zeolite 13X	10	Di-n-butylamine, 1,3,,5-Triethylbenzene (molecules with effective diameter less than 10 Å)	$(C_4F_9)_3$-N, etc. (Larger than 10 Å)

Source: Yang (1987)

2.10.2 Concept of Mixed Matrix Membrane

The development of mixed matrix membrane is a new technique in order to expand the industrial application of membrane separation technology. It is very necessary to enhance the gas permeation flux (productivity) and permselectivity by combining the synthesis of high-performance materials with the innovation of membrane fabrication technology. The improvement is made for membrane gas separation because the further development of polymeric membrane separation technology has been limited by a performance of “upper bound” trade-off curve between the gas productivity and permselectivity. The upper limit for the performance of polymeric membranes in gas separation was predicted by Robeson in early 1990. (Robeson, 1991).

According to Chung (2007), the performance of of various membrane materials that available for the separation of O_2/N_2 is shown in Figure 2.6. The figure presents the permeability of the fast gas O_2 and the O_2/N_2 selectivity performance. For the polymeric materials, a rather general trade-off exists between permeability and selectivity with an "upper bound" evident. It can be seen that, if the materials with separation properties near this limit were modified based on traditional structure property relation, the resultant polymer have permeability and selectivity tracking along this line instead of exceeding it. However, as may be seen in Figure 2.13, the inorganic materials have properties lying far beyond the "upper bound" limit for the organic polymer (Singh and Koros, 2000; Feuters and Centeno, 1999; Kim *et al.*, 2004; Park *et al.*, 2004 and Tin *et al.*, 2004).

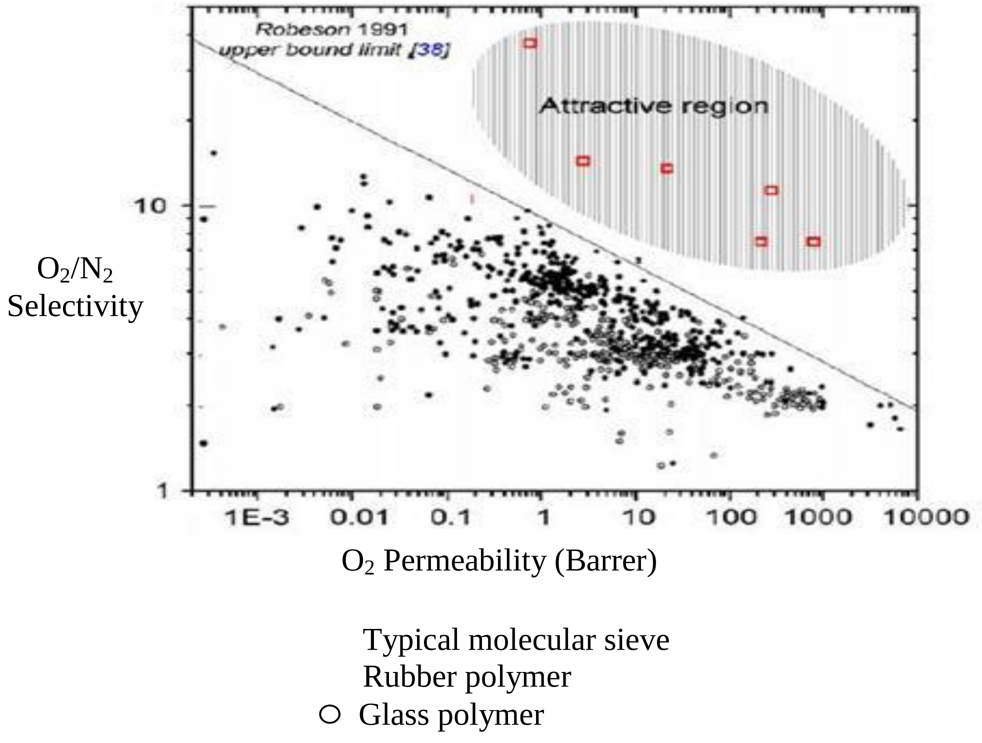


Figure 2.13: Relationship between the O_2/N_2 selectivity and O_2 permeability for polymeric membranes and inorganic membranes

Source: Robeson (1991)

The latest emerging polymer-based organic-inorganic composite membrane materials similar to mixed-matrix membrane may potentially surpass the “upper bound” limit since of combining the easy processability of organic polymer with the excellent gas separation properties of inorganic molecular sieve materials (Kulprathipanja, 1988). During the last two decades, advance progress exceeding the trade off line seems to present a challenge in the near future. All at once, the instantaneous application of inorganic membranes is still delayed by the lack of technology to form continuous and defect-free membranes (Saraco *et al*., 1999 and Caro *et al*., 2000).

According to Chung (2007), a new approach is needed to provide an alternate and cost-effective membrane with separation properties well above the upper-bound limit between permeability and selectivity. Figure 2.14 below shows the schematic of a mixed matrix membrane. As shown in figure, the bulk phase (phase A) is typically a polymer while the dispersed phase (phase B) represents the inorganic particle which may be zeolite, carbon molecular sieve or nano-size particles.

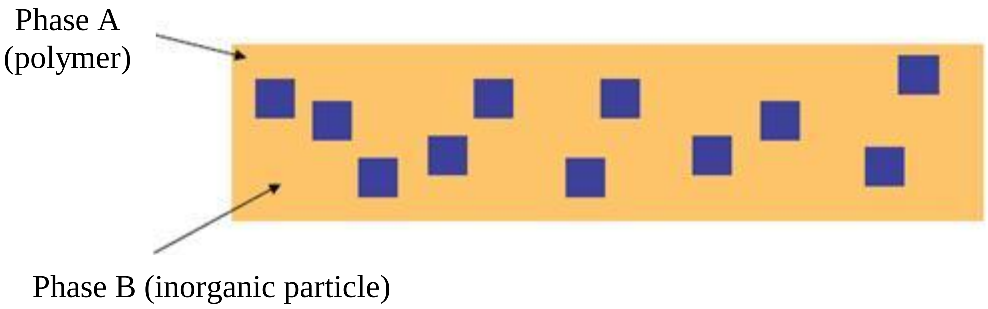


Figure 2.14: Schematic of a mixed matrix membrane (MMM)

Mixed matrix membranes have a potential to achieve higher selectivity and permeability relative to the existing polymeric membrane. It is resulting from the addition of the inorganic particles with their inherent superior separation characteristics. All at once, by using a flexible polymer as a continuous phase, the brittleness intrinsic in the inorganic membranes may be avoided (Chung, 2007).

2.10.3 Molecular Design and Key Advances on Mixed Matrix Membranes (MMMs)

Molecular sieve such as zeolites or carbon molecular sieve shows a much higher selectivity for many gas mixtures than polymeric membranes due to their very defined pore size. The preparation of defect-free zeolite layers on a large scale is extremely difficult and it seems doubtful that this will ever achieved at a competitive price. In spite of this, many researchers has attracted with the combination of the superior gas selectivities of molecular sieves with the processability αof polymeric membranes. Kulprathipanja *et al.* (1988), who have performed the work in the field of polymer/zeolite hybrid membranes and at the same time the term "mixed matrix membrane" was introduced.

Maxwell approach is a simple model for transport in heterogenous medium. The Maxwell equation has been applied to calculate the gas permeability of block copolymers. When the Maxwell equation is applied to mixed-matrix membrane, the following equation is obtained.

$$Peff = Pc\,\frac{(Pd+2Pc-2\emptyset(Pc-Pd))}{(Pd+2Pc+\emptyset(Pc-Pd))} \qquad (2.1)$$

where *Peff* is the effective permeability, ϕ is the volume fraction of the dispersed phase and the subscript d and c refer to the dispersed and continuous phases respectively. If the equation is used to calculate the selectivity of a mixed-matrix membrane, the following equation is obtained.

$$\alpha eff = \alpha c\,\frac{1+2Prel-2\emptyset(Prel-1)}{1+2Prel+\emptyset(Prel-1)} * \frac{\frac{1}{\alpha D}+\frac{2Prel}{\alpha c}+\emptyset(\frac{Prel}{\alpha c}-\frac{1}{\alpha D})}{\frac{1}{\alpha D}+\frac{2Prel}{\alpha c}-2\emptyset(\frac{Prel}{\alpha c}-\frac{1}{\alpha D})} \qquad (2.2)$$

where *αeff* is the effective selectivity of the mixed-matrix membrane, *Prel* is the permeability ratio of continuous phase to dispersed phase for the fast component and *αc* and *αD* are the selectivities of the continuous and dispersed phase.

According to Kusworo *et* al (2008), the permeability and selectivity of gas through mixed matrix membrane can be calculated as follows:

$$P = \frac{Qil}{(\Delta P)(A)} \qquad (2.3)$$

Where Qi is the volumetric flow rate of gas i at standard temperature and pressure, ΔP is the trans membrane pressure difference, A is the membrane area whereas the permeability is expressed in barries (10^{10} cm^3 (STP) cm/cm^2 s cm Hg). The selectivity or in other words, ideal separation factor αi/j can be calculated by using equation below:

$$\alpha(i/j) = \frac{(P)i}{(P)j} \qquad (2.4)$$

2.10.4 Surface Modification of Zeolite External Surface

Since there is a problems of adhesion and wetting between an organic and an inorganic phase, some method have been proposed to solve that problem in order to enhance the separation performance. One of them is the chemical modification of the surface of zeolite with silane coupling agents for instance (γ-aminopropyl)-triethoxy silane, N-β-(aminoethyl)-γ-aminopropyltrimethoxy silane, (γ-glycidyloxy-propyl)-trimethoxy silane and (3-aminopropyl)-dimethylethoxy silane (Mahajan and Koros, 2002; Duval *et al.,* 1994; Liu *et al.*, 2006).

According to Mahajan (2000), the silane coupling agent was used to improve the interfacial adhesion in mixed matrix membrane, where γ-aminopropyldimethylethoxysilane (APDMES) was used to zeolite surface in order to enhance the compatibility of zeolite with polymer. From the previous researchers, by using silane coupling agent, the silane groups will react with the hydroxyl group on the zeolite surface and the amino groups can react with some functional groups in polymers. Therefore, covalent bonding between the phases was formed (Duval, 1995; Kulkarni *et al*.,2003; Guiver *et al*.,2003; Mahajan, 2000; Jia *et al*.,1992; Vankelecom *et al.*, 1996 and Pechar *et al.*, 2002).

According to Guivet et al. (2003), 3-aminopropyltriethoxysilane was used as a silane coupling agent. It shows that the modified zeolite was covalently attached to aldehyde modified polysulfone (PSF). From the result obtained, the hydrogen/carbon dioxide selectivity was only .6 for the pure PSF membrane, 3 for PSF/3A MMMs devoid of covalent bonding while for PSF/3A zeolite with covalent bonding between the polymer and zeolite, the selectivity was 13.

Besides that, Li *et al.* (2006), have applied a novel silane coupling agent which is 3-aminopropyldiethoxymethylsilane (APDMES) to modify the zeolite surface for MMMs. From the occurrence of APDMES, the extent of the partial blockage of zeolite was reduced. Thus, both permeability and gas duo selectivity of PES/A modified zeolite MMMs are higher than those PES/A unmodified zeolite due to a decrease in the negative effect of partial pore blockage. Figure 2.15 shows the flowchart of the chemical modification on zeolite surface.

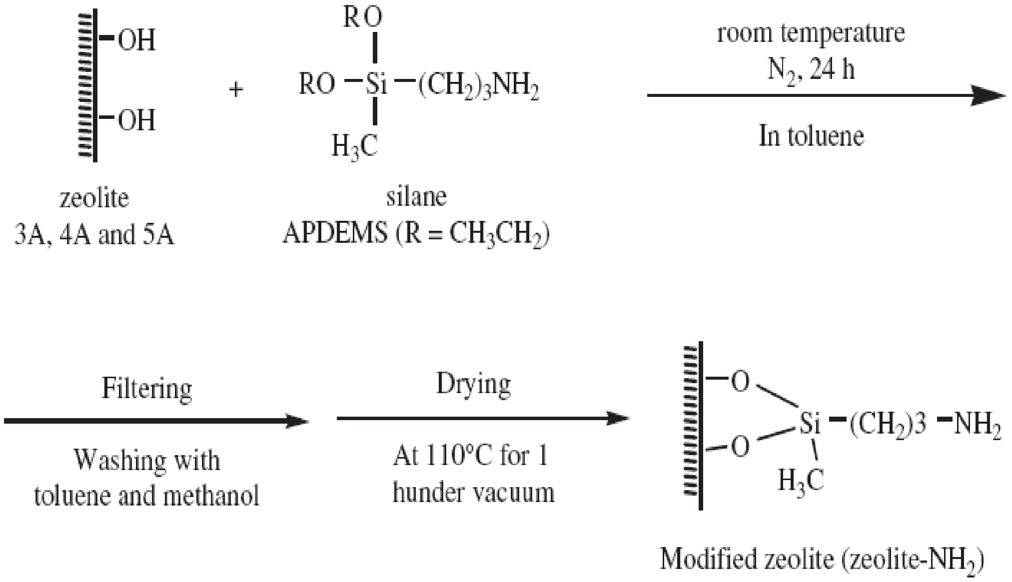


Figure 2.15: Flowchart of the chemical modification on zeolite surface

Source: Li *et al.* (2005)

2.10.5 Non Idealities of Mixed Matrix Membranes

An ideal mixed matrix membrane is highly selective and very permeable composed of organic-inorganic hybrids. This inorganic material such as zeolite that dispersed in a continuos polymeric matrix will leading for the performance of MMMs. Besides that, the ideal additive modelled in terms of the intrinsic properties of the continuous and dispersed phases, thus, that phase may affect the surrounding of polymer matrix at the interface between two phases. For instance, the dispersed phase may caused an undesirable void at the interphase or create varying degree of rigidification in the surrounding polymer (Moore and William, 2005). Figure 2.16 shows the illustration on the non-idealities in MMMs.

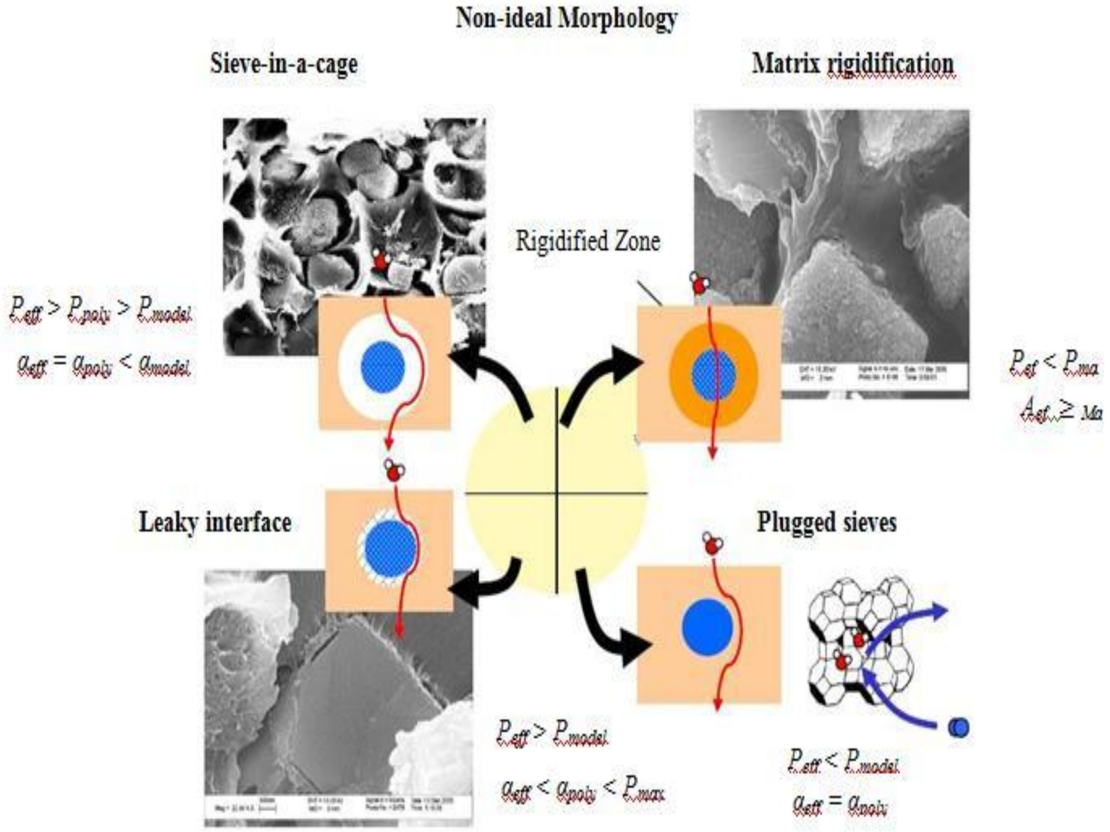


Figure 2.16: Illustration of the morphologies and gas transport properties of non-idealities in mixed matrix membranes

Source: Shu (2007)

According to Shu (2007), the inorganic-organic can caused the performance of a membrane could be greatly impacted by any change at the interfacial region due to the extremely small size of gas molecules and large percentage of interface present in a MMMs. Based on the study, Shu have identified that there are four undesirable morphologies at the polymer-sieve interface. Because of these non-idealities, the successful MMMs are difficult to create. Table 2.9 shows the summarizations of non-idealities occur in mixed matrix membrane.

Table 2.9: Summarization of non-idealities in MMMs

Non-idealities in MMMs	**Description**
Matrix rigidification	• Confinement of polymer chains to a solid surface is an important phenomenon that affects the properties of organic-inorganic composites. • In MMMs, this effect is characterized by reduced permeability at the interface and therefore decreased the overall permeability of the whole membrane. • It is caused by immobilization of polymer chains due to adsorption and chemical tethering on a solid surface.
Sieve in a cage	• This phenomenon is highly detrimental to the membrane performance since the void is much more permeable than the zeolite and gas molecules bypass the zeolite by taking the path of least resistance. • It will cause a higher permeability than the neat polymer with an equivalent selectivity.
Leaky interface	• A leaky interface is look like a special case of sieve-in-a-cage category. It has an effective void that enable partial and less selective bypass of the two gases. • This phenomenon leads to actual loss of separation efficiency since it adds a significant non-selective resistance that undesirable affects the most permeable component. • Knudsen flow and sorption-diffusion is extremely low and as a result, the overall membrane exhibits a higher permeability and lower selectivity than the neat polymer.
Plugged or partially plugged sieves	• This situation is characterized by a permeability lower than the neat polymer with essential no change in selectivity. • It might caused by the use of an impermeable zeolite for instance zeolite 3A or by certain strongly held penetrants such as water, organic solvents and silane coupling agent that prevent the gas molecules from permeating through the internal pores of the sieves.

Source: Shu (2007)

CHAPTER 3

METHODOLOGY

3.1 MATERIALS

3.1.1 Polyethersulfone

A commercial polyethersulfone (PES) (Radel A300 purchased from Amoco) was selected as a continuous phase. It is because PES is a heat-resistant, transparent, amber and non-crystalline. Other than that, PES is a though and rigid resin similar to conventional engineering plastics at room temperature. It also has far better high-temperature properties than conventional engineering plastics. PES also remains in satisfactory condition in long-term continuous use without causing any dimensional change or physical deterioration at temperatures as high as 200 °C. So, it is appear as an adaptable membrane. The polymer structure, physical, mechanical and the other properties are shown in Figure 3.1 and Table 3.1 correspondingly.

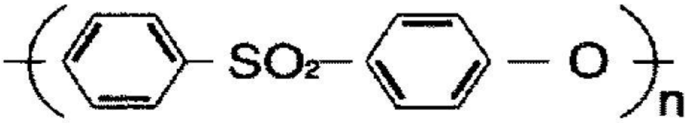


Figure 3.1: Molecular structure of the polyethersulfone

Table 3.1: Physical, mecahnical and thermal properties of polyethersulfone

Properties	**Value**
Molecular weight (Dalton or g/mol)	15000 or 232.26
Density (g/cm^3)	1.4
Glass transition (°C)	230
Tensile strength (yeild) (MPa)	99.4
Tensile modulus (Gpa)	3.7
Elongation at break (%)	30.2%
Compressive strength (yeild) (MPa)	100
Thermal conductivity (Wm^{-1} K^{-1})	0.22
Coefficient of linear thermal expansion K^{-1} [L]	5.5x10^{-5}

Source: www.polymerprocessing.com

3.1.2 1-Methyl-2-Pyrrolidone

The solvent that used in this study was 1-methyl-2-pyrrolidone. It has formula molecular weight of C_5H_9NO. It is also known as NMP. The molecular weight of 1-methyl-2-pyrrolidone is 99.7 g/mol. It has a high boiling point that is 202 °C. Other than that, it has a high solvent power for polyethersulfone, low toxicity and completely miscible with water alcohols and organic acids (www.polymerprocessing.com).

3.1.3 Physical Properties of Nonsolvent Additives and Coagulation Bath

In this study, water was used as nonsolvent additives and methanol was used as coagulation medium. Table 3.2 and Table 3.3 are shown the physical properties of nonsolvent additives and coagulation medium.

Table 3.2: Physical properties of nonsolvent additive

Component	**Distilled Water**
Molecular Weight MW (g/mol)	18.02
Melting Point (°C)	0
Boiling Point (°C)	100
Density (kg/m^3)	998

Source: www.polymerprocessing.com

Table 3.3: Physical properties of coagulation medium

Component	**Methanol (Industrial Grade)**
Molecular Weight MW (g/mol)	32.04
Melting Point (°C)	-98.0
Boiling Point (°C)	65.04
Density (kg/m^3)	790.0

Source: www.polymerprocessing.com

3.1.4 Physical Properties of Zeolites

There have 3 types of zeolites that were used in this study. The zeolites that used are 4A, 5A and 13X.

Table 3.4: Physical properties of zeolites

Zeolite	**Structural Type**	**Formula**	**Pore size (Å)**	**Particle size (µm)**
4A	A type	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].xH_2O$	3.8	3.4
5A	A type	$Ca_nNa_{12\text{-}2n}[(AlO_2)_{12}(SiO_2)_{12}.xH_2O$	4.9	3.2
13X	Faujasite	$Na_2O.Al_2O_3.2.5SiO_2.6H_2O$	7.8	2.6

Source: Kusworo *et al.* (2008)

3.1.5 Properties of Substances for Zeolite Surface Modification

Since polymer and molecular sieve have compatibility problem that leads to voids formation or gaps between the molecular sieve and polymer, it is essential to use silane coupling agent to modify the surface of the zeolite in order to allow polymer to attach to the zeolite (Hussein and Koros, 2007). In this experiment, a combination of chemicals to achieve this objective and they were:

a) 3-Aminopropyl-trimethoxysilane (APTMOS)
b) Ethanol
c) Distilled Water

3.1.6 APTMOS (3-Aminopropyl-trimethoxysilane)

In this experiment, 3-Aminopropyl-trimethoxysilane was selected as a coupling agent for zeolite 4A, 5A and 13X. It is a product form Acros Organics BVBA (Geel, Belgium). The molecular chain of APTMOS can be seen in Figure 3.2 and Table 3.5 shows the physical properties of 3-Aminopropyl-trimethoxysilane.

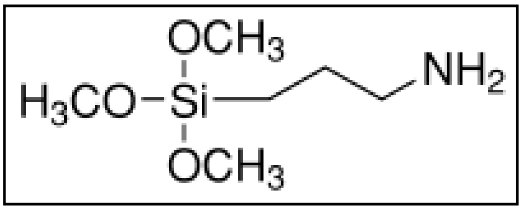


Figure 3.2: Molecular Chain of APTMOS

Source: www.sigmaaldrich.com

Table 3.5: Physical and chemical properties of APTMOS

Physical State at 27^0C and 1 atm	Clear Liquid
Color	Colourless
Boiling Point at 760 mmHg	194^0C
Flash Point	92^0C
Specific Gravity/Density	1.019 g/cm^3
Molecular Formula	$NH_2(CH_2)_3Si(OCH_3)_3$
Molecular Weight	179.29 g/mol

Source: www.acros.com

3.1.7 Ethanol

Ethanol was used together with APTMOS in order to have surface modification for zeolites. Ethanol was chosen in this study due to its strong interaction with water and its relatively self limiting nature (Ismail *et al.*, 2008). The ethanol bought from R&M Chemicals (Essex, UK) as 99.7% V/V denatured and the properties are shown in Table 3.6

Table 3.6: Physical and chemical properties of Ethanol

Molecular Formula	C_2H_5OH
Molecular Weight	46.07 g/mol
Boiling Point	78.8^0C
Density	0.79 kg/m^3

Source: Jiminez *et al.* (2010)

3.1.8 Properties of Test Gases

The membranes have tested using pure oxygen (O_2) and nitrogen (N_2) as test gases. Table 3.3 shows the physical properties of pure oxygen and nitrogen.

Table 3.7: Physical properties of Test gases

Physical property	**O_2**	**N_2**
Molecular weight, Mi (g/mol)a	32	28
Viscosity, ηi (µPa s) [a]	20.7	17.8
Collision diameter, σi × 108 (cm) [a]	3.55	3.7
Permeability of PES dense film (barrer) [b]	0.51	0.084
Permeability of silicone rubber dense film (barrer) [b]	649	354

[a] Data at 25◦C and 1 bar (Lide, 1996)

[b] Data at 30◦C and 145 psi (Wang, 1996) 1 Barrer = 10-10cm^3 (STP) cm/cm^2.s.cmHg

3.2 RESEARCH DESIGN

Figure 3.3 below is the research design for this research, starting from zeolite surface modification until the characterization.

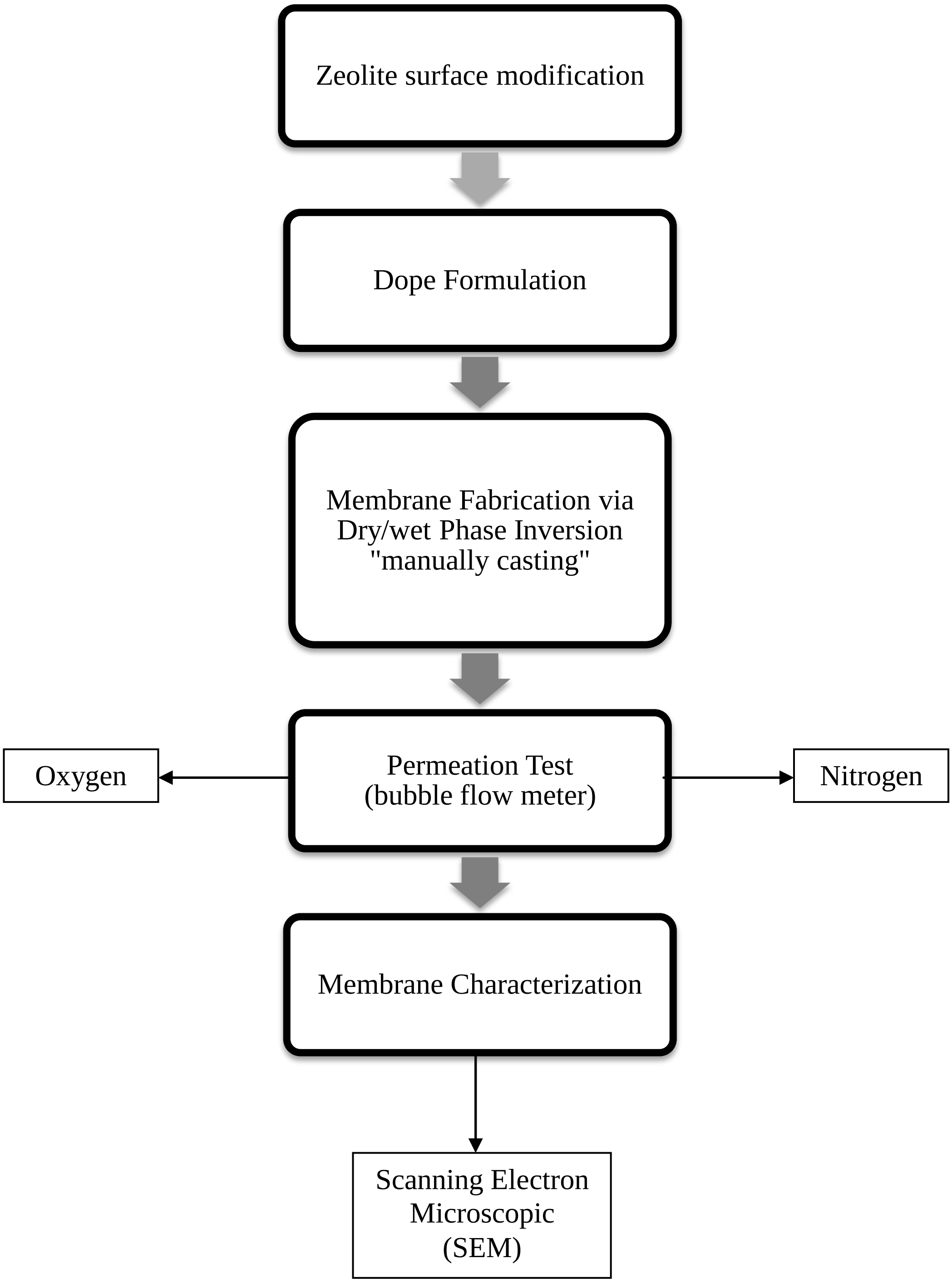


Figure 3.3: Research Design

3.3 PREPARATION OF ZEOLITE SURFACE MODIFICATION

Zeolite was treated with APTMOS which act as a silane coupling agent. The composition of solution for zeolite surface modification was 95 wt% of ethanol / 5 wt% of water, 25 g zeolite (4A, 5A and 13X) and 12.5 ml of APTMOS. According to Ismail (2008), chemical alteration on zeolite surface consists of three steps. Firstly, the mixture of ethanol, water, silane and zeolite were stirred in a beaker at room temperature for 4 hours. Next, the mixture was filtered through a filter paper and then the residue of the solution was washed throughly with ethanol in order to remove the unreacted silane. Lastly, before the modified zeolite was ready to be used in preparation of dope solution, it was dehydrated at 110°C for 2 hours in a vacumm oven.

3.3 PREPARATION OF CASTING SOLUTION (DOPE)

The apparatus for preparing the casting solution is shown in Figure 3.4. The composition of dope solution that was used is shown in Table 3.8. The modified zeolites were dispersed in the solvent and stirred for around 1 hour at a high speed to force particles to separate homogenously. Then, desirable amount of PES was added in the zeolite/solvent mixture and stirred to form the homogenous polymer solution. Then, the PES/zeolite/solvent mixture was stir continuous for 2 hours in order to remove the air trapped around the zeolite surface, which may exacerbate the formation of voids between polymer and zeolite phases. Finally, the nonsolvent was added in the mixture and stirred for at least 1 day. After the dope solution was prepared, they were kept in a storage bottle and were degassed by using ultrasonic bath to remove any traces of micro bubbles inside the casting solution.

Table 3.8: Composition of dope solution

Composition	**PES (wt %)**	**NMP (wt %)**	**Distilled water (wt %)**	**Zeolite (wt %)**
4A	30	60	5	5
5A	30	60	5	5
13X	30	60	5	5

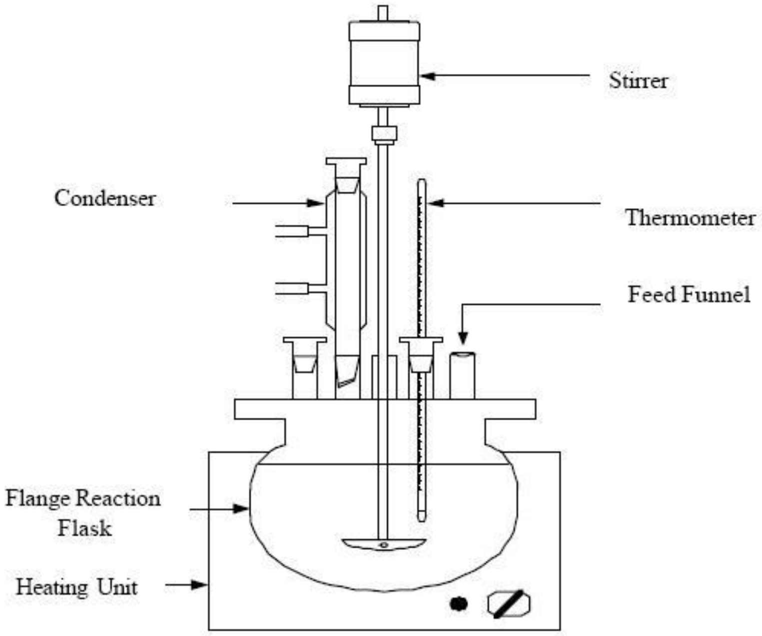


Figure 3.4: Apparatus to prepare dope solution

Source: Norida (2004)

3.4 MEMBRANE CASTING

Asymmetric polyethersulfone mixed matrix membranes were prepared according to dry/wet phase inversion by using manually casting as shown in Figure 3.5. The membranes were cast on the glass plate in order to produce flat sheet membranes. Then, the glass plate was immersed into the coagulation bath (compose of water as coagulation medium). According to Norida (2004), after the process coagulation completed, the membranes were transferred to water bath for 1 day and then washed with methanol for 1 day before air dried for at least 48 hour at room temperature in order to remove any residue of organic compounds. The liquid exchange treatment used is to prevent the changes in structure (Li, 1993).

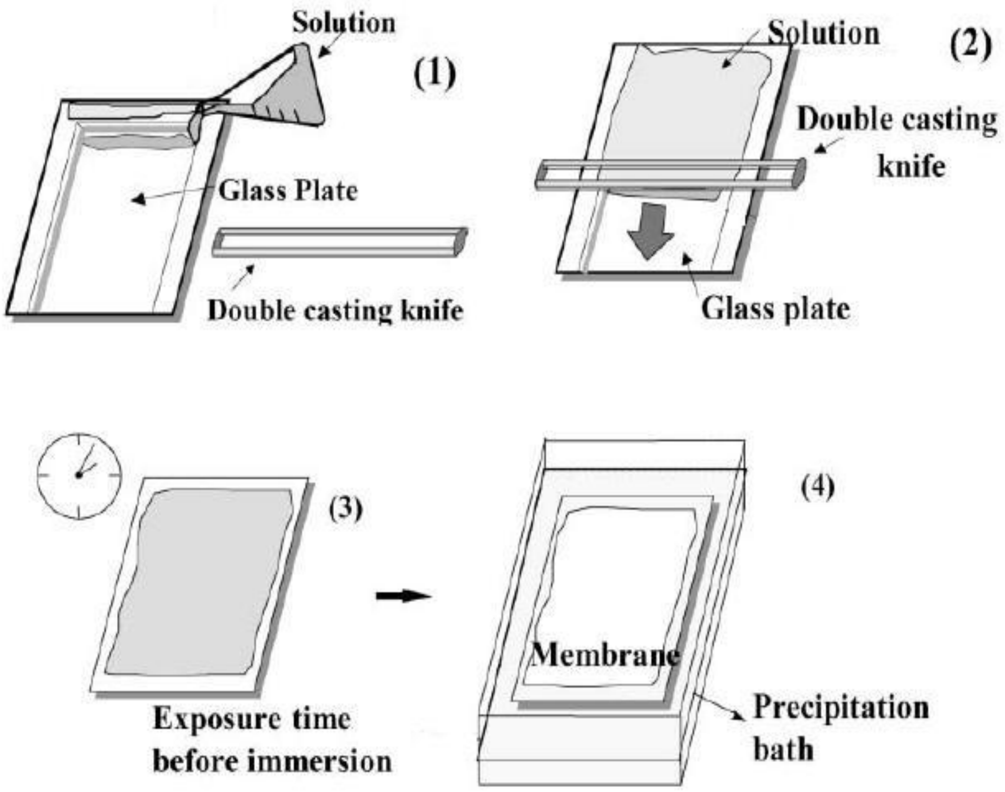


Figure 3.5: Steps involved in the manually casting of polymer solutions (1) Pouring the solution (2) Membrane casting (3) Dry phase inversion (4) Wet phase inversion

3.5 MEMBRANE COATING

In order to repair the defects or in other words to produce defects-free, the membrane should be coated. Membrane coating is an alternative procedure to fill any surface pinholes or imperfections which can reduce the performance of gas separation. Blocking the void will result in a decrease of pressure-normalizes flux but it can improve the selectivity (Rezac *et al*., 1994). The membrane sheets were coated with a highly permeable elastomeric silicone polymer (polydimethyl siloxane). The coating was applied to the circular membrane disc of 12.7 cm^2 in area by immerse the sheet into a 3 wt% silicone solution in n-hexane for 5 minutes. Lastly, the coated membranes were placed in an oven at temperature 40°C for 15 minutes (Norida, 2004).

3.6 GAS PERMEATION TESTS

Gas permeation system was constructed to measure pure gas permeation rate for asymmetric flat sheet membrane. The system consists of flexible hose, permeation cell, plain ball valve, needle valve, pressure regulator and bubble flow meter. Figure 3.6 shows the schematic of gas permeation system that used in this study. The permeation cell is shown in Figure 3.7. The permeation cell is used to measure the pressure – normalized fluxes of flat sheet membranes (Norida, 2004).

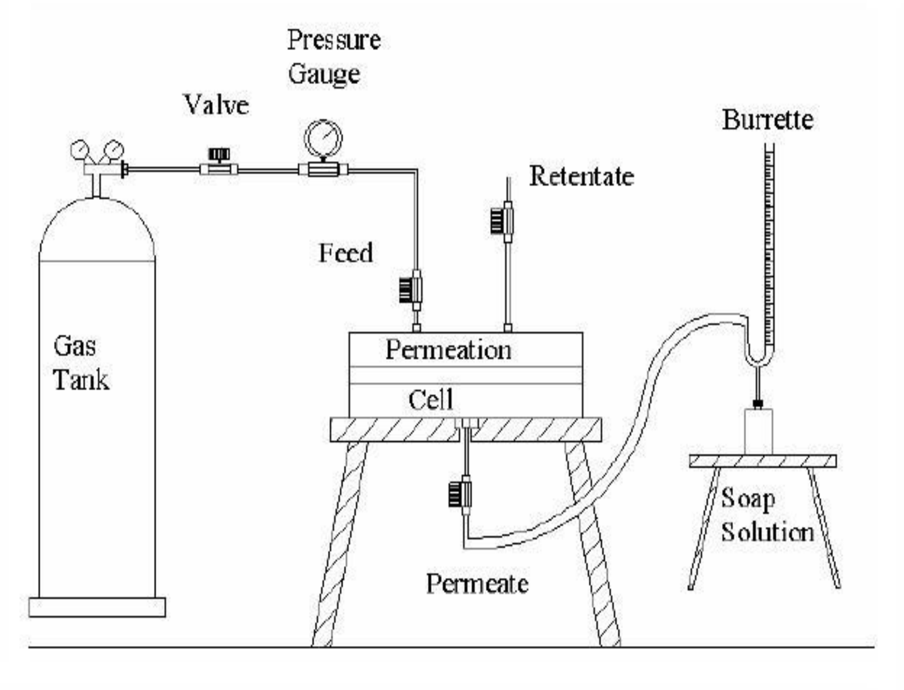


Figure 3.6: Gas Permeation System

Source: Norida (2004)

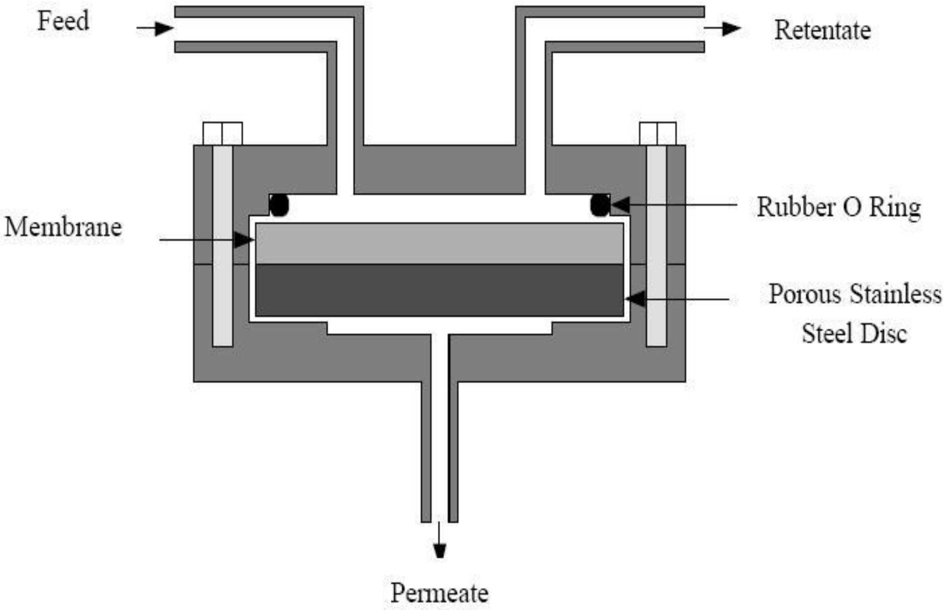


Figure 3.7: Permeation Cell

Source: Norida (2004)

Gas permeation test were performed with a permeation cell by using pure oxygen (O_2) dan nitrogen (N_2) as test gases. Circular membrane disc were used with feed pressure was controlled at 1, 2, 3, 4 and 5 bar while permeate side was maintained at atmospheric pressure. Besides that, the experiment was carried out at ambient temperature which is 30°C. By using soap bubble flow meter, the gas permeation rate was measured and each set of data was determined as an average of three replicates. The gas permeation rate was calculated by:

$$\left(\frac{P}{l}\right) = \frac{Qi}{A\Delta p} \qquad (3.1)$$

where *(P/l)* is defined as pressure-normallized flux or permeability for gas i. The common unit of pressure-normalized gas flux is GPU (1 GPU = 1 × 10^{-6} cm^3 (STP) cm/cm^2scmHg). *Qi* is volumetric flow rate of gas *i*, *Δp* is the pressure difference accross membrane, A is the membrane effective surface area and l is the membrane skin thickness. Selectivity of asymmetric membrane can be determined by:

$$aij = \frac{Pi}{Pj} = \frac{\left(\frac{P}{l}\right)i}{\left(\frac{P}{l}\right)j} \qquad (3.2)$$

3.7 MEMBRANE CHARACTERIZATION

3.7.1 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM Carl Zeiss EVO50) was used to study the membrane morphology. Before the membrane structure is studied, it should be dried and then immersed in liquid nitrogen before the breaking. Next, the samples were coated with a thin platinum layer. The SEM analysis was carried out under high vacuum of the dried membranes after the samples were coated. Then, the morphology of membranes was studied.

CHAPTER 4

RESULT AND DISCUSSION

This chapter is discuss about the effect of different zeolites onto the mixed matrix membranes (MMMs) performance. The morphology of MMMs with different types of zeolite was determined using Scanning Electron Microscope (SEM). SEM gave a better view on the structure and how was the condition of the polymer sieve contact of the MMMs. Polyethersulfone (PES) MMMs content of polyethersulfone, 1-methyl-2-pyrrolidone, distilled water and three different of zeolite types and has been prepared via dry wet phase inversion.

4.1 EFFECT OF DIFFERENT PRESSURE ON GAS SEPARATION PERFORMANCE

4.1.1 Performance of Uncoated Polyethersulfone Mixed Matrix Membranes (MMMs)

In order to achieve both high permeability and selectivity, three different types of zeolite which are 4A, 5A and 13X have been used in preparation of asymmetric flat sheet MMMs. According to Robeson (1991), organic-inorganic hybrid or MMMs have been proposed as a class of materials that can exceed the polymeric upper-bound trade off curves that can improve the performance of gas separation. In addition, Mahajan *et* al (2002) have proved that MMMs have a potential to provide membranes with higher permselectivity and equivalent productivity compared to existing membrane materials. Molecular sieving membrane materials such as zeolites are capable to overcome the limitation that neat polymeric membranes have.

Therefore, to determine the effect of pressure on gas separation performance for three types of MMMs, the pressure in range 1 to 5 bars have been applied. Pure oxygen (O_2) and nitrogen (N_2) pressure-normalized fluxes were measured at 30±2 °C with pressure difference of 1 bar. The permeation properties of uncoated membrane based on O_2 and N_2 gases by applying different pressure for three different MMMs are shown in Table 4.1 to Table 4.3. As shown in the Table 4.1 to Table 4.3, the average range of O_2/N_2 selectivities for MMMs containing zeolite 4A is 0.86 to 0.95, 0.84 to 1.02 for MMMs with zeolite 5A while for MMMs incorporation with zeolite 13X, the average mean selectivity is 0.79 to 0.96.

Table 4.1: Performance of of uncoated MMMs with zeolite 4A at different pressure

Pressure (bar)	**Membrane**	**Pressure-normalized flux (GPU)**		**Selectivity O_2/N_2, α**
		O_2	**N_2**	
1	M1	301.91	346.81	0.87
	M2	366.08	427.09	0.86
	M3	334.88	389.46	0.86
Mean		**334.29±32.09**	**387.79±40.17**	**0.86±0.01**
2	M1	491.61	499.01	0.99
	M2	600.05	607.62	0.99
	M3	550.26	629.24	0.87
Mean		**547.31±54.28**	**578.62±69.79**	**0.95±0.06**
3	M1	726.14	710.10	1.02
	M2	837.99	904.43	0.93
	M3	1178.77	1309.75	0.9
Mean		**914.30±235.77**	**974.76±305.95**	**0.95±0.06**
4	M1	762.14	872.45	0.87
	M2	890.01	1024.03	0.87
	M3	1222.23	1367.13	0.89
Mean		**958.13±237.49**	**1087.87±253.45**	**0.88±0.01**
5	M1	797.67	752.41	1.06
	M2	899.06	982.31	0.92
	M3	1226.47	1483.77	0.83
Mean		**974.40±224.11**	**1072.83±373.99**	**0.93±0.12**

GPU = 1 X 10^{-6} cm^3 (STP) / (cm^2.s.cm Hg)

Table 4.2: Permeation properties of uncoated MMMs with zeolite 5A at different pressure

Pressure (bar)	**Membrane**	**Pressure-normalized flux (GPU)**		**Selectivity O_2/N_2, α**
		O_2	**N_2**	
1	M1	381.89	367.60	1.04
	M2	376.71	356.84	1.06
	M3	282.08	294.86	0.96
Mean		**346.86±56.16**	**399.77±39.26**	**1.02±0.05**
2	M1	660.58	694.30	0.95
	M2	554.86	582.27	0.95
	M3	484.87	532.04	0.91
Mean		**566.77±88.46**	**602.87±83.07**	**0.94±0.02**
3	M1	948.08	1019.11	0.93
	M2	711.53	763.78	0.93
	M3	705.85	755.62	0.93
Mean		**788.49±138.24**	**846.17±149.83**	**0.93±0.002**
4	M1	978.69	1138.30	0.86
	M2	1269.01	1804.24	0.7
	M3	890.01	917.73	0.97
Mean		**1045.90±198.24**	**1286.76±461.53**	**0.84±0.13**
5	M1	906.75	1030.00	0.88
	M2	1894.46	1894.46	1.00
	M3	812.95	895.27	0.91
Mean		**1204.72±599.17**	**1273.24±542.19**	**0.93±0.06**

GPU = 1 X 10^{-6} cm^3 (STP) / (cm^2.s.cm Hg)

Table 4.3: Permeation properties of uncoated MMMs with zeolite 13X at different pressure

Pressure (bar)	Membrane	Pressure-normalized flux (GPU)		Selectivity O_2/N_2, α
		O_2	N_2	
1	M1	1725.03	1807.32	0.95
	M2	2151.92	2461.47	0.87
	M3	1485.85	1567.28	0.94
Mean		**1787.60±337.41**	**1945.28±462.9**	**0.93±0.04**
2	M1	2679.03	2720.24	0.98
	M2	2914.55	3120.28	0.93
	M3	2040.18	2130.31	0.96
Mean		**2544.59±454.42**	**2656.95±498.01**	**0.96±0.03**
3	M1	2373.37	3466.98	0.68
	M2	2922.58	3608.49	0.81
	M3	2455.78	2784.50	0.88
Mean		**2583.91±296.18**	**3286.66±440.6**	**0.79±0.1**
4	M1	2550.23	3195.47	0.80
	M2	3157.43	3633.20	0.87
	M3	2040.18	2247.66	0.91
Mean		**2582.61±559.33**	**3025.44±708.25**	**0.86±0.06**
5	M1	2556.37	2906.56	0.88
	M2	3031.13	3166.85	0.96
	M3	1739.17	1861.22	0.93
Mean		**2442.33±653.5**	**2644.88±691.03**	**0.92±0.04**

GPU = 1 X 10^{-6} cm^3 (STP) / (cm^2.s.cm Hg)

From the observation, all the uncoated MMMs whether incorporation with zeolite 4A, 5A or 13X show to exhibit higher pressure-normalized flux but low selectivity. Possibly, it is because the membranes were extremely permeable due to the skin layer pores. In addition, according to Pinnau and Koros (1992), development of thin-skinned asymmetric membranes would result in defects or pinholes on skin surface due to irregular packing of kinked polymer chains and incompletes coalescence of polymer molecules in skin layer. The gas transport through these membranes was leading from the combination of Knudsen diffusion or viscous flow that occurs through nonselective pores in membrane. Thus, a defective area blocked on the membrane surface can be consider as caused of dramatic loss in selectivity and prevent intrinsic selectivities from being achieved (Ismail and Lai, 2004).

From the analysis, every uncoated MMMs show large value of standard deviation for permeability and it shows that the result collected from uncoated membrane is unreliable. According to previous researcher (Wang, 1996), intrinsic value for O_2/N_2 dense polyethersulfone (PES) is 6.1 However, the results obtained shows that the selectivity of the uncoated is extremely lower compared to the intrinsic value. This situation is might be caused of surface porosity on the MMMs. Figure 4.1 to Figure 4.3 show the summarization of data taken from Table 4.1 to Table 4.3.

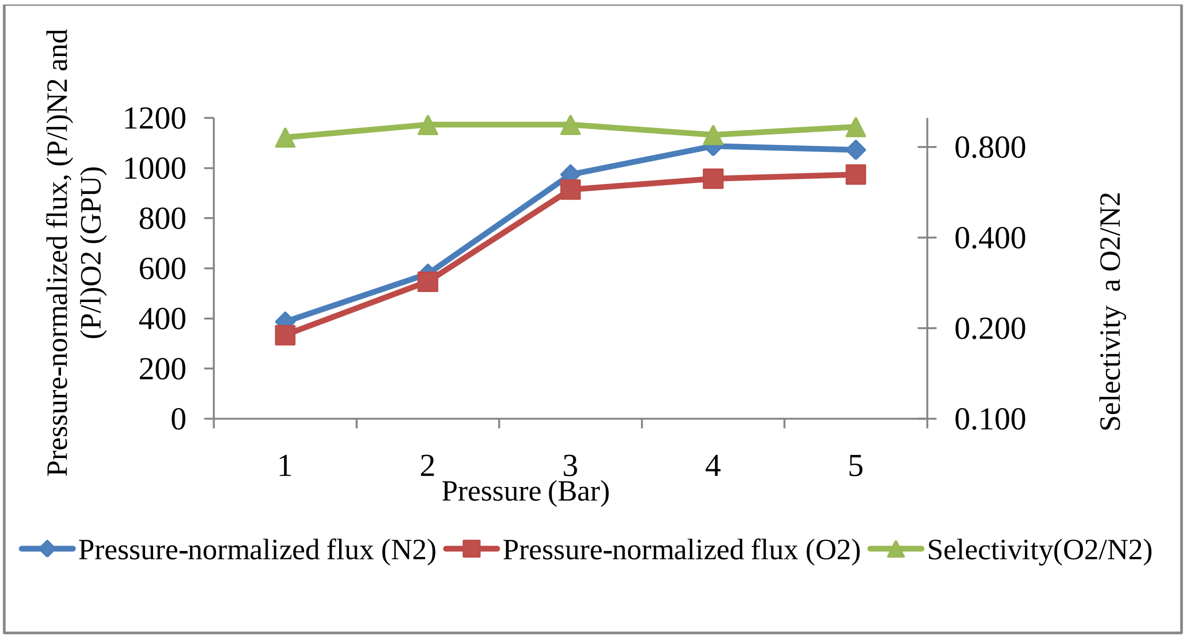


Figure 4.1: Pressure-normalized flux and selectivity of uncoated MMMs with zeolite 4A at different pressure

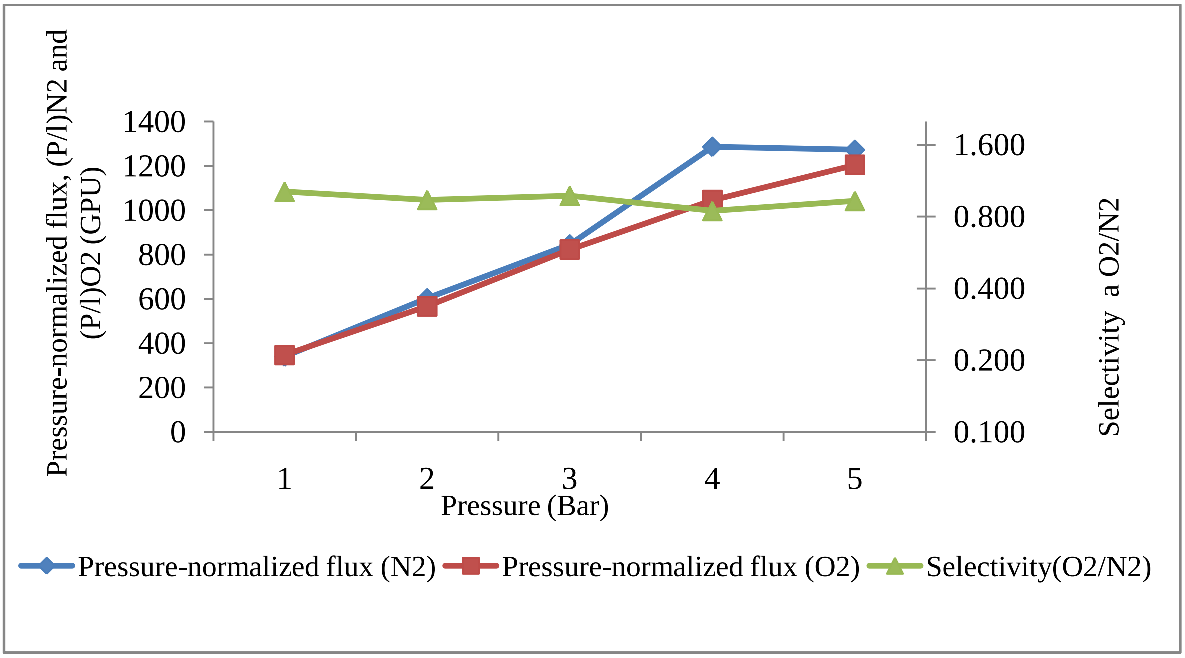


Figure 4.2: Pressure-normalized flux and selectivity of uncoated MMMs with zeolite 5A at different pressure

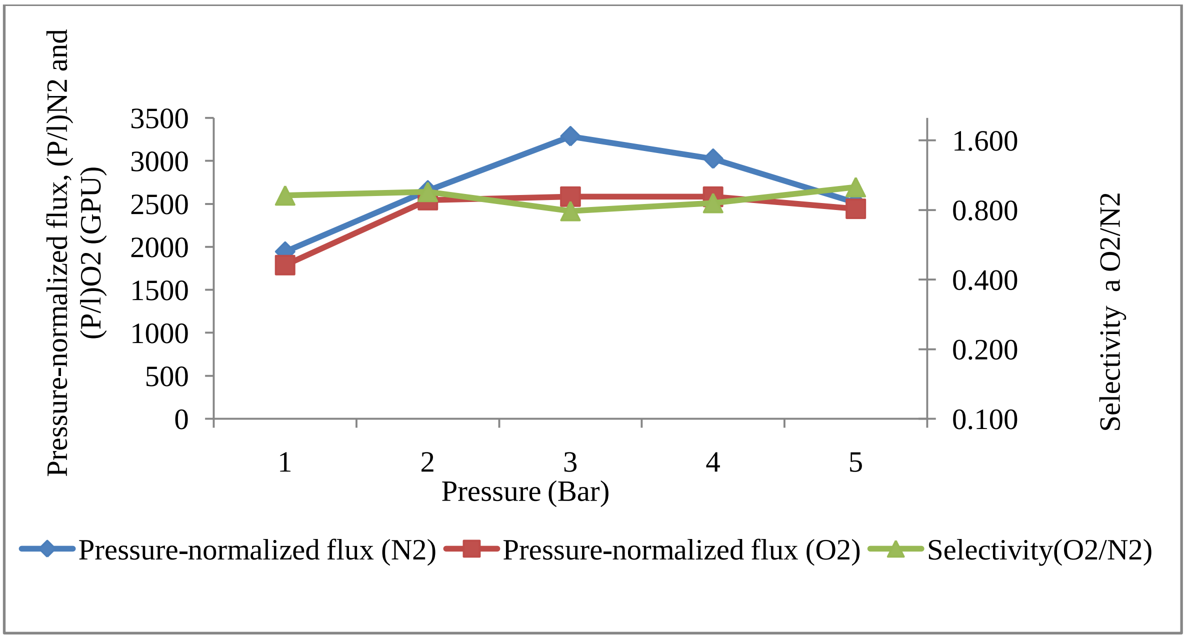


Figure 4.3: Pressure-normalized flux and selectivity of uncoated MMMs with zeolite 13X at different pressure

Figure 4.4 to Figure 4.5 shows the surface layer of uncoated MMMs for zeolite 4A, 5A and 13X.

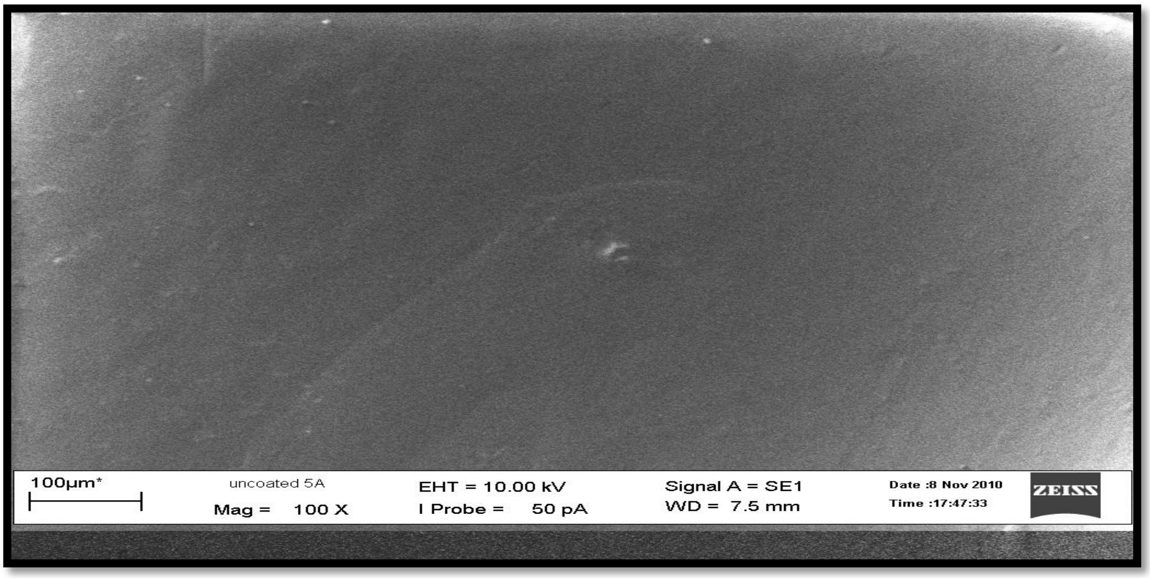


Figure 4.4: SEM for uncoated MMMs with zeolite 4A

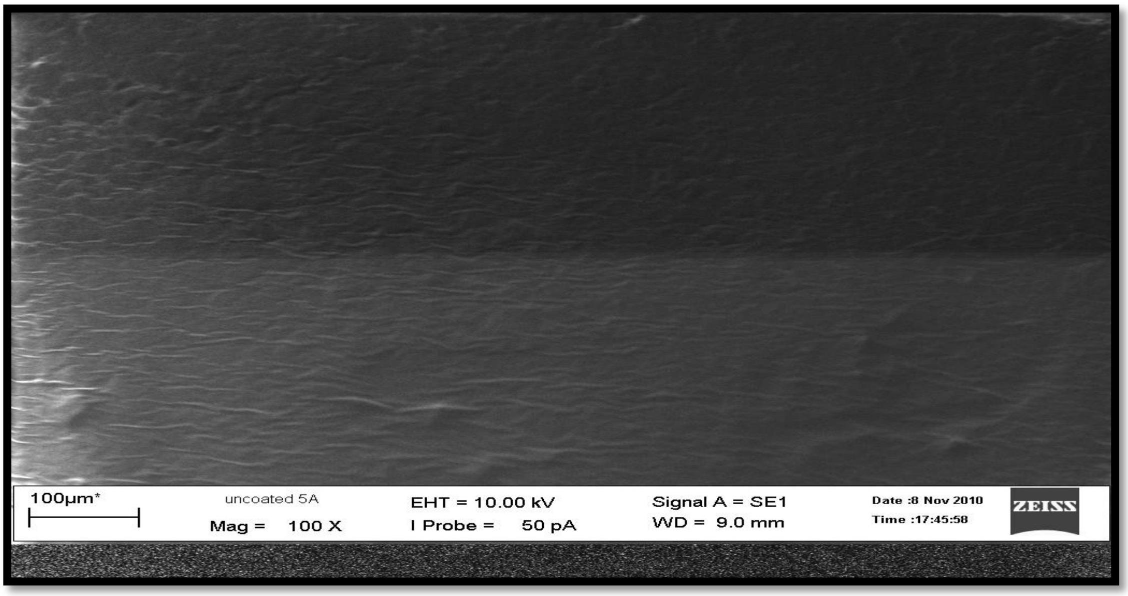


Figure 4.5: SEM for uncoated MMMs with zeolite 5A

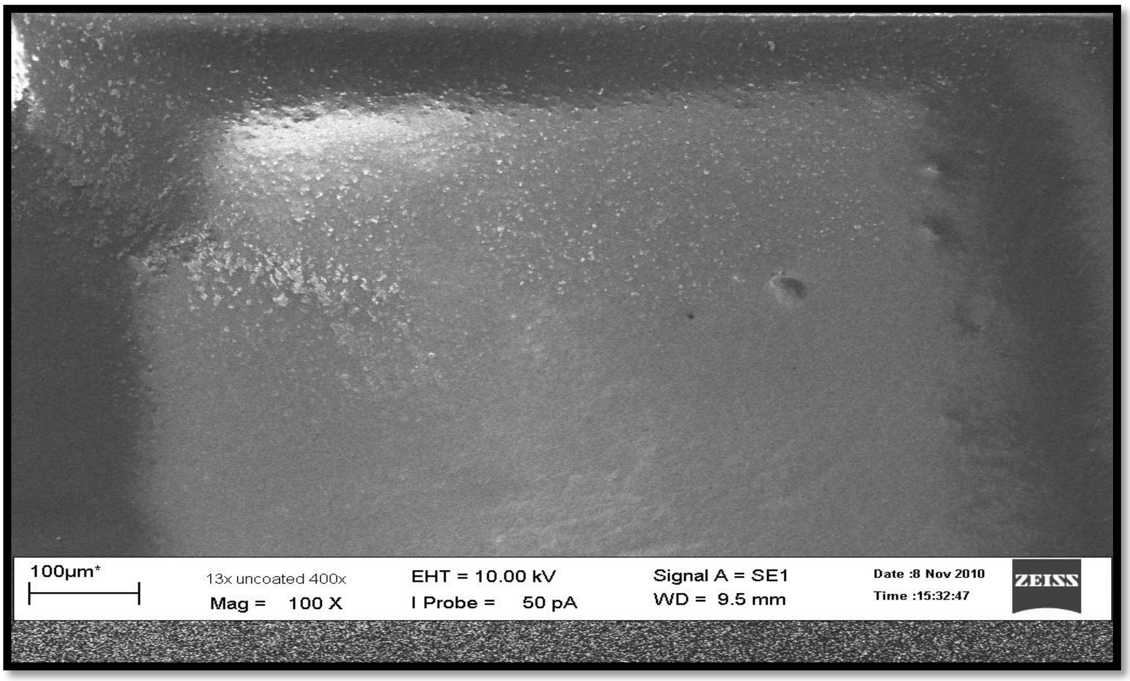


Figure 4.6: SEM for uncoated MMMs with zeolite 13X

For review this section, all of uncoated MMMs were suffered in poor of O_2/N_2 selectivity. As shown in Figure 4.4 to Figure 4.6, all the uncoated MMMs were endured with skin defects and porosity. Besides that, the surface of uncoated MMMs is not smooth since there are have small pinholes or pores that located on the membranes. Thus, Knudsen flow and Poiseuille flow were took place for gas transport mechanism. Nevertheless, these defects can be repaired in order to have a reliable performance of MMMs. So, skin layer should be coated using silicone rubber.

4.1.2 Performance of Coated Polyethersulfone Mixed Matrix Membranes (MMMs)

The performance of asymmetric gas separation MMMs is dependent on a thin and defectiveness skin layer. Basically, asymmetric MMMs suffer from low selectivity because of incomplete coalescence of the nodule aggregates of the composed skin layer and leads to defects during the phase inversion process (Kesting *et al.*, 1990). Since there is a defect on the MMMs surface, it should be coated with suitable coating material (Wang *et al*., 2001).

In this study, silicone rubber which used was polydimethylsiloxane (PDMS) was used as a coating agent. As described in the Chapter 3, coating can plug any surface pinholes or imperfection that caused reduction in performance of gas separation. All the MMMs were coated by 3 wt% of silicone rubber and 97 wt% of n-hexane and it was done under ambient condition (1 atm and 27 °C). By applying the coating procedure, the permeation properties of MMMs can be improve closer to the intrinsic characterization of the polymer membrane itself (Henis and Tripodi, 1981) and also exhibit the potential for higher selectivity (Kesting *et* al, 1993). Pure oxygen (O_2) and nitrogen (N_2) pressure-normalized flux was measured at 30°C±2°C with pressure difference of 1 bar were applied to the MMMs. The permeation results for coated MMMs with different type of zeolite are shown in Table 4.4 to Table 4.6.

Table 4.4: Performance of coated MMMs with zeolite 4A at different pressure applied.

Pressure (bar)	**Membrane**	**Pressure-normalized flux (GPU)**		**Selectivity O_2/N_2, α**
		O_2	**N_2**	
1	M1	4.68	2.14	2.19
	M2	5.00	2.33	2.14
	M3	4.37	2.01	2.17
Mean		**4.68±0.32**	**2.16±0.16**	**2.17±0.02**
2	M1	4.42	1.44	3.08
	M2	5.77	1.59	3.63
	M3	4.64	1.69	2.75
Mean		**4.94±0.72**	**1.57±0.13**	**3.15±0.45**
3	M1	9.37	3.62	2.59
	M2	11.84	5.31	2.23
	M3	15.39	3.96	3.88
Mean		**12.20±3.03**	**4.30±0.89**	**2.90±0.87**
4	M1	15.16	6.19	2.45
	M2	19.16	7.35	2.61
	M3	17.06	6.75	2.53
Mean		**17.13±2.00**	**6.76±0.58**	**2.53±0.08**
5	M1	28.52	10.81	2.64
	M2	25.78	12.09	2.13
	M3	27.84	12.98	2.15
Mean		**27.38±1.43**	**11.96±1.09**	**2.31±0.29**

GPU = 1 X 10^{-6} cm^3 (STP) / (cm^2.s.cm Hg)

Table 4.5: Performance properties of coated MMMs with zeolite 5A at different pressure applied.

Pressure (bar)	**Membrane**	**Pressure-normalized flux (GPU)**		**Selectivity**
		O_2	**N_2**	**O_2/N_2, α**
1	M1	17.20	6.43	2.67
	M2	12.36	6.53	1.89
	M3	11.97	7.16	1.67
Mean		**13.86±2.91**	**6.71±0.39**	**2.08±0.53**
2	M1	16.60	5.60	2.96
	M2	14.36	7.01	2.05
	M3	16.57	8.40	1.97
Mean		**15.84±1.29**	**7.00±1.40**	**2.33±0.55**
3	M1	24.46	22.89	1.11
	M2	38.71	27.80	1.39
	M3	27.31	24.87	1.10
Mean		**30.49±1.20**	**25.19±2.47**	**1.20±0.17**
4	M1	35.27	27.23	1.30
	M2	35.58	28.16	1.16
	M3	30.0	25.70	1.17
Mean		**82.62±2.63**	**27.03±1.24**	**1.21±0.08**
5	M1	87.68	80.68	1.09
	M2	64.30	53.45	1.20
	M3	74.71	64.89	1.15
Mean		**75.56±11.71**	**66.34±13.67**	**1.15±0.06**

GPU = 1 X 10^{-6} cm^3 (STP) / (cm^2.s.cm Hg)

Table 4.6: Performance properties of coated MMMs with zeolite 13X at different pressure applied.

Pressure (bar)	**Membrane**	**Pressure-normalized flux (GPU)**		**Selectivity O_2/N_2, α**
		O_2	**N_2**	
1	M1	53.18	29.74	1.79
	M2	54.27	31.96	1.70
	M3	55.72	37.94	1.47
Mean		**54.39±1.28**	**33.22±4.24**	**1.65±0.16**
2	M1	50.62	31.71	1.60
	M2	54.24	33.15	1.64
	M3	61.39	32.31	1.90
Mean		**55.42±5.49**	**32.39±0.73**	**1.71±0.17**
3	M1	46.84	32.71	1.43
	M2	48.18	36.20	1.33
	M3	50.66	38.78	1.31
Mean		**48.56±1.94**	**35.89±3.04**	**1.36±0.07**
4	M1	47.36	30.66	1.54
	M2	42.17	36.68	1.15
	M3	49.39	34.09	1.31
Mean		**46.31±3.73**	**33.81±3.02**	**1.36±0.07**
5	M1	119.20	76.60	1.54
	M2	73.67	66.10	1.15
	M3	114.69	87.32	1.45
Mean		**102.52±25.09**	**76.67±10.61**	**1.38±0.21**

GPU = 1 X 10^{-6} cm^3 (STP) / (cm^2.s.cm Hg)

From the result in Table 4.4 to Table 4.6, the pressure-normalized flux of O_2 is higher than N_2. Besides that, none of the solution has selectivity less than 1.0. However, none of them also exhibits selectivity above the intrinsic PES dense film for O_2/N_2 selectivity which is 6.1. According to Pesek and Koros (1993), if the membrane has selectivity than 80% of the ideal intrinsic selectivity, it believed that the membrane is defect-free. Nevertheless, from the table 4.4 to 4.6, there are no MMMs that have produced defect-free membrane by comparing the value of selectivity with intrinsic selectivity. The permeability of MMMs is pressure independent if the MMMs are defect-free (Wang, 1995).

Figures 4.6 to Figure 4.9 show the pressure-normalized flux for both O_2 and N_2. The figures show that when pressure is increased the pressure-normalized flux also increased. However, this result is slightly contrary with formation of MMMs with defect-free. Therefore, it has been identified that there is defect on the surface layer of MMMs.

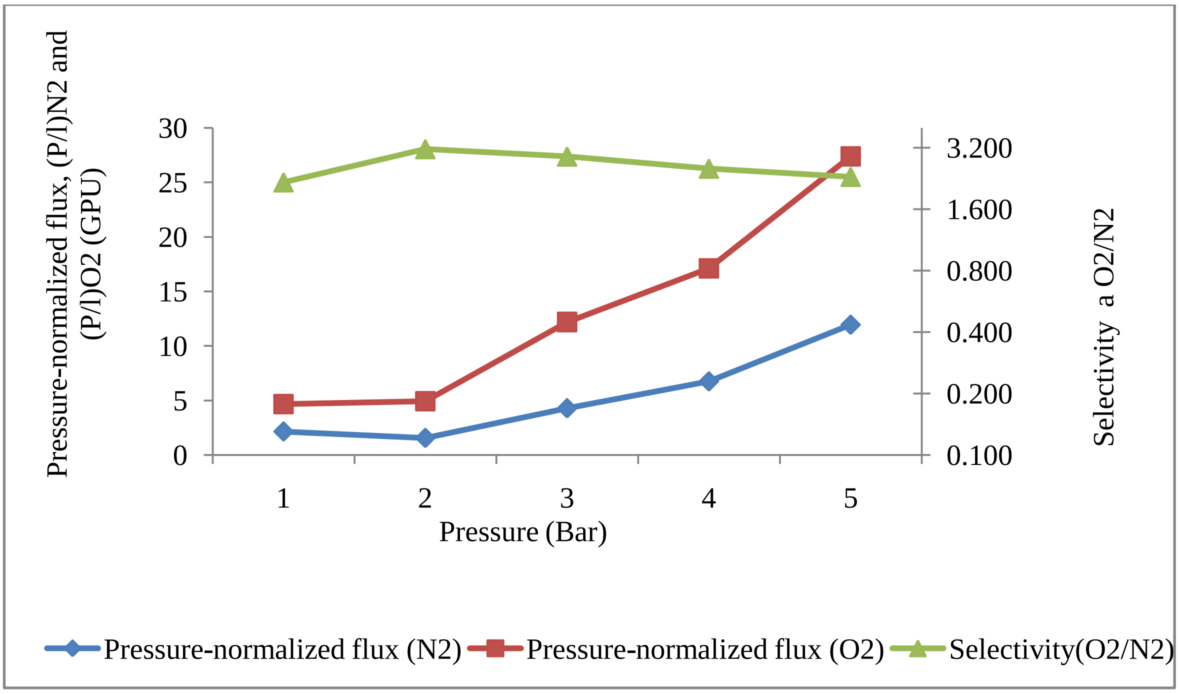


Figure 4.7: Pressure-normalized flux and selectivity of coated MMMs with zeolite 4A at different pressure

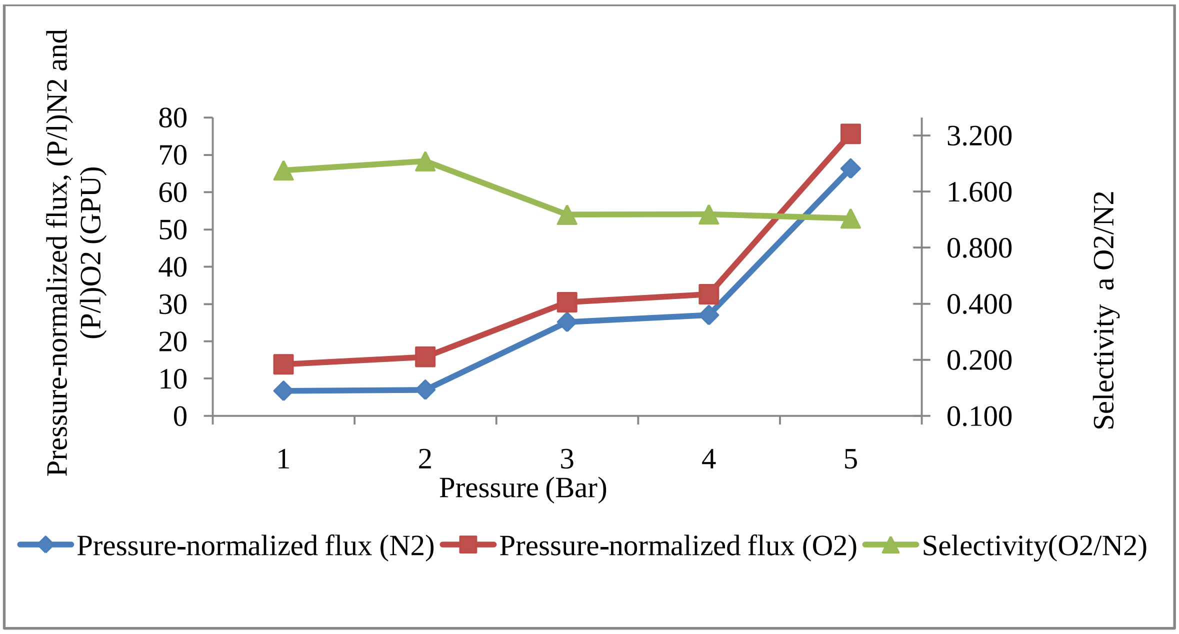


Figure 4.8: Pressure-normalized flux and selectivity of coated MMMs with zeolite 5A at different pressure

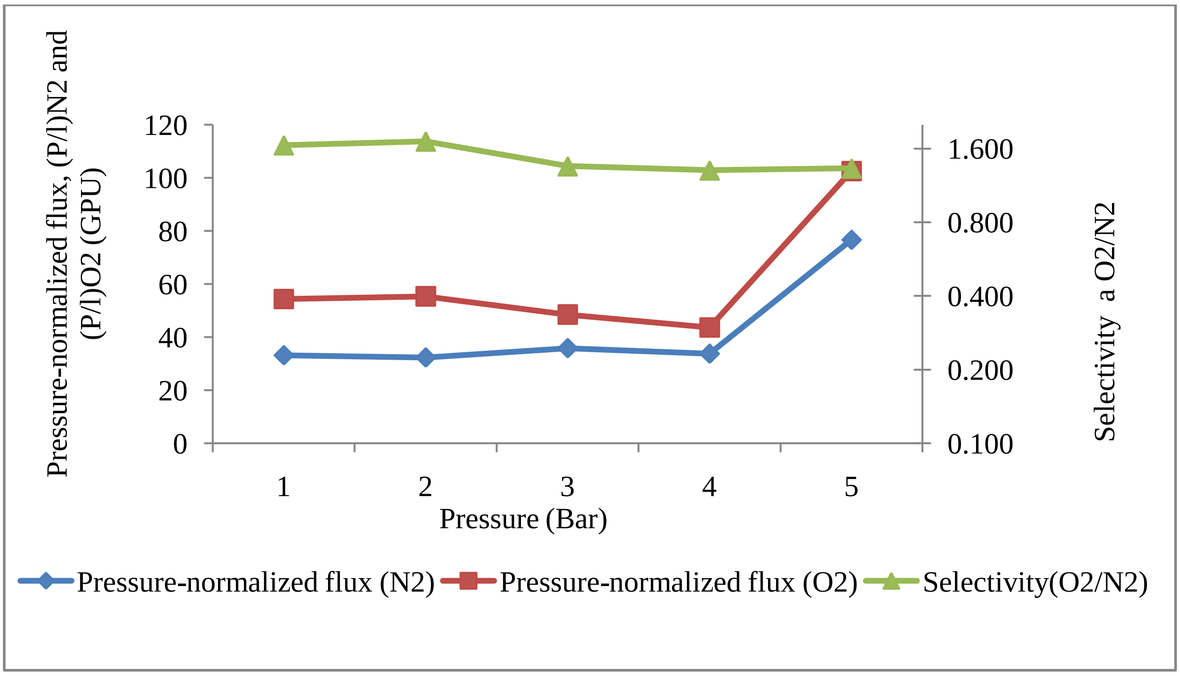


Figure 4.9: Pressure-normalized flux and selectivity of coated MMMs with zeolite 13X at different pressure

Asymmetric membranes that are suitable for gas separation should have two structurally distinct layers, one is thin, dense, selective skin or barrier layer and the other one is thick, porous matrix (substructure) layer whose main function is to provide a physical support for the thin skin (Pandey and Chauhan, 2001). Besides that, the MMMs also should have small enough porosity and pore size so as to increase the membrane selectivity and a thin skin layer for improve the permeation flux (Wang *et al.*, 1995). According to Wang *et al.* (1995), the skin layer that inherent with small fraction or defects, the overall permeation flux that occur when gases transport through this membrane would be the combination of the pore flow and solution-diffusion flow. The pore flow is comparative increased when the pressure is increased. So, this flow will influence the pressure-normalized flux of the O_2/N_2 separation. Based on Henis and Tripodi (1981), they suggested that the surface defect of asymmetric membrane could be repaired by coating with high permeable material which is silicone rubber. However, the incomplete coating membranes surface or not completely plugged the porosity and defect sometimes may do occur (Wang, 1995) and it is suspected that this situation is happened to the produced coated MMMs with all types of zeolite. Because of this small defect, the pore flow is comparative increased when pressure is increased. Thus, it will influence the pressure-normalized flux of O_2/N_2 separation.

From the result obtained, the selectivity of the MMMs is a slightly different. As shown in the Figure 4.7 to Figure 4.9, the selectivity of O_2/N_2 is increased with pressure increased. This condition illustrate that the selectivity of the MMMs increased when the pressure-normalized flux increased. Although this result for MMMs cannot achieve the Robeson 1991 upper bound limit, however, it shows there is an improvement in O_2/N_2 selectivity and O_2 permeability compared to the neat polymer. Figure 4.10 to Figure 4.12 illustrate the surface of coated MMMs by using Scanning Electron Microscope (SEM).

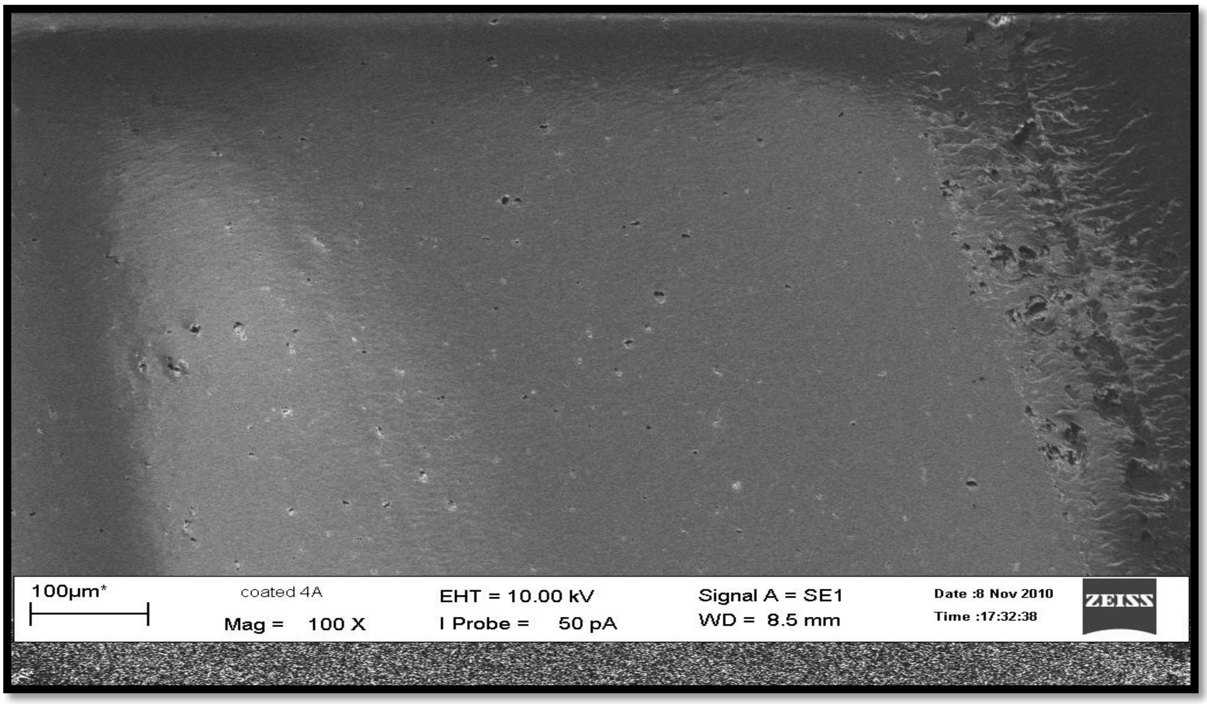


Figure 4.10: Surface layer for coated MMMs with zeolite 4A

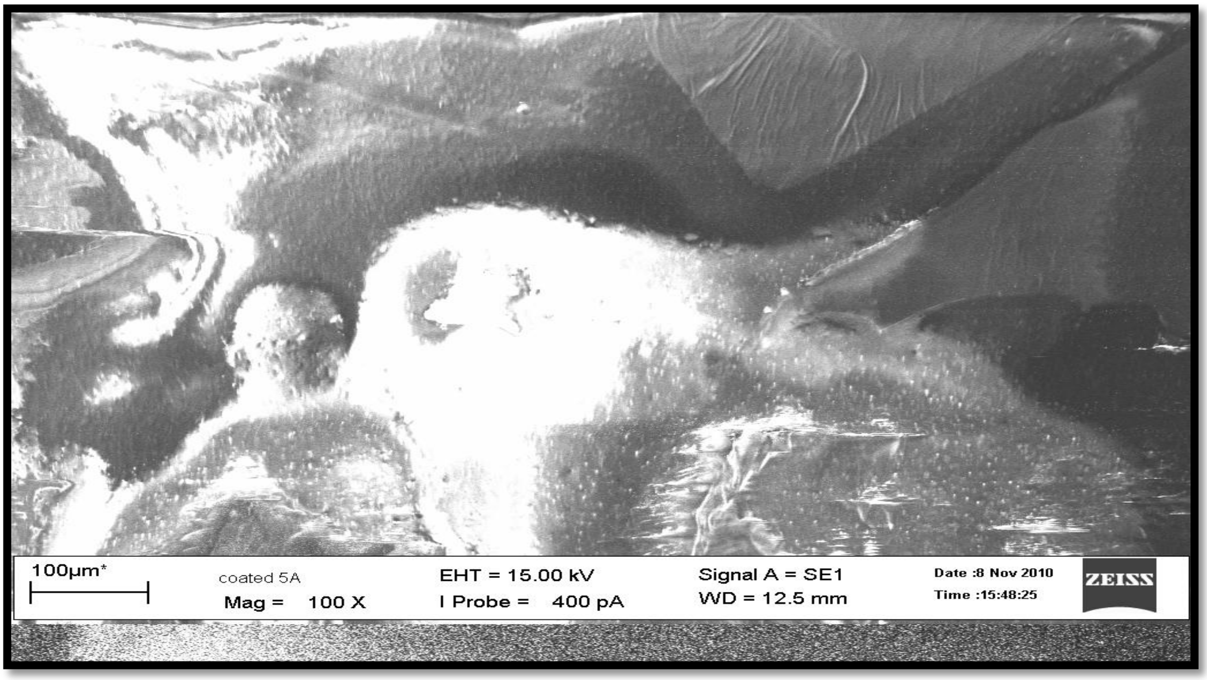


Figure 4.11: Surface layer for coated MMMs with zeolite 5A

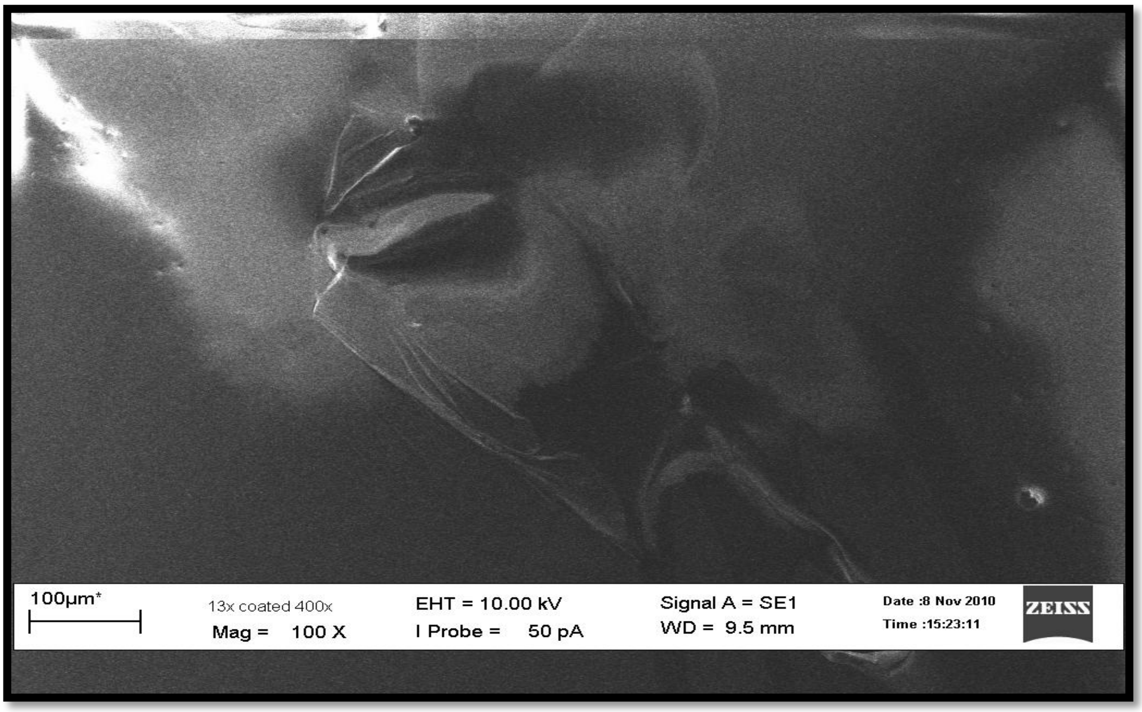


Figure 4.12: Surface layer for coated MMMs with zeolite 13X

The optimum pressure had been found at 2 bars for each type of membrane and the selectivity starts to decreased after pressure 3 bars were applied. Besides that, this position is dominated by solution-diffusion and molecular sieving mechanism. However, Knudsen flow might be contributed but it does not have significant effect since the selectivity increase from pressure 1 to 2 bars. At 3 to 5 bars of pressure, the Poiseuille flow have took place as high pressure was applied. From the result, the selectivity is increased while the permeability is increased. Thus, it suggested that Poiseuille flow was dominated the gas transport at 3 to 5 bars. Therefore, it can be conclude that by incorporation the zeolite in the polymer membrane, it will result in higher permeability and selectivity for gas separation.

4.2 EFFECT OF ZEOLITE TYPES ON GAS SEPARATION PERFORMANCE

4.2.1 Performance of Coated Polyethersulfone Mixed Matrix Membranes (MMMs)

Three different types of zeolite have been used in developing MMMs in order to determine the effect of the gas separation performance. Thus, in this study, zeolite 4A, 5A and 13X have been used. As stated in the literature, all types of zeolite have their own chemical structure, dimension and pore size. Therefore, in this study, the effect of zeolite type was investigated in order to find the suitable zeolite that suitable for polyethersulfone. According to Duval *et al*. (1993), the novel MMMs is considered to be the most practical approach to overcome the limitation of plain polymer membrane. Proper material selection for both matrix and sieve phase is fundamentally important in the development of MMMs. The molecular sieving phase must accurately discriminate between the size and shape differences of the molecules. Polymer matrix selection determines the minimum membrane performance while addition of molecular sieve can only improve the membrane selectivity in the absence of defects (Zimmerman *et al*., 1997).

Since there is a defect from poor polymer sieve contact, the zeolite surface modification have been proposed to improved the interfacial strength in order to enhance the separation performance (Mahajan *et al*., 2002; Mahajan and Koros, 2002; Duval *et al.,* 1994; Liu *et al.,* 2005 and Yong *et al*., 2001). Thus, the zeolite was treated with silane coupling agent. The compositions of prepared MMMs were labeled as Z4A, Z5A and Z13X according to their types of zeolite. Pressure-normalized flux of O_2 and N_2 were measured at 30±2°C and pressure difference of 1 bar. However, in this study, the comparison of performance MMMs with different types of zeolite was observed at optimum pressure of 2 bars. The separation properties of uncoated membranes based on O_2 and N_2 are shown in Table 4.7.

Table 4.7: Performance of uncoated MMMs with different types of zeolite for O_2/N_2 separation (2 bars)

Solution	Membrane	Pressure-normalized flux (GPU)		Selectivity O_2/N_2, α
		O_2	N_2	
Z4A	1	491.61	499.01	0.99
	2	600.05	607.62	0.99
	3	550.26	629.24	0.87
Mean		**547.31±54.28**	**578.62±69.79**	**0.95±0.06**
Z5A	1	660.58	694.30	0.95
	2	554.86	582.27	0.95
	3	484.87	532.04	0.91
Mean		**566.77±88.46**	**602.87±83.07**	**0.94±0.02**
Z13X	1	2679.03	2720.24	0.98
	2	2914.55	3120.24	0.93
	3	2040.18	2130.31	0.96
Mean		**2544.59±452.42**	**2656.95±498.01**	**0.96±0.03**

GPU = 1 X 10^{-6} cm^3 (STP) / (cm^2.s.cm Hg)

*Pressure normalized flux was measured at 2 bars

*Z4A : Solution with zeolite 4A

*Z5A : Solution with zeolite 5A

*Z13X: Solution with zeolite 13X

From the Table 4.7, it shows that the average range of O_2/N_2 selectivity for MMMs with zeolite 4A was about 0.95, MMMs with zeolite 5A was 0.94 while the selectivity for MMMs with zeolite 13X was 0.96. All of the uncoated MMMs seem to have an average value of selectivity. However, all the MMMs look like to have slightly higher pressure-normalized flux. This situation is might be caused of skin layer pores or defect that are dominant for permeability of gas transport through membrane. Basically, the ideal mechanism for gas transport through defect-free membrane is solution-diffusion and molecular sieving. Nonetheless, because of defects occurred on the surface of MMMs prepared, the gas transport is dominated by pore flow which are Knudsen flow and poiseuille flow (Wang *et al.*, 2001) and combine with the solution diffusion and molecular sieving mechanism. Figure 4.13 shows the summarization on performance of uncoated MMMs with different types of zeolite.

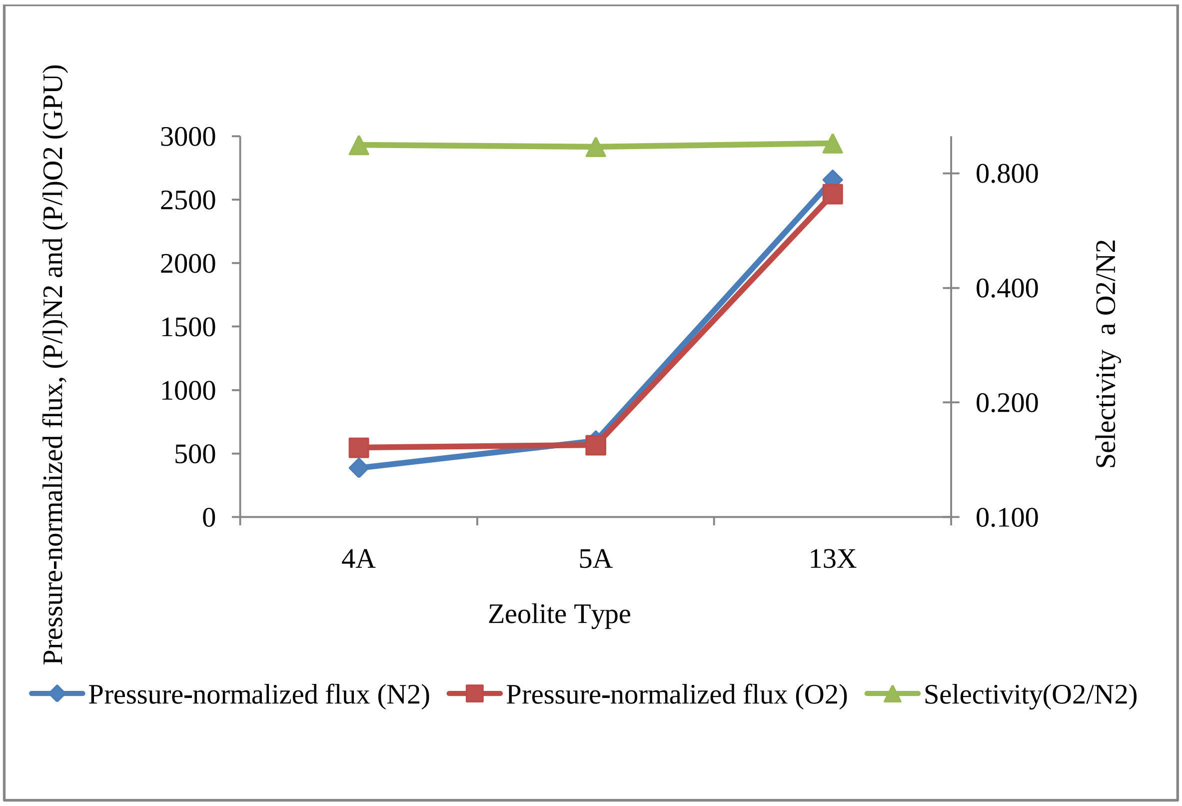


Figure 4.13: Pressure-normalized flux and selectivity of uncoated MMMs with different types of zeolite

In order to know the real performance of MMMs on pressure-normalized flux and selectivity, the surface defect must be covered by silicone rubber. In spite of this, the effect of zeolite on the gas separation performance can be observed since for three types of uncoated MMMs, there are no differences on selectivity.

4.2.2 Performance of uncoated polyethersulfone mixed matrix membranes (MMMs)

All the MMMs were coated using silicone rubber in order to plug the porosity or defect on the surface. By applying the coating, the MMMs should be have a better performance than uncoated MMMs. Table 4.8 summarize the data that have been taken from the experiment.

Table 4.8: Performance of uncoated MMMs with different types of zeolite for O_2/N_2 separation (2 bars)

Solution	Membrane	Pressure-normalized flux (GPU)		Selectivity
		O_2	N_2	O_2/N_2, α
Z4A	1	4.42	1.44	3.08
	2	5.77	1.59	3.63
	3	4.64	1.69	2.75
Mean		**4.94±0.72**	**1.57±0.13**	**3.15±0.45**
Z5A	1	16.60	5.60	2.96
	2	14.36	7.01	2.05
	3	16.57	8.40	1.97
Mean		**15.84±1.29**	**7.00±1.40**	**2.33±0.55**
Z13X	1	50.62	31.71	1.60
	2	54.24	33.15	1.64
	3	61.39	32.31	1.90
Mean		**55.42±5.49**	**32.39±0.73**	**1.71±0.17**

GPU = 1 X 10^{-6} cm^3 (STP) / (cm^2.s.cm Hg)

*Pressure normalized flux was measured at 2 bars

*Z4A : Solution with zeolite 4A

*Z5A : Solution with zeolite 5A

*Z13X: Solution with zeolite 13X

According to Kusworo *et al.* (2008), the phenomenon of the separation performance for PI/PES-zeolite 5A is higher than PI/PES-zeolite 13X in term of selectivity. This condition indicates that the zeolite types have play an important role in determining the gas separation performance of MMMs. In spite of this, the gas transport through the MMMs is affected by the properties of zeolites, pore size and pore structure. Figure 4.14 demonstrate the pressure-normalized flux and selectivity of coated MMMs with different types of zeolite.

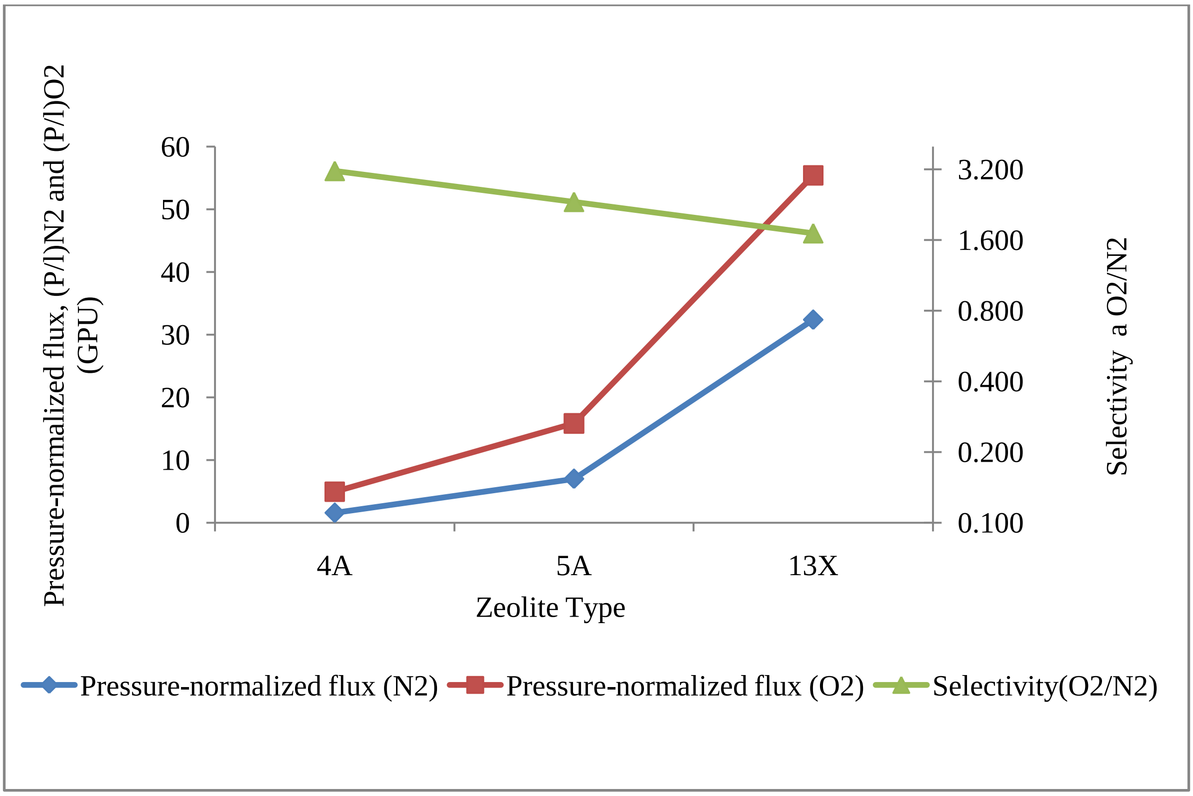


Figure 4.14: Pressure-normalized flux and selectivity of coated MMMs with different types of zeolite

Based on Figure 4.14, it shows that the MMMs with zeolite 4A have a higher selectivity but lowest permeability. However, the MMMs with zeolite 13X has lowest selectivity but higher in permeability. It suggested that, different types of zeolite have their own performance on gas separation. The result on higher in selectivity but lower in permeability indicates that the unselective void or interfacial void between zeolite particle and polymer in MMMs were apparently not formed (Kusworo *et al.*, 2008). Besides that, zeolite 4A has an open crystal structure and relatively small pore size. Thus, it could induce a resistant to the diffusion of the gas penetrate through the zeolite pore. Due to its small pore size, the zeolite 4A can discriminate the gas penetrate on the basis of the differences in molecular size and shape. However, zeolite 13X have a larger pore size, that is why the permeability of MMMs with zeolite 13X is higher than others.

According to Kulprathipanja (2007), mixed-matrix membranes comprising small-pore zeolite will combine the solution-diffusion separation mechanism of the polymer material with the molecular sieving mechanism of the zeolites. The small-pore zeolite molecular sieves in the MMMs are capable of separating mixture of molecular species based on the molecular size or kinetic diameter. However, the separation with the MMMs comprising large or medium pore zeolite is mainly based on solution-diffusion and competitive adsorption when the pores of the large or medium pore zeolite molecular sieve are much larger than all the molecules to be separated. As stated in the literature, zeolite 4A has a pore size of 3.8Å. Thus, it falls between the length of O_2 and N_2 molecules with lengths of 3.75Å and 4.07 Å. Figures 4.15 to Figure 4.17 shows the cross section of MMMs with different types of zeolite and Figure 4.18 to Figure 4.20 shows the location of zeolite in MMMs with different types of zeolite. According to Mahajan *et al*. (2002), the development of MMMs using zeolite 4A that have small pore size showed a significantly increment of O_2/N_2 selectivity compared to the polymer membrane.

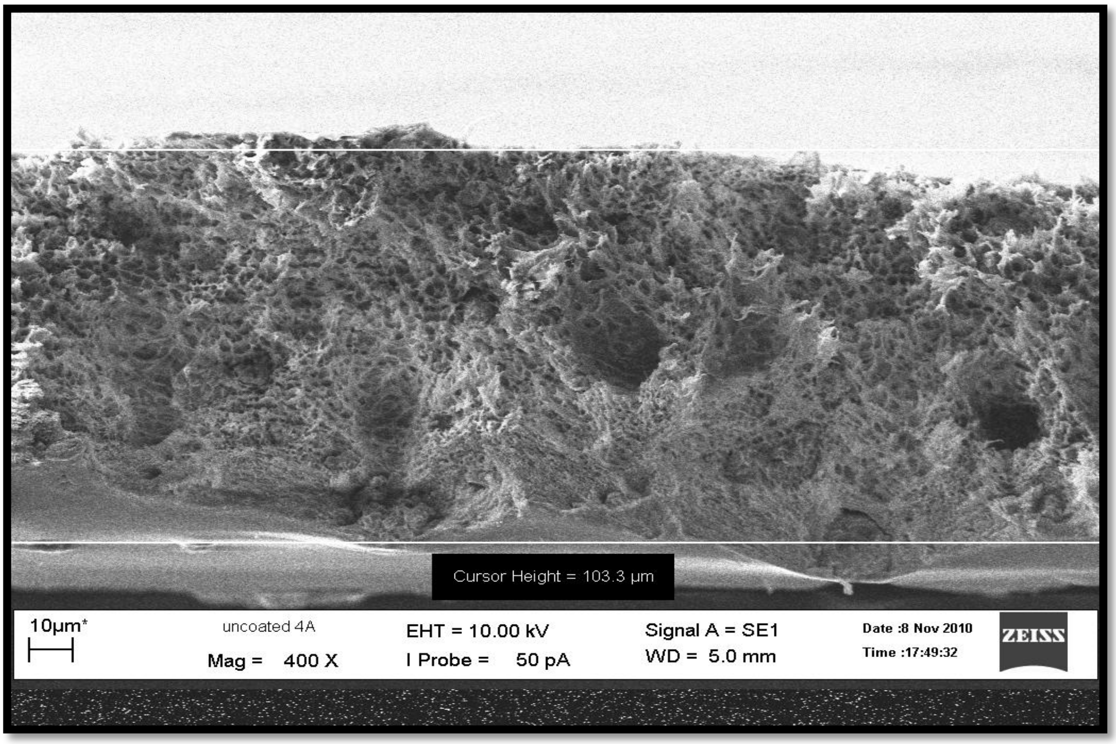


Figure 4.15: Cross section of MMMs with zeolite 4A

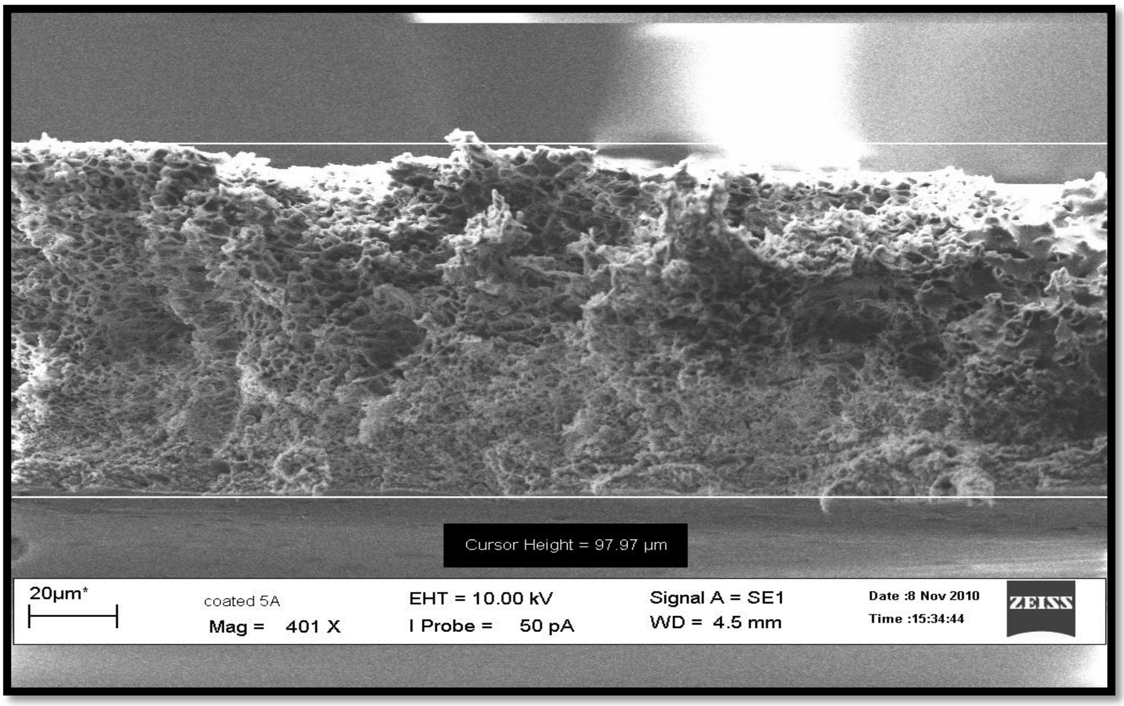


Figure 4.16: Cross section of MMMs with zeolite 5A

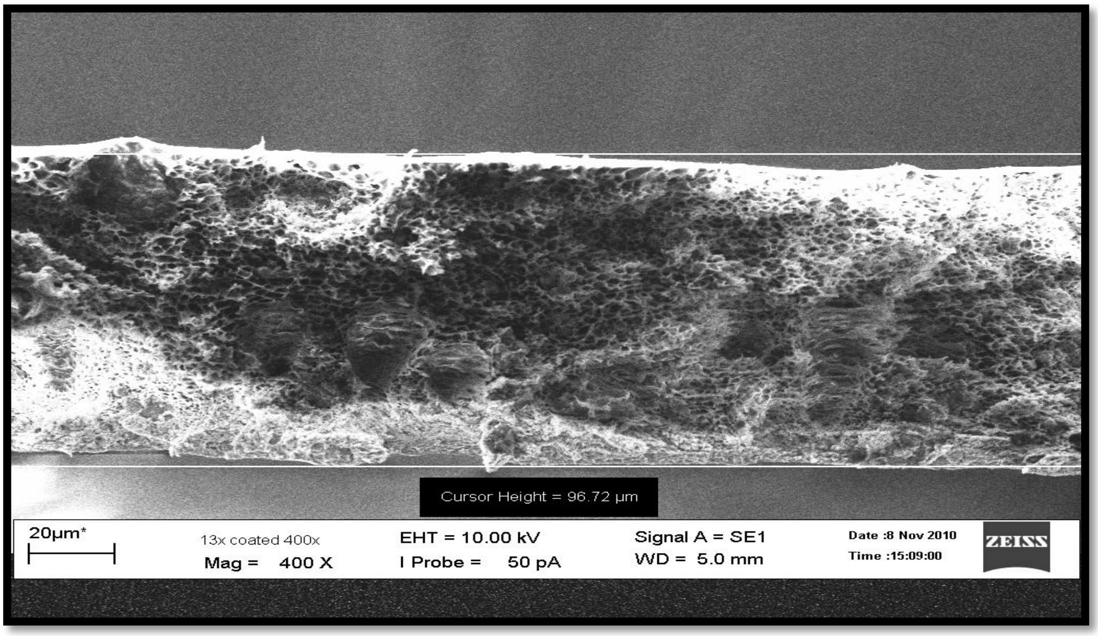


Figure 4.17: Cross section of MMMs with zeolite 13X

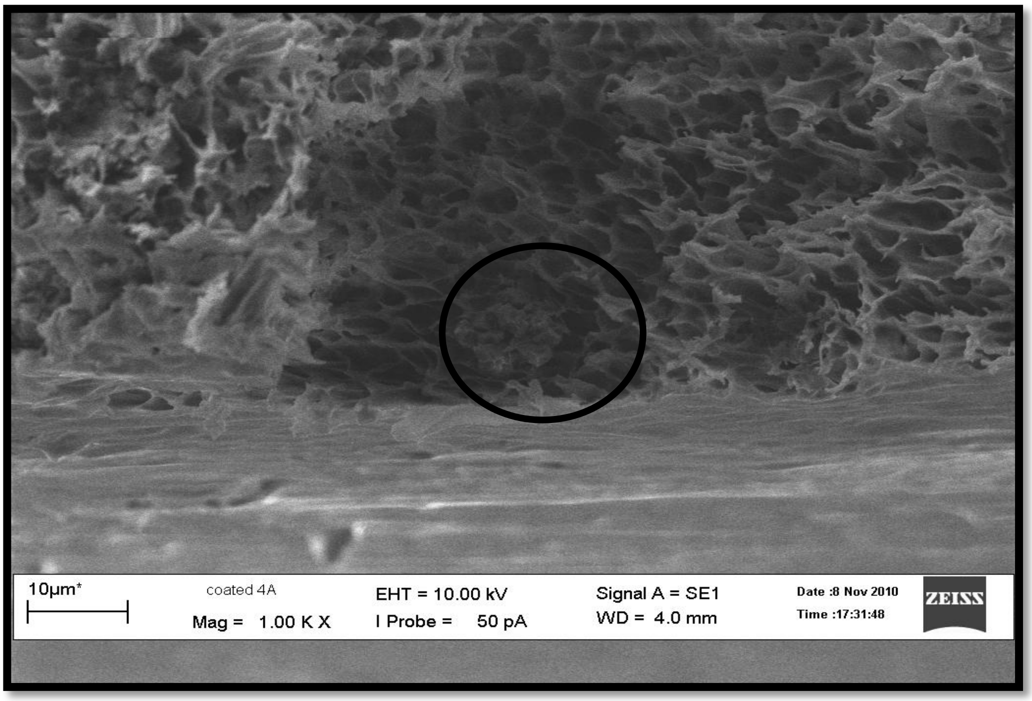


Figure 4.18: Location of the zeolite in MMMs with zeolite 4A

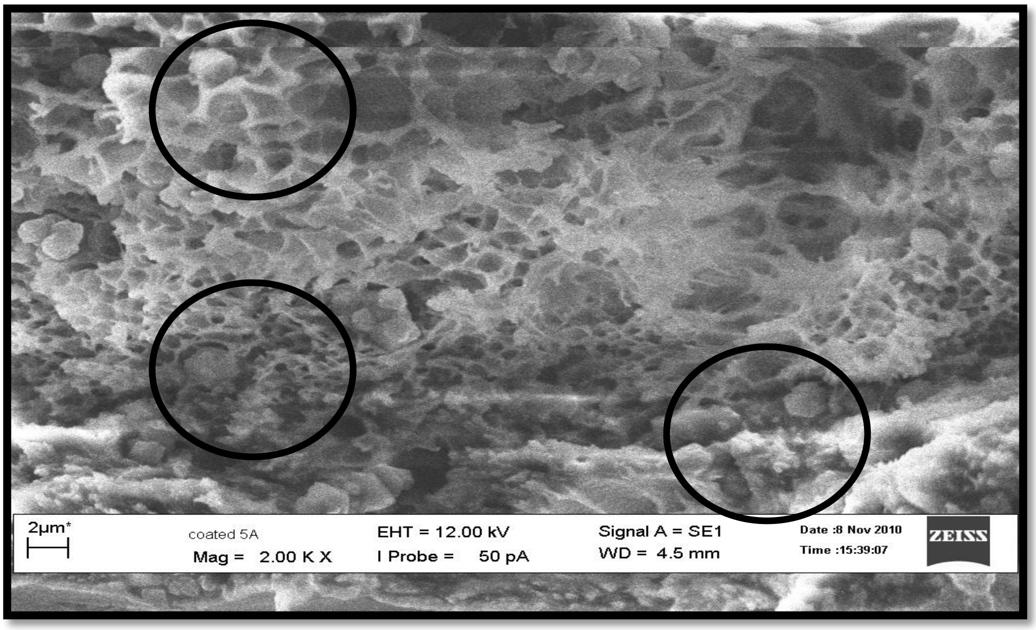


Figure 4.19: Location of the zeolite in MMMs with zeolite 5A

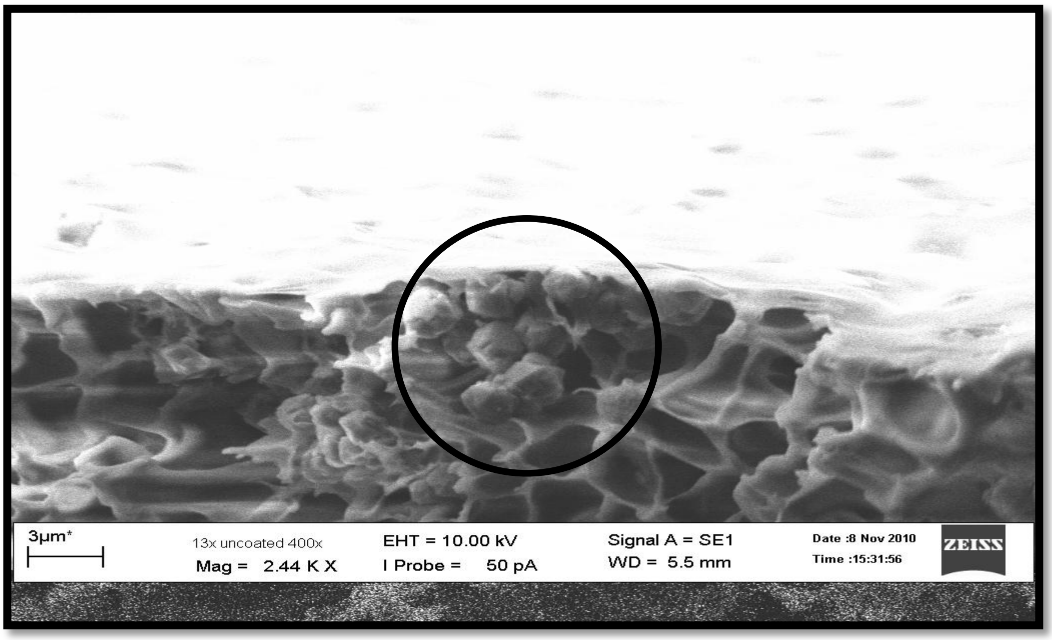


Figure 4.20: Location of the zeolite in MMMs with zeolite 13X

Based on Figure 4.14, it shows that the selectivity of MMMs with zeolite 13X is the lowest. It is suggested that the MMMs have their drawback of the chemical used since the silane coupling agent was used in order to treat the surface of zeolite, it might be contributed to the leaky interface, means that there are no compatibility between polymer and zeolites. Moreover, MMMs itself have their non-idealities on the organic-inorganic interface. This situation is dominated by the leaky interface of the polymer and zeolite. According to Shu (2007), a leaky interface is caused by effective void or high free volume region of sufficient extent to enable partial and less selective bypass of the two gases. However, this type of non-ideality leads to actual loss of separation efficiency. During this condition, the Knudsen diffusion or sorption-diffusion transport is extremely low in selectivity. Thus, it caused the overall membrane exhibits a higher permeability and lower selectivity than the neat polymer. Nevertheless, if the permeability is still quiet high and selectivity is low, that means the zeolite pore size is not suitable for the separation of the gases involve. The pore size might be large enough that it permits both gases to pass through its channel or pores. Therefore, no molecular sieving effects towards the gas separation. This might be happen to the MMMs with zeolite 5A and 13X.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This chapter summarized the results and discussions that have already analyzed in the previous chapter. In this study, the performances of asymmetric mixed matrix membranes (MMMs) were studied by investigating the effect of different types of zeolite and also examined the effect of pressure applied on gas separation performance.

The main material that have been used in this study were polyethersulfone as a polymer matrix while zeolites as the sieve matrix. The effect of different types of zeolite had been investigated using zeolite 4A, 5A and 13X. The MMMs prepared had been tested for gas separation by using pure oxygen (O_2) and nitrogen (N_2) gases. The pressure applied during the permeation test in range 1 to 5 bars. SEM characterizations also have been done in order to view the morphology of MMMs.

Based on the results of this study, a number of conclusions were drawn.

1) Dope solution containing 30 wt% PES, 60 wt%, 5 wt% distilled water and 5 wt% different types of zeolite were used in preparing asymmetric mixed matrix membrane.

2) From the preparation method, by using dry/wet phase inversion process, asymmetric mixed matrix membranes has successfully prepared. It had been confirmed through Scanning Electron Microscope (SEM).

3) The pressure-normalized flux and selectivity of coated MMMs have shown an improvement for gas separation compared to uncoated MMMs. MMMs with zeolite 4A shows the best performance on gas separation compared to MMMs with zeolite 5A and 13X since it has the highest selectivity which is 3.2 while MMMs with zeolite 5A is 2.3 and MMMs with zeolite 13X is 1.7. MMMs with zeolite 13X has the highest permeability of O_2 which is 102.5 GPU while MMMs with zeolite 4A has the lowest value of permeability which is 4.68 GPU and the value of permeability for MMMs with zeolite 5A is 13.8 GPU. However, although MMMs with zeolite 13X has the highest value of permeability, this situation shows that the MMMs with zeolite 13X have poor polymer-sieve contact thus it give an additional path for the gas to pass through without have to pass through the molecular sieve. So, the zeolite 4A is more compatible with PES since it has higher selectivity for MMMs prepared.

4) When the pressure is increased, the pressure-normalized flux of all gases increased while the selectivity of O_2/N_2 is increased until pressure 2 bars was applied then, decreased until pressure 5 bars. It indicates that, the MMMs prepared have 2 bars as optimum pressure. By using different types of zeolite, there is having an improvement based on Robeson upper bound limit compared to neat polymer.

5.2 RECOMMENDATIONS

Based on the results and conclusions obtained, the following recommendations arise in order to further improve the gas separation performance of the MMMs.

1) Asymmetric mixed matrix membrane can be prepared by using other polymer, solvent, non-solvent additive and different zeolites in order to generalize the membrane formation.

2) Gas permeation on asymmetric MMMs should be test by using gas mixture since there are many factors that can make mixed-gases separation have different results from single gas test.

3) The problem that occurs in this study is would be the poor polymer-sieve contact. This could be eliminated by doing the treatment on the zeolite surface. However, in this study the APTMOS have been used as silane coupling agent. Maybe the APTMOS is not suitable for PES. So, the other silane coupling agent should be used such as (γ-aminopropyl)-triethoxy silane, N-β-(aminoethyl)-γ-aminopropyltrimethoxy silane, (γ-glycidyloxy-propyl)-trimethoxy silane and (3-aminopropyl)-dimethylethoxy silane in order to minimize the voids between the polymer and zeolites thus, improve the gas separation performance.

4) Morphology and structure of asymmetric MMMs should be further characterized by using other microscopic or spectroscopic methods such as Atomic Force Microscopy (AFM) that used to study the pore size and pore size distribution, surface roughness and size of macromolar nodules.

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APPENDICES

APPENDIX A

Details calculation for permeability and selectivity

Details calculation for permeability and selectivity

This calculation is based on the data that have highest selectivity which is at 2 bars for mixed matrix membranes (MMMs) with zeolite 4A. Three samples of MMMs were tested.

Pressure applied = 2 bars
Volume changes = 1 cm^3
Membrane area = 12.568 cm^2

	Time (s)	
	O_2	N_2
Membrane 1	119.93	369.2
Membrane 2	91.93	334.13
Membrane 3	114.42	314.37

Calculation of pressure normalized flux and selectivity for membrane 1

$$\text{Permeates flowrates }(O_2) = \frac{\text{volume changes}}{\text{time}} = \frac{1\ \text{cm}^3}{119.93\ \text{s}} = 8.34 \times 10^{-3}\ \frac{\text{cm}^3}{\text{s}}$$

$$\text{Permeates flowrates }(N_2) = \frac{\text{volume changes}}{\text{time}} = \frac{1\ \text{cm}^3}{369.2\ \text{s}} = 2.71 \times 10^{-3}\ \frac{\text{cm}^3}{\text{s}}$$

The pressure normalized flux of membrane is calculated in GPU.

$$\text{Pressure normalized flux (P)} = \frac{\text{permeates flowrate}}{\text{pressure applied} \times \text{membrane area}}$$

$$P(O_2) = \frac{8.34 \times 10^{-3}\ \frac{\text{cm}^3}{\text{s}} \times 1\ \text{GPU} \times 1\ \text{bar}}{2\ \text{bar} \times 12.568\ \text{cm}^2 \times 1 \times 10^{-6} \frac{\text{cm}^3}{\text{cm}^2 . \text{s} . \text{cm Hg}} \times 75\ \text{cm Hg}}$$

$P(O_2)$ = 4.42 GPU

$$P(N_2) = \frac{2.71 \times 10^{-3}\ \frac{\text{cm}^3}{\text{s}} \times 1\ \text{GPU} \times 1\ \text{bar}}{2\ \text{bar} \times 12.568\ \text{cm}^2 \times 1 \times 10^{-6} \frac{\text{cm}^3}{\text{cm}^2 . \text{s} . \text{cm Hg}} \times 75\ \text{cm Hg}}$$

$P(N_2)$ = 1.44 GPU

The calculation of selectivity for membrane 1

$$\text{Selectivity, } \alpha = \frac{\text{Permeability } O_2}{\text{Permeability } N_2}$$

$$\alpha = \frac{4.42 \text{ GPU}}{1.44 \text{ GPU}}$$

$$\alpha = 3.08$$

These calculations also were applied for membrane 2 and membrane 3. From the calculation:

The value of pressure normalized flux and selectivity for membrane 2

Pressure normalized flux, $P(O_2)$ = 5.77 GPU
Pressure normalized flux, $P(N_2)$ = 1.59 GPU

Selectivity, α = 3.63

The value of pressure normalized flux and selectivity for membrane 3

Pressure normalized flux, $P(O_2)$ = 4.63 GPU
Pressure normalized flux, $P(N_2)$ = 1.69 GPU

Selectivity, α = 2.75

The average pressure normalized flux and average selectivity were calculated based on three membranes.

$$\text{Average pressure normalized flux, } P(O_2) = \frac{4.42 \text{ GPU} + 5.77 \text{ GPU} + 4.63 \text{ GPU}}{3}$$

Average pressure normalized flux, $P(O_2)$ = 4.94 GPU

$$\text{Average pressure normalized flux, P}(N_2) = \frac{1.44\ \text{GPU}\ + 1.59\ \text{GPU}\ + 1.69\ \text{GPU}}{3}$$

Average pressure normalized flux, $P(O_2)$ = 1.57 GPU

$$\text{Average selectivity, } \alpha = \frac{3.08\ + 3.63 + 2.75}{3}$$

Average selectivity,α = 3.15

APPENDIX B

Table summarization of all data that have been taken from the experiment

PERMEABILITY AND SELECTIVITY

Type of gas applied: O2, N2 Description: zeolite 4A
Pressure applied: 1,2,3,4,5 bar
Volume changes: 10 cm3
Membrane area: 12.568 cm2

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	35.14	30.59	10.79	10.63	4.87	4.98	3.48	3.04	2.66	2.82
Membrane 2	28.98	24.84	8.84	8.73	4.22	3.91	2.98	2.59	2.36	2.16
Membrane 3	31.68	27.24	9.64	8.43	3	2.7	2.17	1.94	1.73	1.43
Average Flowrate	0.3151	0.36553	1.03178	1.09082	2.58546	2.75643	3.61252	4.10171	4.592344	5.056245
	315.099	365.529	1031.78	1090.82	2585.46	2756.43	3612.52	4101.71	4592.344	5056.245
Permeability (GPU)	334.287	387.788	547.307	578.621	914.302	974.76	958.127	1087.87	974.3994	1072.829
Selectivity	0.86204		0.94588		0.93798		0.88074		0.908252	

Type of gas applied: O2, N2 Description: zeolite 4A
Pressure applied: 1,2,3,4,5 bar
Volume changes: 1 cm3
Membrane area: 12.568 cm2

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	226.78	495.63	119.93	369.2	37.74	97.69	17.5	42.88	7.44	19.63
Membrane 2	212.04	454.39	91.93	334.13	29.87	66.6	13.84	36.09	8.23	17.55
Mmebrane 3	242.87	527.13	114.42	314.37	22.98	89.19	15.55	39.31	7.62	16.35
Average Flowrate	0.00441	0.00204	0.00932	0.00296	0.0345	0.01215	0.06457	0.02549	0.12905	0.056362
	4.41436	2.03848	9.31859	2.96079	34.4972	12.1545	64.5686	25.4894	129.0496	56.36152
Permeability (GPU)	4.68317	2.16262	4.94302	1.57054	12.1993	4.29822	17.1251	6.7604	27.38163	11.95874
Selectivity	2.16551		3.14733		2.83822		2.53316		2.289676	

Dope Formulation: 30%PES 60%NMP 5%NSA 5%Zeolite 5A GPU = 1 x 10^-6 cm3/cm2 .s.cmHg

PERMEABILITY AND SELECTIVITY

Type of gas applied: O2, N2 Description: zeolite 5A
Pressure applied: 1,2,3,4,5 bar
Volume changes: 10 cm3
Membrane area: 12.568 cm2

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	27.78	28.86	8.03	7.64	3.73	3.47	2.71	2.33	2.34	2.06
Membrane 2	28.17	29.73	9.56	9.11	4.97	4.63	2.09	1.47	1.12	1.12
Membrane 3	37.61	35.98	10.94	9.97	5.01	4.68	2.98	2.89	2.61	2.37
Average Flowrate	0.32695	0.32026	1.06848	1.13653	2.22968	2.39281	3.94348	4.85159	5.67783	6.00078
	326.949	320.264	1068.48	1136.53	2229.68	2392.81	3943.48	4851.59	5677.83	6000.78
Permeability (GPU)	346.858	339.767	566.771	602.872	788.486	846.173	1045.9	1286.76	1204.72	1273.24
Selectivity	1.02087		0.94012		0.93183		0.81282		0.94618	

Type of gas applied: O2, N2 Description: zeolite 5A
Pressure applied: 1,2,3,4,5 bar
Volume changes: 1 cm3
Membrane area: 12.568 cm2

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	61.67	164.96	31.95	94.68	13.89	15.45	7.52	9.74	2.42	2.63
Membrane 2	85.82	162.47	36.95	75.72	9.135	12.72	8.14	9.42	3.3	3.97
Membrane 3	88.62	148.21	32.02	63.18	12.95	14.22	8.84	10.32	2.84	3.27
Average Flowrate	0.01305	0.00632	0.02986	0.0132	0.08623	0.07122	0.12298	0.10191	0.35612	0.31264
	13.0506	6.32141	29.8643	13.1987	86.2278	71.2216	122.984	101.909	356.122	312.643
Permeability (GPU)	13.8453	6.70636	15.8415	7.00124	30.4929	25.1862	32.6182	27.0286	75.5616	66.3362
Selectivity	2.0645		2.26266		1.2107		1.2068		1.13907	

Dope Formulation: 30%PES 60%NMP 5%NSA 5%Zeolite 13X GPU = 1 x 10^-6 cm3/cm2 .s.cmHg

PERMEABILITY AND SELECTIVITY

Type of gas applied: O2, N2 Description: zeolite 13X
Pressure applied: 1,2,3,4,5 bar
Volume changes: 10 cm3
Membrane area: 12.568 cm2

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	6.15	5.87	1.98	1.95	1.49	1.02	1.04	0.83	0.83	0.73
Membrane 2	4.93	4.31	1.82	1.7	1.21	0.98	0.84	0.73	0.7	0.67
Mmebrane 3	7.14	6.77	2.6	2.49	1.44	1.27	1.3	1.18	1.22	1.14
Average Flowrate	1.68499	1.83362	4.79705	5.00887	7.30677	9.29401	9.73748	11.40713	11.5102	12.4653
	1684.99	1833.62	4797.05	5008.87	7306.77	9294.01	9737.48	11407.13	11510.2	12465.3
Permeability (GPU)	1787.6	1945.28	2544.59	2656.95	2583.91	3286.66	2582.61	3025.444	2442.23	2644.88
Selectivity	0.91894		0.95771		0.78618		0.85363		0.92338	

Type of gas applied: O2, N2 Description: zeolite 13X
Pressure applied: 1,2,3,4,5 bar
Volume changes: 1 cm3
Membrane area: 12.568 cm2

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	19.95	35.67	10.48	16.73	7.55	10.81	5.6	8.65	1.78	2.77
Membrane 2	19.55	33.19	9.78	16	7.34	9.77	6.29	7.23	2.88	3.21
Membrane 3	19.04	27.96	8.64	16.42	6.98	9.12	5.37	7.78	1.85	2.43
Average Flowrate	0.05127	0.03131	0.10447	0.06106	0.13732	0.1015	0.17459	0.127485	0.48319	0.36135
	51.2657	31.3099	104.47	61.0581	137.319	101.503	174.591	127.4847	483.187	361.353
Permeability (GPU)	54.3876	33.2165	55.4159	32.3881	48.5603	35.8948	46.3058	33.81199	102.522	76.6716
Selectivity	1.63737		1.71099		1.35285		1.36951		1.33716	

OVERALL RESULTS ZEOLITE 4A and SKIN THICKNESS

polyethersulfone oxygen permeability coefficient (0.51 x 10-10 cm3 (STP) cm/ cm2. s.cmHg (Wang, 1996)

Angstrom (A) = 1 x10^-8 cm

Type of gas applied: O2, N2

Description: zeolite 4A (uncoated)

Pressure applied: 1,2,3,4,5 bar

Volume changes: 10 cm3

Membrane area: 12.568 cm2

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	35.14	30.59	10.79	10.63	4.87	4.98	3.48	3.04	2.66	2.82
Membrane 2	28.98	24.84	8.84	8.73	4.22	3.91	2.98	2.59	2.36	2.16
Membrane 3	31.68	27.24	9.64	8.43	3	2.7	2.17	1.94	1.73	1.43

Pressure (Bar)	Permeates Flowrates, Q x(10^-3 cm3/s)		Pressure Normalized Flux		Selectivity, α	Average Pressure Normalized flux		Average Pressure Normalized flux (Barrer)		Average Selectivity, α	Skin Layer Thickness , A	Average Skin Layer Thickness , A	Average Active Skin Layer Thickness , cm	Average STDEVA O2	Average STDEVA N2	Average STDEVA Selectivity	Average STDEVA Skin Thickness
	O2	N2	P*l* (O2)	P*l* (N2)		P*l* (O2)	P*l* (N2)	P*l* (O2)	P*l* (N2)								
1	284.576	326.9042	301.9053	346.8112	0.870517928	334.2874708	387.788352	0.513170834	0.595301019	0.86250309	16.8927116	15.3511836	1.53512E-07	32.09064239	40.1663532	0.00707166	1.484387649
	345.0656	402.5765	366.0785	427.0915	0.857142857						13.9314395						
	315.6566	367.1072	334.8786	389.4623	0.859848485						15.2293997						
2	926.7841	940.7338	491.6105	499.0101	0.985171455	547.3071252	578.6209713	0.513405098	0.54277926	0.949069781	10.3740671	9.38056668	9.38057E-08	54.28188938	69.7876366	0.0646065	0.942435502
	1131.222	1145.475	600.054	607.6148	0.987556561						8.49923568						
	1037.344	1186.24	550.2569	629.2381	0.874481328						9.26839728						
3	2053.388	2008.032	726.1433	710.104	1.022587269	914.3020098	974.7601892	0.531390256	0.566528413	0.949709184	7.02340686	5.81197734	5.81198E-08	235.7667631	305.945893	0.06449425	1.369157948
	2369.668	2557.545	837.99	904.4292	0.926540284						6.08599116						
	3333.333	3703.704	1178.773	1309.747	0.9						4.326534						
4	2873.563	3289.474	762.1375	872.4469	0.873563218	958.1267105	1087.870139	0.529992948	0.601761225	0.878899984	6.69170592	5.53155384	5.53155E-08	237.4885889	253.446828	0.01327161	1.271202927
	3355.705	3861.004	890.0129	1024.03	0.87						5.73025392						
	4608.295	5154.639	1222.23	1367.133	0.894009217						4.17270168						
5	3759.398	3546.099	797.6657	752.4081	1.060150376	974.3994238	1072.829473	0.52697153	0.580204149	0.93399807	6.3936558	5.4081675	5.40817E-08	224.1083999	373.988959	0.11790317	1.140901659
	4237.288	4629.63	899.0639	982.3106	0.915254237						5.6725668						
	5780.347	6993.007	1226.469	1483.77	0.826589595						4.1582799						

Type of gas applied: O2, N2 Description: zeolite 4A (coated)

Pressure applied: 1,2,3,4,5 bar

Volume changes: 1 cm3

Membrane area: 12.568 cm2

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	226.78	495.63	119.93	369.2	37.74	97.69	17.5	42.88	7.44	19.63
Membrane 2	212.04	454.39	91.93	334.13	29.87	66.6	13.84	36.09	8.23	17.55
Membrane 3	242.87	527.13	114.42	314.37	22.98	89.19	15.55	39.31	7.62	16.35

Pressure (Bar)	Permeates Flowrates, Q x(10^-3 cm3/s)		Pressure Normalized Flux		Selectivity, α	Average Pressure Normalized flux		Average Pressure Normalized flux (Barrer)		Average Selectivity, α	Skin Layer Thickness , A	Average Skin Layer Thickness , A	Average Active Skin Layer Thickness , cm	Average STDEVA O2	Average STDEVA N2	Average STDEVA Selectivity	Average STDEVA Skin Thickness
	O2	N2	P*l* (O2)	P*l* (N2)		P*l* (O2)	P*l* (N2)	P*l* (O2)	P*l* (N2)								
1	4.40956	2.017634	4.678082	2.140499	2.185510186	4.683174307	2.162618297	0.511568273	0.236234408	2.166291768	1090.19042	1092.35369	1.09235E-05	0.317589623	0.16222527	0.02158098	74.12759068
	4.716091	2.200753	5.00328	2.334768	2.142944727						1019.33141						
	4.117429	1.897065	4.368162	2.012588	2.17042039						1167.53924						
2	8.338197	2.708559	4.422978	1.436749	3.078462436	4.943024601	1.57054446	0.516879821	0.164227938	3.153528302	1153.06938	1045.675195	1.04568E-05	0.724164482	0.1261558	0.44829074	142.6150307
	10.87784	2.992847	5.770126	1.587549	3.634613293						883.862824						
	8.739731	3.180965	4.63597	1.687336	2.747509177						1100.09338						
3	26.49709	10.23646	9.370212	3.619939	2.588500265	12.19930602	4.298217292	0.531267192	0.187182929	2.899787726	544.277977	435.4896834	4.3549E-06	3.02536447	0.89286549	0.86866007	106.5109071
	33.47841	15.01502	11.83903	5.309787	2.229661868						430.778569						
	43.5161	11.21202	15.38868	3.964927	3.881201044						331.412504						
4	57.14286	23.3209	15.15565	6.185258	2.450285714	17.12513916	6.760398691	0.514695878	0.203183712	2.52863965	336.5082	300.5498952	3.0055E-06	2.004851451	0.58196555	0.07868873	35.21435258
	72.25434	27.70851	19.16357	7.348957	2.61						266.129914						
	64.30868	25.43882	17.0562	6.746982	2.527974277						299.011572						
5	134.4086	50.94244	28.51869	10.80892	2.63844086	27.38163101	11.95873623	0.510946188	0.223152181	2.305517479	178.830072	186.601809	1.86602E-06	1.426376448	1.09013846	0.28839595	9.952111903
	121.5067	56.98006	25.78118	12.08998	2.132442284						197.818749						
	131.2336	61.16208	27.84502	12.97731	2.145669291						183.156606						

OVERALL RESULTS ZEOLITE 5A and SKIN THICKNESS

polyethersulfone oxygen permeability coefficient (0.51 x 10-10 cm3 (STP) cm/ cm2. s.cmHg (Wang, 1996)

Angstrom (A) = 1 x10^-8 cm

Type of gas applied: O2, N2 Description: zeolite 5A (uncoated)

Pressure applied:	1,2,3,4,5	bar
Volume changes:	10	cm3
Membrane area:	12.568	cm2

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	27.78	28.86	8.03	7.64	3.73	3.47	2.71	2.33	2.34	2.06
Membrane 2	28.17	29.73	9.56	9.11	4.63	4.63	2.09	1.47	1.12	1.12
Membrane 3	37.61	35.98	10.94	9.97	4.68	4.68	2.98	2.89	2.61	2.37

Pressure (Bar)	Permeates Flowrates, Q x(10^-3 cm3/s)		Pressure Normalized Flux		Selectivity, α	Average Pressure Normalized flux		Average Pressure Normalized flux (Barrer)		Average Selectivity, α	Skin Layer Thickness , A	Average Skin Layer Thickness , A	Average Active Skin Layer Thickness , cm	Average STDEVA O2	Average STDEVA N2	Average STDEVA Selectivity	Average STDEVA Skin Thickness
	O2	N2	P*l* (O2)	P*l* (N2)		P*l* (O2)	P*l* (N2)	P*l* (O2)	P*l* (N2)								
1	359.9712	346.5003	381.8918	367.6006	1.03887689	346.8582	339.767	0.520018	0.509387	1.0169718	13.3545683	14.9922415	1.49922E-07	56.16351	39.26337	0.05287878	2.67581062
	354.9876	336.3606	376.6047	356.8434	1.05537806						13.5420514						
	265.8867	277.9322	282.078	294.857	0.95666046						18.0801049						
2	1245.33	1308.901	660.5824	694.3033	0.95143213	566.7713	602.8723	0.518222	0.551231	0.93856518	7.72045956	9.14340852	9.14341E-08	88.45961	83.06853	0.02359429	1.39953202
	1046.025	1097.695	554.8616	582.2697	0.95292887						9.19148112						
	914.0768	1003.009	484.8699	532.0438	0.91133455						10.5182849						
3	2680.965	2881.844	948.0745	1019.112	0.93029491	822.4939	846.173	0.515594	0.530438	0.97676497	5.37932394	6.26866704	6.26867E-08	108.8325	149.825	0.04024425	0.77103715
	2159.827	2159.827	763.7836	763.7836	1						6.67728414						
	2136.752	2136.752	755.6235	755.6235	1						6.74939304						
4	3690.037	4291.845	978.6858	1138.3	0.8597786	1045.904	1286.758	0.521564	0.641671	0.84430885	5.21106984	4.98673104	4.98673E-08	198.24	461.5265	0.13389661	0.87747091
	4784.689	6802.721	1269.014	1804.244	0.70						4.01886936						
	3355.705	3460.208	890.0129	917.7296	0.96979866						5.73025392						
5	4273.504	4854.369	906.7482	1029.996	0.88034188	1204.717	1273.241	0.585895	0.619221	0.92946262	5.6244942	4.8633447	4.86334E-08	599.17	542.1892	0.06263801	1.90817543
	8928.571	8928.571	1894.456	1894.456	1						2.6920656						
	3831.418	4219.409	812.9467	895.2704	0.90804598						6.2734743						

Type of gas applied: O2, N2		Description:	zeolite 5A (coated)
Pressure applied:	1,2,3,4,5 bar		
Volume changes:	1 cm3		
Membrane area:	12.568 cm2		

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	61.67	164.96	31.95	94.68	13.89	15.45	7.52	9.74	2.42	2.63
Membrane 2	85.82	162.47	36.95	75.72	9.135	12.72	8.14	9.42	3.3	3.97
Membrane 3	88.62	148.21	32.02	63.18	12.95	14.22	8.84	10.32	2.84	3.27

Pressure (Bar)	Permeates Flowrates, Q x(10^-3 cm3/s)		Pressure Normalized Flux		Selectivity, α	Average Pressure Normalized flux		Average Pressure Normalized flux (Barrer)		Average Selectivity, α	Skin Layer Thickness , A	Average Skin Layer Thickness , A	Average Active Skin Layer Thickness , cm	Average STDEVA O2	Average STDEVA N2	Average STDEVA Selectivity	Average STDEVA Skin Thickness
	O2	N2	P*l* (O2)	P*l* (N2)		P*l* (O2)	P*l* (N2)	P*l* (O2)	P*l* (N2)								
1	16.21534	6.062076	17.20278	6.431228	2.67488244	13.84531	6.706359	0.523834	0.253733	2.08015082	296.463724	378.347386	3.78347E-06	2.914204	0.394273	0.52674411	71.231985
	11.6523	6.154982	12.36187	6.529793	1.89314845						412.559053						
	11.28413	6.747183	11.97129	7.158055	1.67242158						426.019381						
2	31.2989	10.56189	16.60243	5.602532	2.96338028	15.84146	7.001244	0.512364	0.226443	2.32859261	307.183914	323.432453	3.23432E-06	1.28673	1.396647	0.55105796	27.5624997
	27.0636	13.20655	14.35582	7.005384	2.04925575						355.256514						
	31.23048	15.82779	16.56614	8.395817	1.97314179						307.85693						
3	71.99424	64.72492	25.45945	22.88879	1.11231102	30.49289	25.18622	0.527348	0.435573	1.20094238	200.318524	172.941179	1.72941E-06	7.177463	2.471578	0.16600034	36.3168608
	109.4691	78.61635	38.71175	27.80124	1.39244663						131.74296						
	77.22008	70.32349	27.30747	24.86862	1.0980695						186.762051						
4	132.9787	102.6694	35.26913	27.23037	1.29521277	32.6182	27.02859	0.512227	0.424449	1.20662725	144.602381	157.03716	1.57037E-06	2.633394	1.240081	0.07688574	12.6989333
	122.8501	106.1571	32.58278	28.1554	1.16						156.524386						
	113.1222	96.89922	30.0027	25.69999	1.16742081						169.984714						
5	413.2231	380.2281	87.67731	80.67646	1.08677686	75.56165	66.33621	0.518229	0.454957	1.14707187	58.167846	68.583576	6.85836E-07	11.7135	13.67318	0.05824792	10.5796132
	303.0303	251.8892	64.29669	53.44561	1.2030303						79.31979						
	352.1127	305.8104	74.71094	64.88657	1.15140845						68.263092						

OVERALL RESULTS ZEOLITE 13X and SKIN THICKNESS

polyethersulfone oxygen permeability coefficient (0.51 x 10-10 cm3 (STP) cm/ cm2. s.cmHg (Wang, 1996)

Angstrom (A) = 1 x10^-8 cm

Type of gas applied: O2, N2
Description: zeolite 13X (uncoated)
Pressure applied: 1,2,3,4,5 bar
Volume changes: 10 cm3
Membrane area: 12.568 cm2

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	6.15	5.87	1.98	1.95	1.49	1.02	1.04	0.83	0.83	0.73
Membrane 2	4.93	4.31	1.82	1.7	1.21	0.98	0.84	0.73	0.7	0.67
Mmebrane 3	7.14	6.77	2.6	2.49	1.44	1.27	1.3	1.18	1.22	1.44

Pressure (Bar)	Permeates Flowrates, Q x(10^-3 cm3/s)		Pressure Normalized Flux		Selectivity, α	Average Pressure Normalized flux		Average Pressure Normalized flux (Barrer)		Average Selectivity, α	Skin Layer Thickness , A	Average Skin Layer Thickness , A	Average Active Skin Layer Thickness , cm	Average STDEVA O2	Average STDEVA N2	Average STDEVA Selectivity	Average STDEVA Skin Thickness
	O2	N2	P*l* (O2)	P*l* (N2)		P*l* (O2)	P*l* (N2)	P*l* (O2)	P*l* (N2)								
1	1626.016	1703.578	1725.033	1807.318	0.95447154	1787.6	1945.282	0.521909	0.567946	0.92563006	2.9564649	2.91960924	2.91961E-08	337.4139	462.8959	0.04461672	0.53216028
	2028.398	2320.186	2151.918	2461.474	0.87423935						2.36997918						
	1400.56	1477.105	1485.848	1567.054	0.94817927						3.43238364						
2	5050.505	5128.205	2679.029	2720.245	0.98484848	2544.587	2656.946	0.52192	0.544966	0.95886891	1.90367496	2.0510976	2.0511E-08	452.4204	498.0105	0.02541171	0.39610578
	5494.505	5882.353	2914.548	3120.281	0.93406593						1.74984264						
	3846.154	4016.064	2040.183	2130.312	0.95769231						2.4997752						
3	6711.409	9803.922	2373.368	3466.978	0.68456376	2583.907	3286.656	0.514251	0.654112	0.79214185	2.14884522	1.99020564	1.99021E-08	296.1769	440.5963	0.09988373	0.2153631
	8264.463	10204.08	2922.577	3608.488	0.80991736						1.74503538						
	6944.444	7874.016	2455.776	2784.502	0.88194444						2.07673632						
4	9615.385	12048.19	2550.229	3195.468	0.79807692	2582.613	3025.444	0.526408	0.61667	0.85827228	1.99982016	2.03827824	2.03828E-08	559.3252	708.2471	0.05559644	0.44352021
	11904.76	13698.63	3157.427	3633.203	0.87						1.61523936						
	7692.308	8474.576	2040.183	2247.66	0.90769231						2.4997752						
5	12048.19	13698.63	2556.374	2906.563	0.87951807	2442.226	2515.627	0.538102	0.554275	1.00566293	1.9950129	2.2033275	2.20333E-08	653.4988	911.873	0.15616428	0.65046213
	14285.71	14925.37	3031.13	3166.852	0.95714286						1.682541						
	8196.721	6944.444	1739.173	1473.466	1.18032787						2.9324286						

Type of gas applied: O2, N2 Description: zeolite 13X (coated)
Pressure applied: 1,2,3,4,5 bar
Volume changes: 1 cm3
Membrane area: 12.568 cm2

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	19.95	35.67	10.48	16.73	7.55	10.81	5.6	8.65	1.78	2.77
Membrane 2	19.55	33.19	9.78	16	7.34	9.77	6.29	7.23	2.88	3.21
Membrane 3	19.04	27.96	8.64	16.42	6.98	9.12	6.37	7.78	1.85	2.43

Pressure (Bar)	Permeates Flowrates, Q x(10^-3 cm3/s)		Pressure Normalized Flux		Selectivity, α	Average Pressure Normalized flux		Average Pressure Normalized flux (Barrer)		Average Selectivity, α	Skin Layer Thickness , A	Average Skin Layer Thickness , A	Average Active Skin Layer Thickness , cm	Average STDEVA O2	Average STDEVA N2	Average STDEVA Selectivity	Average STDEVA Skin Thickness
	O2	N2	P*l* (O2)	P*l* (N2)		P*l* (O2)	P*l* (N2)	P*l* (O2)	P*l* (N2)								
1	50.12531	28.03476	53.17771	29.74195	1.78796992	54.38759	33.21653	0.510186	0.31159	1.65138518	95.904837	93.8056668	9.38057E-07	1.275164	4.24166	0.16469956	2.19262356
	51.1509	30.12956	54.26575	31.96431	1.69769821						93.981933						
	52.52101	35.76538	55.7193	37.94333	1.46848739						91.5302304						
2	95.41985	59.77286	50.61524	31.70638	1.59637405	55.41588	32.38811	0.513261	0.299978	1.71094294	100.7601696	92.619876	9.26199E-07	5.485269	0.726876	0.16532021	8.92926169
	102.2495	62.5	54.23801	33.15298	1.63599182						94.0300056						
	115.7407	60.90134	61.39441	32.30498	1.90046296						83.0694528						
3	132.4503	92.50694	46.83865	32.71339	1.43178808	48.56032	35.89483	0.510538	0.377379	1.35648034	108.884439	105.134776	1.05135E-06	1.940809	3.042188	0.06635636	4.1573767
	136.2398	102.3541	48.17872	36.19568	1.33106267						105.8558652						
	143.2665	109.6491	50.66358	38.77542	1.30659026						100.6640244						
4	178.5714	115.6069	47.3614	30.66172	1.54464286	43.72125	33.81199	0.511717	0.395738	1.3051455	107.682624	117.040757	1.17041E-06	3.163563	3.020683	0.21050386	8.14079828
	158.9825	138.3126	42.16595	36.6838	1.15						120.9506616						
	156.9859	128.5347	41.6364	34.09047	1.22135008						122.4889848						
5	561.7978	361.0108	119.2017	76.59895	1.55617978	102.5221	76.67161	0.534743	0.39991	1.32809221	42.784614	52.158771	5.21588E-07	25.08541	10.60873	0.2211589	14.8033169
	347.2222	311.5265	73.67329	66.0994	1.11458333						69.224544						
	540.5405	411.5226	114.6914	87.31649	1.31351351						44.467155						

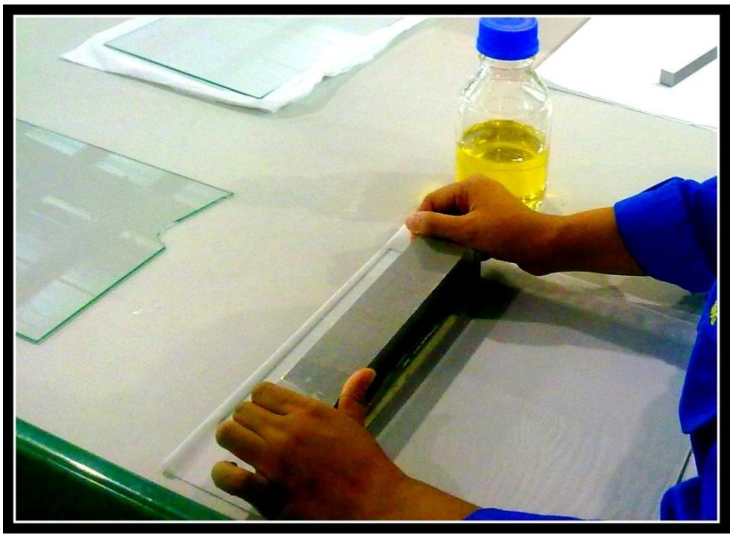
APPENDIX C

APPENDIX C

(i) Preparation casting solution

(ii) Ultrasonic bath to remove microbubble

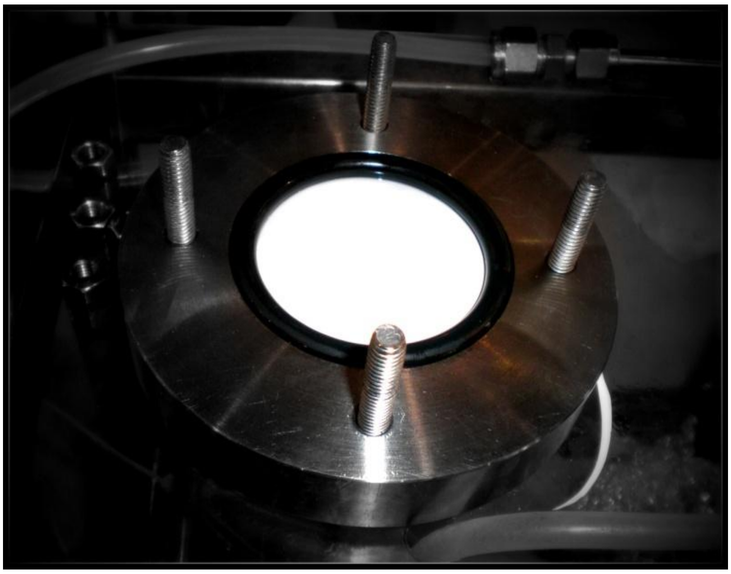
(iii) Membrane casting



(iv) Coagulation medium (water – 1 day and methanol – 1 day)

(v) Cut a membrane after drying in 2 days with ambient condition (1 atm and 30°C)

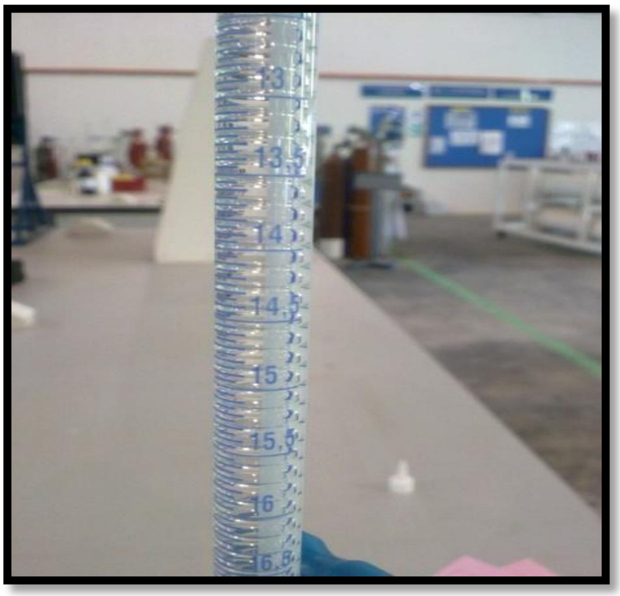
(vi) Coating with solution of 3% PDMS and 97% n-hexane



(vii) Drying the membrane coating at ambient condition or 30°C in oven

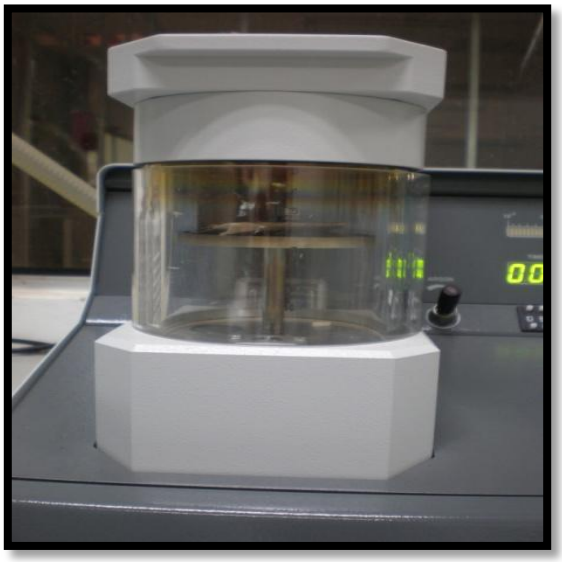
(viii) Gas permeation test

(ix) Bubble flow meter



(x) Liquid nitrogen

(xi) Coating the membrane sample with platinum



(xii) Characterize the structure of the membrane using SEM