EFFECT OF ZEOLITE CONCENTRATION ON DEVELOPEMENT OF POLYETHERSULFONE MIXED MATRIX MEMBRANES (MMMs) FOR O₂/N₂ SEPARATION

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UNIVERSITI MALAYSIA PAHANG **BORANG PENGESAHAN STATUS TESIS** JUDUL : EFFECT OF ZEOLITE CONCENTRATION ON DEVELOPMENT OF POLYETHERSULFONE MIXED MATRIX MEMBRANES (MMMs) FOR O₂/N₂ **SEPARATION** SESI PENGAJIAN: 2010/2011 MUHAMMAD HIDAYAT BIN MUSA Sava (HURUF BESAR) mengaku membenarkan tesis Projek Sarjana Muda (PSM) ini disimpan di Perpustakaan Universiti Malaysia Pahang dengan syarat-syarat kegunaan seperti berikut: 1. Hakmilik kertas projek adalah di bawah nama penulis melainkan penulisan sebagai projek bersama dan dibiayai oleh UMP, hakmiliknya adalah kepunyaan UMP. 2. Naskah salinan di dalam bentuk kertas atau mikro hanya boleh dibuat dengan kebenaran bertulis daripada penulis. 3. Perpustakaan Universiti Malaysia Pahang dibenarkan membuat salinan untuk tujuan pengajian mereka. 4. Kertas projek hanya boleh diterbitkan dengan kebenaran penulis. Bayaran royalti adalah mengikut kadar yang dipersetujui kelak. *Sava membenarkan/tidak membenarkan Perpustakaan membuat salinan kertas projek ni 5. sebagai bahan pertukaran di antara institusi pengajian tinggi. 6. **Sila tandakan (✓) SULIT dungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972) (Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di TERHA mana penyelidikan dijalankan) TIDAK Disahkan oleh (TANDATANGAN PENULIS) (TANDATANGAN PENYELIA)

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A thesis submitted in fulfillment of the requirements for the award of the Degree of Bachelor of Chemical Engineering (Gas Technology)

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NOVEMBER 2010

I declare that this thesis entitled "Effect of Zeolite Concentration on Development of Polyethersulfone Mixed Matrix Membranes (MMMs) for O_2/N_2 Separation" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

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Special Thanks to supervisor, Madam Norida Binti Ridzuan for all of your Care, Support and Best Wishes.

And,

Special Dedication to my beloved parents, siblings and all my friends for their love and encouragement.

ACNOWLEDGEMENT

With the completion of my study I would like to say grace to Allah S.W.T for His blessings and guidances throughout this project particularly and throughout the life given to me.

I would take this opportunity to give my special thanks to my supervisor Madam Norida Binti Ridzuan for her knowledge, consistency and motivations that help me throughout the project until the end.

Thank you also to the staffs of University Malaysia Pahang especially laboratory staffs that have been supplying all the apparatus and equipment that I used for this study. The cooperation and help will never be forgotten

To my beloved family, thank you for the motivation and reminder. My sincere appreciation to friends that had been giving suggestions, ideas, motivation and companies. Thank you for your support and care. Your deeds will always be remembered.

ABSTRACT

The membrane gas separation is an effective economical process to separate gas such as oxygen (O_2) and nitrogen (N_2) gases. The limited selectivity and permeability trade off of plain polymeric membrane have force researchers in finding alternatives to improve polymeric membrane performance. With the insertion of inorganic filler in polymer solution such as zeolite, mixed matrix membranes (MMMs) was produced. In this study, the effect of concentration zeolite loading was studied in order to identify optimum composition for the best separation performance. The polymer solution contains Polyethersulfone (PES) as the polymer, N-Methyl Pyrrolidone (NMP) as the solvent and distilled water (H₂O) as the non-solvent. The zeolite concentration valued between 5 to 20 wt % was applied. To increase the compatibility of zeolite with the polymer, 3-Aminopropyl-Trimethoxysilane (APTMOS) was used to treat the zeolite prior to dope formulation to modify the zeolite surface. The dry/wet phase inversion method was used to produce the asymmetric flat sheet membrane. The prepared membrane was coated with silicone and N-Hexane to decrease the surface defect of the membrane. In order to determine the membrane performance, the membranes were tested using O₂ and N₂ as the test gases using permeability test rig. The surface and cross section image of the prepared membrane was identified by using Scanning Electron Microscope (SEM). The results show that the MMMs with 15 % concentration of zeolite possessed the highest selectivity of 3.3 while the lowest selectivity is at 5 % zeolite concentration that is 1.3 and the optimum pressure was found at 3 bar. Therefore it proves that by insertion of zeolite at 15 wt% provides an interconnected channel that will only allow the flow of O_2 and preventing N_2 . As a conclusion by increasing concentration of zeolite loading, the high selectivity and high permeability of MMMs will be increased.

ABSTRAK

Proses pengasingan gas menggunakan membran adalah salah satu dari proses yang ekonomikal dan berhemat untuk mengasingkan gas oksigen (O_2) dan nitrogen (N₂).Kadar pemilihan dan resapan terhadap gas yang terhad oleh membran polimer telah mendesak para penyelidik untuk mencari alternatif untuk mempertingkatkan prestasi dan kemampuan polimer membran. Dengan penambahan bahan bukan organik di dalam larutan polimer contohnya seperti zeolit, membran campuran matrik (MMMs) akan terhasil. Dalam kajian ini, efek kepekatan zeolit yang ditambah dikaji untuk mendapatkan komposisi optimum terbaik. Larutan polimer terdiri daripada Poliethersulfona (PES) sebagai polimer, N-Metil Pyrrolidona (NMP) sebagai pelarut dan air suling (H₂O) sebagai bahan tambah bukan pelarut. Kepekatan zeolit yang dikaji adalah di antara 5 hingga 20 % jisim. Untuk meningkatkan keserasian antara zeolit dan polimer, 3-Aminopropil-Trimetoksisilan (APTMOS) digunakan untuk mengubahsuai permukaan zeolit sebelum penghasilan larutan polimer. Proses fasa balikan kering/basah digunakan untuk memghasilkan membran asimetrik kepingan rata. Membran yang terhasil akan disalut dengan silikon dan N-Heksana untuk tujuan mengurangkan kecacatan pada permukaan membran. Membran yang terhasil diuji mengunakan gas O₂ dan gas N₂ sebagai gas ujian pada mesin penguji kadar penembusan dan imej permukaan serta keratin rentas membran yang terhasil, didapati menggunakan Mikroskop Pengimbas Elektron (SEM). Keputusan kajian menunjukkan MMMs yang berkepekatan zeolit 15% mempunyai kadar pemilihan yang tertinggi iaitu, 3.3 manakala pemilihan yang paling rendah didapati pada kepekatan zeolit 5% iaitu 1.3 dan tekanan optimum adalah pada 3 bar .Oleh itu dapat dibuktikan bahawa penambahan zeolit sebanyak 15 % menjadikan ikatan zeolit dan zeolit yang mana akan hanya membenarkan pengaliran gas O_2 dan menghalang pengaliran gas N_2 . Oleh yang demikian, dapat disimpulkan peningkatan kepekatan zeolit dalam membran, kedua-dua kadar penyerapan dan pemilihan MMMs pasti meningkat.

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LIST OF SYMBOLS

Abbreviations

CO ₂	-	Carbon Dioxide		
H_2	-	Hydrogen		
MMMs	-	Mixed Matrix Membranes		
AlO ₄	-	Aluminium Oxide		
SiO_4	-	Silicone Oxide		
O ₂	-	Oxygen		
N_2	-	Nitrogen		
NH2	-	Amino Group		
SEM	-	Scanning Electron Microscopic		
GS	-	Gas Separation		
H ₂ O	-	Water		
PES	-	Polyethersulfone		
NMP	-	1-methyl-2-pyrrolidone		
APTMOS	-	3-Aminopropyl- Trimethoxysilane		
UK	-	United Kingdom		
GPU	-	Gas Permeation Unit		
MW	-	Molecular Weight		
Wt% °C	- -	Weight percentage Degree celcius		
V/V	-	Volume over volume total		
STP	-	Standard Pressure and Temperature		

Parameters/Symbols

Р	-	Overall permeability
P _c	-	Permeability of the continuous polymer phase $(\frac{cm^3}{cmHg \ s \ cm^2})$
P _d	-	Permeability of the dispersed zeolite phase $\left(\frac{cm^3}{cmHg \ s \ cm^2}\right)$
α	-	Selectivity (Unitless)
Q	-	Flow rate of gas species (cm ³ /s)
А	-	Area of membrane (cm^2)
ΔP	-	Pressure difference across membrane (cm Hg)
М	-	Charge balancing cation
n	-	cation valence
W	-	Moles of water contained in the zeolitic voids
Å	-	Amstrong
μm	-	Micrometer
cm	-	Centimeter
%	-	Percentage
Kg	-	Kilogram
g	-	Gram
M_i	-	Molecular weight species i (g/mol)
η_i	-	Viscosity species i (µPa s)
σ_i	-	Collision diameter i (cm)
(P/ <i>l</i>)	-	Pressure Normalized Flux (cm ³ (STP)/ cm ² . s. cmHg)

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Gas separation is one of the technologies that become wider and getting more attention each year. By applying gas separation we can obtain more pure products. The examples of gas separation processes are absorption, cryogenic distillation and gas permeation (Bernardo *et. al*, 2009). Gas separation process is applied in many processes in the chemical industry such as separation of acid gases like CO_2 from natural gas, separation of H₂ from CO_2 for the product of fermentation using carbohydrate rich substrate (Khan *et. al*, 2010).

Gas permeation process is a gas separation process that uses polymeric membrane and it is an attractive process because of its low energy consumption, simple operation and low maintenance requirements (Sen *et. al*, 2007; Khan *et. al*, 2010). The application of polymeric membranes is limited by the permeability and selectivity trade off (Robeson, 1991). Both membrane's permeability and selectivity influence the economics of a gas separation membrane process.

As stated before the polymeric membrane have a limitation on the trade-off between permeability and selectivity. As the selectivity increase, the permeability tends to decrease and vice versa (Bernardo *et. al*, 2009). Chain stiffness and interchain separation increases are recognized as ways to systematically improve separation performance until the interchain separation becomes large enough that the polymer segmental motion no longer controls penetrant diffusion. Other than that, polymeric membrane cannot withstand high temperature and aggressive chemical environments (Bernardo *et. al*, 2009). The development of inorganic membranes such as silica membranes, zeolites membrane and carbon based molecular sieve was introduced because they can with stand aggressive chemicals as well as high temperatures. But these material also present drawbacks such as high cost, modest reproducibility, brittleness, low permeability in the case of highly selective dense membrane and difficult sealing at high temperature (Bernardo *et. al*, 2009).

The combination of the polymer membrane and inorganic membrane produce a new type of materials called Mixed Matrix Membranes (Bernardo *et. al*, 2009). Mixed Matrix Membranes (MMMs) have recently emerged as promising membrane morphology for gas separation. Their microstructure consists of an inorganic materials incorporated into a polymeric matrix by embedding a filler material into the polymer matrix (Bernardo *et. al*, 2009; Sen *et. al*, 2007). The examples of the fillers are carbon molecular sieve and zeolite molecular sieve. MMMs combine the easy processability of the polymer with the size sieving properties of the molecular sieving material (Khan *et. al*, 2010).

Zeolite is a mineral and they are crystalline alumino-silicates consisting AlO_4 and SiO_4 tetrahedral that are connected to form a network of channels and cavities (Khan *et. al*, 2010). The insertion of Zeolite in the polymeric membrane does increase the permeability and selectivity of the membrane towards the gases. The successful development of MMMs depends on several factors, such as the proper selection of polymer matrix and inorganic fillers and the elimination of interfacial defects between the two phases. It is also important to control the filler concentration, shape and dimensions to obtained best results (Bernardo *et. al*, 2009).

A result of a research on gas permeation characteristics of polymer-zeolite mixed matrix membranes (the MMMs of the polyethersulfone and zeolite [4A and 13X]) by Suer, for mixed matrix membrane between PES and zeolite 13X, for zeolite loading rate between 0.0% to 8.3% the permeability of N₂ gas decreases from 0.14 to 0.077 barrer. For loading rate of zeolite from 16.6% to 50.0%, the permeability of N₂ gas increases from 0.088 to 0.12 barrer. While for the selectivity of O_2/N_2 gas, with the increase of zeolite loading rate, from 0.0% to 50.0%, the selectivity increases from 3.71 to 4.18 (Suer *et. al*, 1994). Therefore, by varying the zeolite concentration, it will expect to produce membrane with the best separation performance for gas separation.

1.2 Problem Statement

The concentration or the loading rate of the zeolite into the polymer matrix during membrane fabrication plays an important role on determining and production of the expected membrane that will allow maximum gas separation process. According to Sen and co-worker, the increasing zeolite loading rate will increase the membrane selectivity and the permeability of the membrane. But at high loading rate, the selectivity of the membrane will decrease and increase the permeability for certain membrane morphology (Mixed matrix membrane of polyethylene imene and silicate-1) (Sen *et. al*, 2007). While on the other hand, Suer and co-worker, reported that, at low zeolite loading rate, the permeability decrease, while the selectivity increase for the MMMs of the polyethersulfone and zeolite (Suer *et. al*, 1994). But at high zeolite loading rate both selectivity and permeability increases. This shows that the concentration of the zeolite must be at the optimum point to have the highest permeability and selectivity. Therefore this study will focus on the effect of zeolite

concentration on the development of polyether sulfone mixed matrix membranes for O_2 and N_2 gas separation

1.3 Objective

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

- To develop MMMs for O₂/ N₂ gas separation by varying the composition of zeolite during dope formulation.
- Correlating membrane performance with fabrication conditions hence producing MMMs for O₂/ N₂ gas separation.
- 3. To study membrane morphology.
- 4. To identified the optimum zeolite loading by analyzing the membrane performance.

1.4 Scope of Study

In order to achieve the above mentioned objective the following scopes were drawn:

- 1. Characterization of coated and uncoated membrane using pure N_2 and O_2 as test gas.
- 2. Morphological studies of the surface layer and cross section of the developed membrane using Scanning Electron Microscopy (SEM).
- 3. Varying the percentage of zeolite loading in dope formulation.

1.5 Benefit and Significant of Research

By doing a research on the development of mixed matrix membrane, with the insertion a certain concentration of zeolite in the matrix of the polymeric membrane, possibly the permeability and selectivity will increase, therefore we will get a better separation of gas and it leads to more cost and energy saved. More pure product will be obtained, so the product receive by the consumer will be at a satisfactory level and if there is a downstream process waits, this will ensure a better result for downstream processes that use the product.

CHAPTER 2

LITERATURE REVIEW

3.1 Historical Development of Membranes

Studies of membrane can be traced back to the eighteenth century. A good example is Abbé Nolet started the use of the word Osmosis for the description of permeation of water from a lower concentration to a higher concentration through a diaphragm in 1748. For next two centuries the application of membrane are still limited with no commercial used but still it was used as a laboratory tools in developing physical and chemical theories (Baker, 2000). Table 2.1 show the overall events on the membrane technology development 1960s to 1980s.

Table 2.1: Historical background and the development of membrane technology
(Baker, 2000)

Year/ century	Researcher/ scientist	Events
1748	Abbé Nolet	Introduced the word osmosis for water permeation through diaphragm
1867	Moritz Traube and W.Pfeffer	Introduced a fortified copper-ferrocyanide membrane that allows water to move from diluted to the concentrated parts.
1887	Van't Hoff	Introduction of Van't Hoff equation that explain the behaviour of ideal dilute solutions
1907	Bechhold	Devised a technique called dry phase inversion method to prepare nitrocellulose (collodion) membranes
1918	Zsigmondy and Bachmann	Improve Bechhold method and patent the dry phase inversion method
1930s	-	Microporous collodion membranes were commercially available.
1940s	US army	Develop filters to test water safety for drinking at the end of World War II
1945	W.J.Kolf	Demostrated the first successful artificial kidney based on membrane separation concept
1947	Goetz	Produce cellulose acetate-cellulose nitrate microfiltration membrane by vapor induced phase inversion
1954	Milipore corp.	Commercialized Goetz'smembrane
1960s	Sidney Loeb and S. Sourirajan	Development and introduction of their method of making defect-free, high flux, anistropic reverse osmosis membrane
1966	Alex Zaffaroni	Founder of membranes for controlled drug delivery systems
1980s	-	 -First major development of membrane application in industry -Mansato Prism membrane produce for hydrogen separation
1980s	GFT(Germany engineering company)	Introduction of the first commercial pervaporation systems for dehydration of alcohol

In the 1980s separation by using membranes, emerged as a commercial process on a large scale. In this period, significant progress was made in virtually every aspect of membrane technology, including improvements in membrane formation processes (including interfacial polymerization and multiplayer composite casting and coating), chemical and physical structures, configuration and applications.

2.2 Membrane Separation Technology

Membrane can be defined as a thin barrier between the two bulk phases and it is either a homogeneous phase or a heterogeneous collection of phases (Pandey and Chauhan, 2001). The membrane is a permselective barrier that permits transport of some component but retains others. The flow of material across a membrane is kinetically driven by the application of pressure concentration, vapour pressure, hydrostatic pressure, electrical potential, or temperature (Norida, 2004). According to Baker, the category, process and the status of types of membrane technology can be seen in Table 2.2.

Category	Process	Status
Developed industrial	Microfiltration	Well establish unit operation. No
membrane separation	Ultrafiltration	major breakthrough seem imminent
technology	Reverse Osmosis	
	Electrodialysis	
Developing industrial	Gas separation	A number of plants have been
membrane separation	Pervaporation	installed. Market size and number of
technologies		applications served are expanding
To-be-developed industrial	Carrier facilitated	Major problems remain to be solved
membrane separation	transport	before industrial systems will be
technology	Membrane contractors	installed on large scale
	Piezodialysis	_
Medical application of	Artificial Kidneys	Well establish processes. Still the
membrane	Artificial Lungs	focus of research to improve
	Controlled drug	performance, for example,
	deliveries	improving biocompatibility

Table 2.2: Membrane Processes (Bake

The four developed industrial application of membrane separation processes are microfiltration, ultrafiltration, reverse osmosis, and electrodialysis. Figure 2.1 showing the range of application for reverse osmosis, ultrafiltration, microfiltration, pervaporation and gas separation according to their gas transport mechanism and also based on their pore size (Baker, 2000).



Figure 2.1: Schematic representation of nominal pore size for the principal membrane separation processes (Baker, 2000)

Reverse osmosis, ultrafiltration, microfiltration and conventional filtration are related processes differing principally in the average pore diameter of the membrane filter. Microfiltration membranes filter colloidal particles and bacteria from 0.1 to 10 μ m in diameter. Ultrafiltration membranes can used to filter dissolve macromolecules such as proteins, from solutions. The mechanism of separation by reverse osmosis is quite different. Reverse osmosis membranes are so dense that discrete pores are so small, from 3 to 5 Å in diameter that they are within the range of thermal motion of the polymer chains that form the membrane does not exist and therefore the transport

occurs via statistically distributed free volume areas. This mechanism is called solutiondiffusion (Baker, 2000).

The fourth fully developed membrane process is electrodialysis in which charged membranes are used to separate ions from aqueous solutions under the driving force of an electrical potential difference. The process utilizes the electrodialysis stack, built on the filter-press principle and containing several hundred individual cells, each formed by pairs of anion and cation exchange membranes. The principal application of electrodialysis is the desalting of brackish groundwater (Baker, 2000).

There are two developing membrane application, gas separation and pervaporation. In gas separation, a gas mixture at an elevated pressure is passed across a surface of membrane that is selectively permeable to one component of the feed mixture and the membrane permeates will enriched with that species (Baker, 2000). Pervaporation is relatively new process that has element in common with reverse osmosis and gas separation. In pervaporation, a liquid mixture contacts on membrane at one side, and the permeates escape on the other side as vapour. The main industrial application of pervaporation is the dehydration of ethanol solutions (Baker, 2000).

2.3 Mixed Matrix Membrane

Mixed-matrix membranes (MMMs) microstructure consists of an inorganic material incorporated into a polymeric matrix. The use of two materials with different flux and selectivity provides the possibility to better design a Gas Separation (GS) membrane, allowing the synergistic combination of polymers' easy processability and the superior GS performance of inorganic materials (Bernardo *et. al*, 2009)

In principle, the incorporation of the inorganic component can be seen as a relatively easy modification of existing methods for fabricating large-surface area polymeric membranes; therefore, MMMs possess an economic advantage over inorganic membranes. In addition, they may offer enhanced physical, thermal, and mechanical properties for aggressive environments and could be a way to stabilize the polymer membrane against change in permselectivity with temperature (Hu *et. al*, 1997).

The performance of various membrane materials available for the separation of O_2/N_2 is depicted in Figure 2.2.



Figure 2.2: Relationship between the O_2/N_2 selectivity and O_2 permeability for polymeric membranes and inorganic membranes (Robeson, 1991)

From Figure 2.2, the selectivity and permeability limit has become an obstacle for polymeric membrane to exceed beyond the upper bound limit. On the other hand, inorganic membranes was way far beyond the upper limit bound showing it have high selectivity and permeability. However, inorganic membranes is still seriously hindered by the lack of technology to form continuous and defect-free membranes, the extremely high cost for the membrane production, and handling issues (Saracco *et.al*, 1999). The latest membrane morphology emerging involves MMMs, consisting of organic polymer and inorganic particle phases.

At relatively low loadings of zeolite particles, permeation occurs by combination of diffusion through the polymer phase and diffusion through the permeable zeolite particles. The relative permeation rates through two phases are determined by their permeability. At low loadings of zeolite, the effect of the permeable zeolite particle on permeation can be expressed mathematically by the expression shown in equation 2.1, developed first by Maxwell in 1970s (Baker, 2000; Nunes and Peinemann, 2001; Chung *et. al*, 2007).

$$P = P_{C} \left[\frac{P_{d} + 2P_{c} - 2\Phi(P_{c} - P_{d})}{P_{d} + 2P_{c} + \Phi(P_{c} - P_{d})} \right]$$
(2.1)

Where P is the overall permeability of the mixed matrix material, Φ is the volume fraction of the dispersed zeolite phase, P_c is the permeability of the continuous polymer phase and P_d is the permeability of the dispersed zeolite phase. If this equation is used to calculate the permeability of the mixed matrix membrane, the equation to be used to calculate the selectivity is as equation 2.2 (Nunes and Peinemann, 2001)

$$\alpha = \frac{\alpha_c (\frac{1}{P_{c1}} + \left(\frac{2}{P_{d1}}\right) - 2\Phi(\frac{1}{P_{d1}} - \frac{1}{P_{c1}})(\frac{\alpha_c}{P_{c1}} + \frac{2}{P_{d2}} + \Phi\left(\frac{1}{P_{d2}} - \frac{\alpha_c}{P_{c1}}\right))}{(\frac{1}{P_{c1}} + \left(\frac{2}{P_{d1}}\right) + \Phi(\frac{1}{P_{d1}} - \frac{1}{P_{c1}})(\frac{\alpha_c}{P_{c1}} + \frac{2}{P_{d2}} - 2\Phi\left(\frac{1}{P_{d2}} - \frac{\alpha_c}{P_{c1}}\right))}$$
(2.2)

Where α is the overall selectivity, and α_c is the selectivity of the continuous polymer phase. The indices 1 and 2 are referring to gas 1 and 2. At low loadings of dispersed zeolite, individual particle can be considered to be well separated. At higher loadings rate, some small islands of interconnected particles form and at even higher loadings, these islands will grow and connect to form extended pathways. Continuous channel will form within membranes and all zeolite particles are connected to the channels. This is called the percolation threshold and this threshold can only be achieved at particle loadings of about 30% The highly permeable zeolite only has a large effect on polymer permeability when the percolation threshold is reached (Baker, 2000).

However, according to Ismail, the permeability and selectivity of mixed matrix membrane can be calculated using formula for normal plain polymeric membrane. The permeability can be calculated by using equation 2.3.

$$P = \frac{Q}{A \times \Delta P}$$
(2.3)

Where P is the permeability of the membrane, Q is the flowrate of gas species in, A is the area of the membrane and ΔP is the pressure difference across the membrane. The unit for permeability is in GPU and it can be calculated by using equation 2.4 (Norida, 2004).

$$1 \text{ GPU}=1 \times 10^{-6} \frac{cm^3}{cmHg \ s \ cm^2} \qquad (2.4)$$

For the selectivity, α , of the membrane of species A from species B, it can be calculated by using this equation 2.5

$$\alpha = \frac{P_A}{P_B} \tag{2.5}$$

To properly choose the dispersed and continuous phases, one must take the transport mechanisms and the gas component preferentially transporting through the membrane into consideration. In some cases, it is more sensible to allow the smaller component to pass through; therefore, inorganic fillers with molecular sieving characteristics and polymers based on the size selection should be combined to produce MMMs. On the other hand, the selective transport of more condensable molecules through the membrane is more economical in some industrial applications. To fulfil this target, the MMMs may include microporous media that favour a selective surface flow mechanism and polymers that separate the mixtures by solubility selectivity (Anand *et. al*, 1997; Rao and Sircar, 1996).

2.4 Zeolite and Surface Modification

2.4.1 Zeolite

Molecular sieve zeolites of the most important aluminosilicates can be represented by the chemical formula $M_{2/n}O.Al_2O_{3.y}SiO_{2.w}H_2O$ 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 (Wan Aizan *et. al*, 2006).

Zeolite framework is made up of SiO₄ tetrahedral linked together by sharing of oxygen ions. The example of this kind of structure can be seen in Figure 2.3. This structure makes up channels and interconnected voids and this allows water molecules to occupy the space. (Wan Aizan *et. al*, 2006) Therefore we need to dry zeolite when we want to use it in order to remove water. The example of zeolite and its water sorption properties are shown in Table 2.3.



Figure 2.3: The tetrahedral molecular structure of zeolite 4A (Wan Aizan et. al, 2006)

Zeolite (examples)	Chemical structure	Si/Al ratio	Pore aperture (Å)	Water sorption (wt %)
Silicalite-1	Pure silica form of ZSM-5	>500	5.3*5.6 < - >5.1*5.5	1
ZSM-5	Nan(AlnSi96–nO192)- ~16H2O	10– 500	5.3*5.6 < ->5.1*5.5	4
Faujasite (KY,13X)	(Na2,Ca,Mg)29[Al58Si134O384]- 240H2O	1.5–3	7.4	26
Offretite	(Ca,Mg)15K[Al4Si14O36]-14H2O	3–4	6.7 < ->3.6*4.9	13
Mordenite	Na8[Al8Si40O96]-24H2O	5-5	6.5*7.0 < ->2.6*5.7	14

Table 2.3: Examples of zeolite and its properties (Chung et. al, 2007)

2.4.2 Non Idealities of MMMs

Even though zeolite has proven that it can increase the permeability and selectivity of a membrane, it is found that with the insertion of zeolite do sometimes decrease the selectivity of the membrane under certain circumstances. These circumstances occur when there are voids formation between the zeolite and the polymer itself (Wan Aizan *et. al*, 2006).

The inorganic-organic interface is clearly important in a composite material. Indeed 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 given membrane. Study has identified four undesirable morphologies at the polymer-sieve interface, which need to be overcome in order to create successful mixed matrix membranes (Shu Shu, 2007).

Incompatible of the zeolite with the polymer will result in several conditions that presumed to be the major cause for the more or less deteriorated performance as gas molecules take this non-selective and less resistant by-pass instead passing through pores in the particle (Jia *et. al*, 1992). These conditions can be seen in Figure 2.4.



Figure 2.4: Illustration of the morphologies and gas transport properties of non-idealities in mixed matrix membranes

There are actually for types of non idealities in mixed matrix membrane. They are sieve in a cage, matrix rigidification, leaky Interface and plugged sieve (Shu Shu, 2007). From Figure 2.4, Case 1 is called Sieve in a cage condition. 'Sieve-in-a-cage' is a term describes the voids present at the polymer-sieve interface. The SEM image on the upper-left corner of Figure 1.3 depicts zeolite 4A dispersed in a polyether imide, which is an example of 'sieve-in-acage' morphology. 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. The net result of such morphology is to cause a higher permeability than the neat polymer with an equivalent selectivity.

Matrix rigidification is the second case of non idealities in mixed matrix membrane. Upon the formation of intimate contact between polymer and particles, this condition might occur. The mobility of polymer chains in the region directly contacting the particles can be inhibited relative to that for the bulk polymer (Chung *et. al*, 2007). Confinement of polymer chains to a solid surface is an important phenomenon that affects properties of organic-inorganic composites and is not accounted for in regular models. In mixed matrix membranes, this effect is characterized by reduced permeability at the interface and therefore decreased overall permeability of the whole membrane. It is believed to be caused by immobilization of polymer chains due to adsorption and/or chemical tethering on a solid surface. This morphology is undesirable because it negatively affects the productivity of a membrane; however, if it affects both penetrants in a similar manner, selectivity enhancement still occurs consistent with the expectation based on the Maxwell model (Shu Shu, 2007).

Another type of non-idealities of MMMs can be seen in Case 3 of Figure 2.4. A 'leaky interface' is essentially a special case of 'sieve-in-a-cage' category, with an effective void or high free volume region of sufficient extent to enable partial and less selective bypass of the two gases. This non-ideality leads to actual loss of separation efficiency, since it adds a significant non-selective resistance that undesirably affects the most permeable component, as opposed to the negligible non-selective resistance present in the 'sieve-in-a-cage' situation. Knudsen diffusion or sorption-diffusion transport with extremely low selectivity is dominant at this dimension in the interfacial region. As a result, the overall membrane exhibits a somewhat higher permeability and lower selectivity than the neat polymer (Shu Shu, 2007).

The last type of MMMs non idealities is called Plugged Sieve and it can be seen in Case 4. This case is characterized by permeability lower than the neat polymer with essentially no change in selectivity. It could be caused by the use of an impermeable zeolite (e.g. zeolite 3A) or by certain strongly held penetrants that prevent the gas molecules from permeating through the internal pores of the sieves. Zeolites have lost selective ability under such circumstances and simply add an additional resistance to both penetrants. Gas sorption experiment is an excellent technique to probe this morphology by analyzing the dynamic rate and equilibrium sorption capacity of the molecular sieves (Shu Shu, 2007).

2.4.3 Zeolite Surface Modifications

The incompatibility of polymer and zeolite is one of the causes to void formation between zeolite phase and polymer phase. This leads to the non idealities of the MMMs morphology and as a result the gas separation performance will also decrease (Suer *et. al*, 1994). The origins of the imperfect interphases are complicated. Poor compatibility between molecular sieve and polymer matrix where by the tendency to develop voids between polymer and zeolite phases are very high, uneven shrinkages and stresses of these two components during the membrane formation may be some of the possible causes.

In order to reduce the voids formation between zeolite and polymer, several studies have indicate that by the modification of zeolite surface using silane coupling agent, the compatibility of polymer and zeolite will increase, therefore the gas separation characteristics will increase (Ismail *et. al*, 2008; Li *et. al*, 2006).



Figure 2.5: Chemical modification on zeolite surface (Ismail et. al, 2008)
Figure 2.5 is illustrating the chemical modification steps on zeolite surface based on a research done by Ismail. The silane coupling agent has a typical general structure and it is shown as in Figure 2.6.

$(RO)_3$ -Si-CH₂-CH₂-CH₂-X

Figure 2.6: General formula for silane coupling agent

Silane coupling agent is a silicon based chemical that contain two types of reactivity, one is organic and the other is inorganic in the same molecule. From the Figure 2.6, the RO is a hydrolysable group, followed by ethoxy while X is a organofucntional group of amino. The silane coupling agent will act as an interface between an inorganic substrate, zeolite and an organic material, polymer to bond, or couple, these two dissimilar materials. The silicon at the centre is connected to two different functional groups; the organophilic amino group (NH₂) and the ethoxy group .Surface treatment of zeolites with silane coupling agent was carried out to produce silanol groups through hydrolysis reaction. Silanol groups, a product of a hydrolysis reaction, react with hydroxyl groups found on zeolite surfaces to form siloxane bonds (– Si–O–zeolite) through a condensation reaction. The silane agent consists of ethoxy groups that are the reactive centres which can be used for the formation siloxane bonds with the zeolite channel. These –Si–O–zeolite bonds formed a stable structure on the surface of zeolite (Ismail *et. al*, 2008).

The modification of zeolite surface has show significant selectivity improvement since there are decrease volume of voids form between the zeolite and the polymer. The silane coupling acts as a connector between the polymer, an organic material and the zeolite, an inorganic material (Li *et. al*, 2006; Ismail *et. al*, 2008). Generally, zeolites with hydrophilic surfaces do not interact well with hydrophobic polymers. By adding a coupling agent, it increases the adherence between the polymer and the zeolite. Therefore to get a better separation performance, zeolite surface modification is an essential part that needs to be done prior to dope formulation.

CHAPTER 3

METHODOLOGY

3.1 Materials

3.1.1 Polyethersulfone (PES)

Polyethersulfone (PES) was chose to be the polymer in this research. The repeat unit structure of Polyethersulfone posses a certain degree of rigidity (Suer *et. al*, 1994). PES has a glass transition temperature of 225°C and thus a glassy polymer at preparation and application temperatures (Chiou *et. al*, 1987). Polyethersulfone is an amorphous polymer with good thermal resistance and mechanical strength (Norida, 2004). Thus, it appears to be a more versatile membrane.

3.1.2 1-Methyl-2-Pyrrolidone

1-methyl-2-pyrrolidone with formula molecular of C_5H_9NO was also known as NMP. It was used in this research because It has a high solvent power for PES, low toxicity and completely miscible with water, alcohols and organic acids (Norida, 2004).

3.1.3 Physical Properties of Non solvent Additives and Coagulation Bath

Water was used as non solvent additives used and water along with methanol was used as the coagulation. The physical properties are shown in Table 3.1.

Table 3.1: The Non solvent additives and coagulation bath properties (Norida, 2004)

Component	Molecular	Melting Point	Boiling Point	Density	
	w eight	(°C)	(°C)	kg/m ³	
	MW (g/mol)				
Non solvent Additive					
Distilled water	18.02	0	100	998	
Coagulation Bath					
Tap water	18.02	0	100	998	
Methanol	32.04	-98	65.04	790	

3.1.4 Zeolite 4A

This study used zeolite 4A as a filler to form MMMs. The properties of zeolite 4A are listed in Table 3.2 and the molecular structure of zeolite 4A can be seen in Figure 3.1.

Table 3.2: The zeolite 4A properties (Chung et. al, 2007; Wan Aizan et. al, 2006)

Zeolite	Chemical structure	Si/Al	Structure	Pore	Water
		ratio		aperture (Å)	sorption (wt %)
4A	{Na12(Al12Si12O48)- 27H2O}8	1	3D	3.8	23



Figure 3.1: Molecular structure of Zeolite 4A (Wan Aizan et. al, 2006)

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 to modify the surface of the zeolite in order to allow polymer to attach to the zeolite (Hussein and Koros, 2007). This research uses a combination of chemicals to achieve this objective and they were:

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

3.1.5.1 APTMOS

For this research, APTMOS or 3-Aminopropyl-trimethoxysilane was selected as a coupling agent for zeolite 4A and PES. It is a product form Acros Organics BVBA (Geel, Belgium). The molecular chain of APTMOS can be seen in Figure 3.2.



Figure 3.2: Molecular Chain of APTMOS (www.sigmaaldrich.com)

The physical properties of 3-Aminopropyl-trimethoxysilane can be seen in Table 3.3.

Table 3.3: Physical and chemical properties of APTMOS (www.acros.com)

Physical State at 27 ⁰ C and 1 atm	Clear Liquid
Color	Colorless
Boiling Point at 760 mmHg	194°C
Flash Point	92°C
Specific Gravity/Density	1.019 g/cm^3
Molecular Formula	NH ₂ (CH ₂) ₃ Si(OCH ₃) ₃
Molecular Weight	179.29 g/mol

3.1.5.2 Ethanol

The APTMOS was mixed with mixture of ethanol and distilled water. 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 used in this research was bought from R&M Chemicals (Essex, UK) as 99.7% V/V denatured. The physical and chemical properties of ethanol can be seen on Table 3.4.

Molecular Formula	C ₂ H ₅ OH
Molecular Weight	46.07 g/mol
Boiling Point	78.8°C
Density	0.79 kg/m^3

Table 3.4: Physical and chemical properties of Ethanol (Jiminez et. al, 2010)

3.1.6 Properties of Test Gases

The membranes were tested using pure oxygen and nitrogen as test gases. Table 3.5 shows the physical properties of both gases.

Table 3.5: Physical properties of Test gases

Physical property	O ₂	N_2
Molecular weight, <i>Mi</i> (g/mol)a	32	28
Viscosity, ηi (µPa s) ^a	20.7	17.8
Collision diameter, $\sigma i \times 10^8 (\text{cm})^a$	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^{-10} cm³ (STP) cm/cm².s.cmHg

3.2 Research Design

The research design for development of MMMs is summarized in the Figure 3.3.



Figure 3.3: Research Design

3.2.1 Zeolite Surface Modification

This process was done prior to dope solution formulation. In order to increase the compatibility of zeolite and PES, the zeolite surface must be modified first by silane coupling agent (Ismail *et. al*, 2008). The zeolite 4A was dried in an oven at 80°C for 24 hours prior to the modification. 200 ml ethanol solution was prepared (95% ethanol, 5% distilled water) and it was stirred with APTMOS and zeolite 4A for 4 hours under room temperature. Based on a study by Shu Shu, for 5g of zeolite 4A, 5ml of APTMOS was used (Shu Shu, 2007). Based on this ratio, Table 3.6 is showing the mass of zeolite and volume of APTMOS used for each 400 g dope solution. The mixture was then filtered through a filter paper and the residue was washed thoroughly with ethanol to remove the unreacted silane. Finally, the modified zeolite was dehydrated at 110 °C for 2 hours in a vacuum oven to remove the adsorbed water vapor or other organic vapors before it was ready to be used in preparation of dope solution.

Solution	Zeolite mass (g)	APTMOS volume (ml)
CZ1	20	20
CZ2	40	40
CZ3	60	60
CZ4	80	80

Table 3.6: Mass of Zeolite and volume APTMOS used for 400 g dope solution

3.2.2 Dope Solution Preparation

Dope solution was prepared by adding all four PES, NMP, Zeolite 4A and distilled water into the casting solution preparation system. Before the insertion of PES, PES is dried for 4 hours at the temp of $150 \pm 2^{\circ}$ C. As stated at previous section, zeolite need to be dried for 2 hours at the temperature of 110° C prior to the addition into the casting solution due to its hydrophilic properties.

It took 5 hours to prepare the dope solution. At first zeolite was added into the solvent and stirred for 1 hour. After that, PES was inserted into the NMP-Zeolite solution and stirred for about 2 and a half hour. Next the distilled water was inserted and stirred for another hour and a half. After stirring of the dope formulation, the solution was degassed under vacuum for 3 hours in the ultrasonic bath to remove any micro bubbles inside the solution. Figure 3.4 is showing the casting solution preparation system.



Figure 3.4: Dope solution preparation system

3.2.3 Membrane Preparation

A layer of dope solution was poured on a glass plate. By using stainless steel casting block, the solution was slowly spread to have a smooth and uniform layer. Figure 3.5 shows the manual hand membrane casting. After the layer of membrane was formed, it was inserted to the water bath for 1 day and then it was washed with industrial grade methanol for 1 day. Lastly it was dried at room temperature for 48 hours.



Figure 3.5: Manual hand casting block and glass plate

3.2.4 Membrane Coating

In order to repair the skin layer from any defects, the membranes were coated because during membrane fabrication, the membrane skin layer suffers from some defects. These defects caused by gas bubbles, dust particles and support fabric imperfections, can be very difficult to eliminate. To overcome these problems, coating method was applied. The membrane was cut into circular area of 12.57 cm². Then the skin layer of the membrane was dip into 3 wt% of silicone in n-hexane for 5 minutes and placed in oven at temperature of 40°C for 15 minutes. After that the membrane is left at room temperature for 24 hours.

3.2.5 Permeation Test

Pure O_2 and N_2 gases were applied in the permeation test to identify the membrane performance. The volume of the gas permeates were determined by using bubble flow meter. The bubble flow meter is consist of a burette containing soap solution and the expansion of bubble over time was the gas flow rate of the permeates. Figure 3.6 showing the membrane permeation unit.



Figure 3.6: Permeation test unit

In order to calculate the permeability of the membrane, equation 2.3, 2.4 and 2.5 in chapter 2 was used (Ismail *et. al*, 2008).

3.2.6 Membrane characterization

Scanning Electron Microscopic (SEM) was used to analyze the surface and cross section image of MMMs produced. The model used for this study was SEM Carl Zeiss EVO50. A portion of membrane was cut and it was condition in liquid N_2 in order to leave the membrane in an undeformed structure. The membrane then coated with platinum by sputter coating under vacuum. The structure and morphology of the membrane then observe under microscope the magnification of 300 X-1000 X.

CHAPTER 4

RESULT AND DISCUSSION

The resultant mixed matrix membranes (MMMs) was produce using PES as the polymer, NMP as the solvent, distilled water as the non-solvent and zeolite 4A as the inorganic filler material. It was produced by using the dry/wet phase inversion method. Since there were several zeolite concentrations used during the formulation, this gives the major effect on the membrane performance. Other than that, the pressure applied and the coatings also give effects on the MMMs performance. The membrane produced from this study are based on the composition listed in Table 4.1

Solution	Material	Concentration (wt %)			
CZ1	PES	30	30	30	30
CZ2	NMP	60	55	50	45
CZ3	Zeolite 4A	5	10	15	20
CZ4	Distilled H ₂ O	5	5	5	5

Table 4.1: Concentration of materials for dope solution formulation

4.1 Effect of Zeolite Concentration on the Permeability and Selectivity of the MMMs

4.1.1 Performance of Uncoated MMMs

The insertion of inorganic filler such as zeolite was actually to acquire both high permeability and selectivity. Plain polymeric membranes have a limit that avoids it to have high selectivity at high permeability rates. This has been proves by many researchers (Robeson, 1991; Bernardo *et. al*, 2009). Therefore with the insertion of zeolite, it will increase the membrane free-volume and also increases the sorption of the desired gas component (Bernardo *et. al*, 2009). In this study, zeolite concentrations between 5 wt% to 20 wt% were used and their performances were observed. The purpose of using variety of zeolite concentration was to find the optimum zeolite concentration that makes the membrane posses the highest permeability and selectivity.

The zeolite 4A was treated with silane coupling agent prior to the dope formulation to increase the compatibility between the zeolite and the PES (Ismail *et. al*, 2008; Li *et. al*, 2006). The compositions of dope formulation were labeled as CZ1, CZ2, CZ3 and CZ4 based on the different zeolite loading rates. Pure oxygen and nitrogen pressure-normalized fluxes were measured at 30 ± 2 °C and pressure difference of 1 bar were applied for the membranes. Table 4.2 demonstrated that the average range of O_2/N_2 selectivity for membrane samples was about 0.91 to 1.26. According Table 4.2, it can be seen that for all of the solution formulation, each of it exhibits quite high permeability for both gases. However the selectivity observed was rather low.

Solution	Pressure -no G	Selectivity $O_2/N_{2,} \alpha$	
	(P / <i>l</i>) O ₂	(P / <i>l</i>) N ₂	
CZ1	768.76	862.52	0.89
	841.98	785.85	1.07
	278.45	263.90	1.06
Mean	629.73±306.41	637.42±325.74	1.01±0.10
C72	1262.97	1473.47	0.86
	5051.88	5051.88	1.00
	2210.20	2525.94	0.88
Mean	2841.68±1971.81	3017.10±1839.07	0.91±0.26
CZ3	3214.84	2720.245	1.18
	3536.32	2525.94	1.40
	3536.32	2946.93	1.20
Mean	3429.16±185.61	2731.04±210.70	1.26±0.12
C7 4	3536.32	2210.20	1.60
	3536.32	2720.25	1.30
	2720.25	3214.84	0.85
Mean	3264.29±471.16	2715.09±502.34	1.25±0.38

 Table 4.2: Separation properties of uncoated MMMs at different zeolite concentration

*Pressure normalized flux was measured at 3 bar

*GPU=1 X 10^{-6} cm² (STP)/ (cm².s.cmHg)

*CZ1: Solution with 5 wt% zeolite loading

CZ2: Solution with 10 wt% zeolite loading

CZ3: Solution with 15 wt% zeolite loading

CZ4: Solution with 20 wt% zeolite loading

This might have been caused by the significant present of pin-holes defects that eventually decrease the capability of the membrane to have a high selectivity. When there are porosity and defects on the membrane, other than molecular sieveing mechanism, the gas transports through the membrane is the combination of three transports mechanism and they are solution-diffusion contribution in the nonporous portion of the dense skin layer, Knudsen molecular flow and Poiseuille flow in the porous medium of the dense skin layer (Wang *et. al*, 2001).

The Knudsen flow and the Poiseuille flow are gas transport mechanisms that happen through the pores on the defected dense selective skin layer of the membrane. The first mechanism occurs when the pressure is so low that the mean free path greatly exceeds the pore diameter. The second one occurs when the pressure is high enough so that the mean free path is very small compared to the diameter of the pore. For intermediate pressures the transition from the Poiseuille to the Knudsen flow will take place (Izquerdo-Gil, 2008).

However these two types of gas transport do not reflect the real capability and performance of the membrane since the gas was transport through the pores. An ideal membrane for gas separation must have a selective layer that should be defect-free so that gas transport takes places exclusively by solution/ diffusion, not by poorly selective flow through pores (Paul and Yampol'skii, 1994).



Figure 4.1: SEM for uncoated surface of CZ1 membrane



Figure 4.2: SEM for uncoated surface of CZ2 membrane



Figure 4.3: SEM for uncoated surface of CZ3 membrane



Figure 4.4: SEM for uncoated surface of CZ4 membrane

From Figure 4.1 to Figure 4.4, all of the membranes showing that all of it suffers from skin defects of porosity and resulted bad performance as shown in Table 4.2. This support that the membranes gas separation was mainly dominated by the Knudsen and Poiseuille flow mechanism due the pores formed on the membranes. Small pin holes can be located on the membranes, and these pin holes or pores leads to Knudsen and Poiseuille flow.

Other than that, the standard deviations of the tested membrane were also high and that show that the result collected from uncoated membrane is unreliable. However from a study done on the plain PES membrane performance on the selectivity and permeability of O_2 and N_2 , the standard deviation for the selectivity is in between 0.12 and 0.72 (Norida, 2004). It is higher than the standard deviation of selectivity obtained in this study that is in the range of 0.10 to 0.38. This shows that the selectivity of an uncoated MMMs is still more reliable compared to an uncoated plain PES membrane.

However, solution CZ3, which contain 15 wt% zeolite loading rate posses the slightly higher selectivity compare to the other with 1.26 of selectivity followed by CZ4 with selectivity of 1.25. This shows that with the increase in the zeolite concentration the selectivity increases even though the increment was not significant. The result of different zeolite concentration on the selectivity and permeability of membrane can be seen in Figure 4.5.



Figure 4.5: Pressure-normalized flux and selectivity of uncoated membrane at different zeolite concentration at 3 Bar

From the result of uncoated membrane, it suggesting that at 15 wt% zeolite loading is at the optimum. However the selectivity of the membrane was low and limited caused by the defects of the skin layer. Even when the zeolite have already modified by using silane coupling agent to decrease the pore, unselective voids that in the skin outermost layer may still exist (Ismail *et. al*, 2008). Therefore to obtain higher level of selectivity, the membrane must be coated with silicone rubber in order to get a membrane with high selectivity

4.1.2 Performance of Coated MMMs

Asymmetric membrane mostly suffers from low selectivity compared with that of a dense film made of the same polymer. This was often attributed to the incomplete coalescence of the nodule aggregates of the composed skin layer and leads to defects (pores) formed during the phase inversion process (Kesting *et. al*, 1990; Kesting *et. al*, 1993). These defects can be eliminated by coating the membrane with suitable coating material (Wang. *et. al*, 2001).

In this study silicone rubber was used as the coating material. The membrane was coated at ambient condition (1 atm and 27° C). Pure oxygen and nitrogen pressurenormalized fluxes were measured at 30 ± 2 °C and pressure difference of 1 bar were applied for the membranes. The results for coated MMMs can be seen in the Table 4.3.

From the result obtained the selectivity of coated MMMs within ranges of 1.32 to 3.25. Each of the coated membrane from CZ1, CZ2, CZ3 and CZ4 exhibits higher selectivity compare to the result from uncoated MMMs but with lower permeability. This was caused by the covering of the skin defects using silicone rubber and prevents the gas to transport through pores on the defected skin layer. With this method, the permeation of gas species was dominated by solution diffusion mechanism and molecular sieving mechanism only, thus the real performance of membrane can be observed.

The standard deviation tabulated in Table 4.2 is lower compared the ones in Table 4.1. This means that the data for this result is more reliable compared to uncoated MMMs. Figure 4.6 to Figure 4.9 show the surface layer of the coated MMMs by using SEM.

	Pressure -noi		
Solution	G	PU	Selectivity
	(P / <i>l</i>) O ₂	(P / <i>l</i>) N ₂	$O_2/N_{2,} \alpha$
	4.88	3.50	1.39
C Z 1	4.52	2.54	1.29
CLI	4.52	5.54	1.28
	4.86	3.72	1.31
Mean	4.75±0.20	3.59±0.12	1.32±0.06
	25.26	20.80	1.21
CZ2	16.84	13.60	1.24
	11.67	7.52	1.55
Mean	17.92±6.85	13.98±6.65	1.34±0.18
	86.25	26.00	3.32
CZ3	104.01	36.84	2.82
	153.75	42.61	3.61
Mean	114.67±34.99	35.15±8.43	3.25±0.40
	33.36	23.11	1.44
CZ4	43.66	31.29	1.40
	72.17	57.97	1.24
Mean	49.73±20.10	37.46±18.23	1.36±0.10

 Table 4.3:
 Separation properties of coated MMMs at different zeolite concentration

*Pressure normalized flux was measured at 3 bar

*GPU=1 X 10^{-6} cm² (STP)/ (cm².s.cmHg)

*CZ1: Solution with 5 wt% zeolite loading

CZ2: Solution with 10 wt% zeolite loading

CZ3: Solution with 15 wt% zeolite loading

CZ4: Solution with 20 wt% zeolite loading



Figure 4.6: SEM for coated surface of CZ1 membrane



Figure 4.7: SEM for coated surface of CZ2 membrane



Figure 4.8: SEM for coated surface of CZ3 membrane



Figure 4.9: SEM for coated surface of CZ4 membrane

Based on Figure 4.6 to Figure 4.8 the surface appear smoother compare to the uncoated MMMs because of the silicone rubber have filled the holes and pores on the skin surface. For the Figure 4.9 show MMMs with 20 wt% zeolite have more rough and unlevelled surface layer. This is due to the significant presence of the zeolite bulk on the surface of the MMMs and it makes it look more rough compared to the others. The result of selectivity and permeability for coated membrane had been compiled as shown in Figure 4.10.



Figure 4.10: Pressure-normalized flux and selectivity of coated membrane at different zeolite concentration at 3 Bar

Based on Figure 4.10, it shows that with the increase of the zeolite loading rate, the permeability of both gases increase. This happens due to the formation of interconnected channels between the zeolites particles. At low loading rate of zeolite particles, permeation occurs by combination of diffusion through the polymer phase and diffusion through the permeable zeolite particles. At this stage individual particle of zeolite can be considered to be well separated. At higher loadings rate, some small islands of interconnected particles form and at even higher loadings, these islands will grow and connect to form extended pathways. Continuous channel will form within membranes and almost all zeolite particles are connected to the channels and this is called the percolation threshold (Baker, 2000).

With the increasing zeolite loadings rates more permeates can go through the zeolite interconnected channels. From all of the four solutions, CZ3, that is MMMs with 15% zeolite loading rates have the highest selectivity with 3.25. It is believed that at 15% zeolite loading rate, the percolation threshold have been achieved where all the zeolite is interconnected to form a continuous channel.

The crossed section of the CZ1, CZ2, CZ3 and CZ4 MMMs can be observed in Figure 4.11 to Figure 4.14, while the zeolite bulk embedded in the MMMs matrix can be seen in Figure 4.15.



Figure 4.11: Cross section of MMMs for CZ1



Figure 4.12: Cross section of MMMs for CZ2



Figure 4.13: Cross section of CZ3 MMMs



Figure 4.14: Cross section of CZ4 MMMs



Figure 4.15: Zeolite embedded in MMMs matrix

There are certain optimum zeolite concentration that will possess the highest selectivity and permeability. Below or above this optimum zeolite concentration, the selectivity will be lowered (Ismail *et. al*, 2008; Duval *et. al*, 1993).At this optimum value the molecular sieving effect of the zeolite was observed in the gas separation performance, even with the presence of free voids. However, beyond this amount, the free voids were likely to govern the direction of the gas molecules to pass through the membrane instead of absorb through the open pore of zeolite particles (Ismail *et. al*, 2008).

The optimum zeolite loading for this study was found at 15 wt % for this study. However, since this section is discussing on the performance of the coated membrane, it is unlikely that the free voids will affects the overall performance of the membrane. Plus, the membrane was treated already with silane coupling agent in order to increase the compatibility of the zeolite and PES thus lowering the formation of free voids around the zeolitic areas. At 20% zeolite loading rate, it is observed that pressurized normal flux of O_2 decrease and the selectivity also decrease by 58% to 1.36, even though the pressure normalized flux of N_2 increases. Comparing to a research done by another worker for surface modified zeolite and also used PES as the polymer, the increase of zeolite insertion from 0 to 50% result in the increase of selectivity and O_2 permeability of the MMMs (Li *et. al*, 2006). The reason that might be possible to explained for the decreasing of selectivity and pressure normalized flux of O_2 at 20 wt % of zeolite is that it might be caused by the blockage of the pore in the zeolite.

These pores in the structures of zeolite can only allow the gas species that have kinetic diameters smaller than the zeolite's pore diameter. The gas species that have bigger kinetic diameter compared to the zeolite pore diameter will not permeates through the MMMs. This kind of mechanism is called molecular sieving gas transport (Pandey and Chauhan, 2001). The pore size must be between the size of the smaller gas and the larger gas molecule. With the blockage of these pores, both gas species will not be able to go through the zeolite.

The pore blockage caused by the impermeable of the zeolite particle due to the strongly held penetrant and in this case the silane coupling agent (Shu Shu, 2007). The addition of silane coupling agent, actually was to increase the compatibility of the polymer and zeolite and preventing the formation of holes or pores between them (Ismail *et. al*, 2008). However, this coupling agent might plug the pores of zeolite and preventing the formation of interconnected channel between the zeolite particles. With the plugging of the zeolite pores, even the smaller gas species could not go through and the MMMs lost its selectivity (Shu Shu, 2007).

At 20% zeolite loading rate or CZ4, the silane coupling agent used is rather high compare to the other solutions formulation. The silane might be in excessive and plugged the pores of zeolite. From the result obtained, it suggest the same conclusion as the previous section that the optimum zeolite loading rate is at 15% where the selectivity is 3.25 with the pressurized normal flux of O_2 and N_2 is 144.67 and 35.15 GPU respectively. The permeability and selectivity increases from CZ1 to CZ3 and this also shows that with the increase of zeolite loading rate the permeability and the selectivity increases.

4.2 Effect of Pressure on Selectivity and Permeability of MMMs

Different pressures are applied to membranes according to their designated operating condition. By applying the membrane in a range of pressure, it allows us to determine whether the pressure does or does not affect the permeability and selectivity of the membrane. In this study the membrane was tested under pressure difference of 1 bar in the range of 1 bar to 5 bars. The result of pressure normalized flux and selectivity of coated MMMs at different pressure can be seen in Table 4.4.

From the result showed in Table 4.4, the pressure normalized flux of O_2 is higher than N_2 . The selectivity achieved from this study is between the ranges of 1.07 to 3.25. None of the membrane exhibits selectivity above the intrinsic PES dense polymer for O_2/N_2 selectivity that is 6.1 (Wang *et. al*, 1996).

A membrane that has selectivity more than 80% of the ideal intrinsic selectivity can be considered as defect-free (Pesek and Koros, 1993). In this study the defect free membrane was not achieved. By comparing with the result of Table 4.4 and the intrinsic value, the membrane produce does not have defects-free skin and this ultimately influence the permeability and selectivity of the membrane. The effects of pressure on the membrane performance are show in Figure 4.16 to Figure 4.19.

		Pressure -nor		
Solution	Pressure (Bar)	GP	Selectivity	
		(P / <i>l</i>) O ₂	(P / <i>l</i>)N ₂	Ο ₂ /Ν ₂ , α
	1	4.73	4.32	1.09
CZ1	2	4.76	4.01	1.19
	3	4.75	3.59	1.33
	4	6.11	5.73	1.07
	5	14.44	11.39	1.28
	1	8.20	6.66	1.23
CZ2	2	10.01	9.20	1.09
	3	17.92	13.98	1.33
	4	128.93	97.46	1.36
	5	165.84	142.88	1.18
~~~	1	10.01	8.70	1.25
CZ3	2	30.63	15.17	1.99
	3	114.67	35.15	3.25
	4	110.96	41.54	2.73
	5	141.45	78.75	1.80
	1	4.15	3.41	1.23
CZ4	2	19.16	15.48	1.25
	3	49.73	37.46	1.36
	4	93.66	84.84	1.11
	5	146.96	115.35	1.26

Table 4.4: Separation properties of coated MMMs at different pressure

*Membrane was coated at ambient condition (cm².s.cmHg) (1 atm and  $27^{\circ}C$ )

*GPU=1 X  $10^{-6}$  cm² (STP)/

*CZ1: Solution with 5 wt% zeolite loading

CZ2: Solution with 10 wt% zeolite loading

CZ3: Solution with 15 wt% zeolite loading

CZ4: Solution with 20 wt% zeolite loading



Figure 4.16: Pressure-normalized flux and selectivity of coated MMMs of CZ1



Figure 4.17: Pressure-normalized flux and selectivity of coated MMMs of CZ2



Figure 4.18: Pressure-normalized flux and selectivity of coated MMMs of CZ3



Figure 4.19: Pressure-normalized flux and selectivity of coated MMMs of CZ4

From Figure 4.16 to Figure 4.19 it can be concluded that with the increase of pressure, the pressure normalized flux for both gases also increases. An asymmetric membrane consist of two regions, one is the thin dense selective skin layer while the other is a porous substructure for the support of the membrane (Nunes, 2001). For a membrane that has a defect-free skin layer, the pressure does not have a significant influence to the permeability of the membrane (Wang *et. al*, 1995). For a skin layer of membrane that suffers from porosity or defects, the overall permeation flux will be the combination of the pore flow and solution-diffusion flow (Wang *et. al*, 1995).

The pore flow will affect the permeability since it will proportionally increase with the increase of pressure. From the result provided in the Figure 4.16 to Figure 4.19, it can be assumed that the membranes produced do suffer from skin defects due to the increase of pressure normalized flux increase with the increase of the pressure. The idea of coating the membrane skin with silicone proposes by Henis and Tripodi was actually to repair the skin defects. However, the incomplete of plugging or covering of the surface defects on an asymmetric during coating may sometimes occur (Wang *et. al*, 1995). This same condition predicted to happen to the membrane produced from this study.

However for the selectivity of the membrane, a slightly different result was obtained. From the Figure 4.16 to Figure 4.19, it shows that the selectivity increases with the pressure increase until 3 bar and after 3 bars the selectivity decrease. The selectivity of the produced membrane increased with the increasing of the permeability. Based on the permeability/selectivity trade-off limit for  $O_2/N_2$  separation, for a plain asymmetric polymer membrane, the selectivity of the membrane will decrease with the increase in permeability (Robeson, 1991).

This trade off limit was also support by another research done by Wang and it also shows that the selectivity between  $O_2$  and  $N_2$  gas decreases with the increase of pressure from 0 to 6 bars. With the insertion of zeolite, the limit was breakthrough. The mechanism of transport for zeolite particle is called the molecular sieving flow. This type of transport only allows the smaller size gas molecule will go through the zeolite, while the bigger size molecule will be prevented (Pandey and Chauhan, 2001). With this kind of separation, even with the increase of permeability of both gas species, the only one can go through more is the one with smaller size and in this case it is the  $O_2$  gas.

From this study, it can be seen that the selectivity only increases until 3 bars and started to decrease towards 5 bars for all of the membrane. This is suggesting that for the membrane produced the optimum operating pressure to get the highest selectivity is at 3 bars. This might because by Poiseuille flow. This flow can only occur with the presence of pores on the selective skin layer with high pressure is applied (Wang *et. al*, 1995). As discussed before, even with the coatings, not all of the membrane defects are plugged and therefore the chances for Poiseuille flow to happen still exist.

At high pressure, the pressure is believed to be high enough that can lead to Poiseuille flow. At first the gas transport mechanism was dominated by Solution Diffusion and Molecular sieving mechanism. As the pressure increase, with the existence of uncoated pores, the transport of gas species of the MMMs is the combination of solution diffusion, molecular sieving and Poiseuille flow. The Poiseuille flow becomes the alternative ways for gas to transport across the membrane without a selective barrier. Therefore with the pressure increase, the permeability increases also but the selectivity decrease. But based on the result, the decrease in selectivity is not at a significant rate proving that the Poiseuille flow does not dominate the transport mechanism at high pressure. It is more to coexisting in the dominat flow mechanism that are solution diffusion and molecular sieving flow. Even so, it can be agreed that the insertion of zeolite in the matrix of polymer membrane do increase the selectivity and permeability and has the potential for application in the gas separation industry.

# **CHAPTER 5**

#### CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusion

This chapter summarize all of the important points that have been discussed on the previous chapters. From the research of membrane for gas separation it has already shows that the insertion of inorganic in the plain polymeric membrane can enhance the performance of the membrane. With careful consideration of the zeolite insertion loading for mixed matrix membranes (MMMs) can provide a more optimum performance of permeability and selectivity. In this study, MMMs of polyethersulfone (PES) with zeolite 4A was produced. From all of the experiment, result and study several conclusions can be made.

The first conclusion from this study is the performance of a membrane only reliable when it is been coated. The membrane performance was observed for both uncoated and coated. It shows that for an uncoated membrane, the permeability of both gases was high however the selectivity was low due to the existence of an alternative ways for the gas permeates through the membrane. The alternative way was provided by pores on the defected selective skin layer and as we all know an ideal membrane performance must be based on the solution diffusion of the gases not by flow through poor defects skin layer. By coating of the membranes, the permeability decreased but the selectivity increased and provides a reliable performance of the membrane.
All the pores are covered and the mechanism of gas transport was dominated by solution diffusion. The second conclusion is that the best concentration of zeolite that can provide the best separation performance in this study is at 15 wt %. The selectivity and permeability increased from 5 to 15 wt % and decreased towards 20 wt % zeolite loading rate. The blockage of the pore for 20 wt % zeolite caused the decreased on the permeability and selectivity of the MMMs. This is due to the excessive usage of silane coupling agent. However, if the silane coupling agent used to treat the zeolite for 20 wt % is at the optimum amount, it might change the result and the selectivity and permeability will keep increasing with the increase of zeolite loading rate. The increased in the zeolite insertion, zeolite particles tends to form interconnected channels between particles and this increased the selectivity and permeability of the MMMs.

The optimum pressure was found at pressure of 3 bar when the membranes were tested between pressure range of 1 to 5 bars. The pressure actually will give a significant towards the membrane if the membrane was a defect free membrane. However form the observation the permeability of both gases through the MMMs keep increasing even for coated MMMs. These shows that the membrane produce suffers from skin defects. The uneven coatings of the membrane might occur that cause the pore flow still happen after the membrane was coated. The selectivity was observed to be increasing from 1 to 3 bar and started to decrease from 4 to 5 bars. It is suspected that at high pressure, the poiseuille flow happen. This contributes to the increase of permeability and decrease of selectivity from 4 to 5 bar.

As an overall conclusion the optimum condition and settings for the MMMs produced from this study were, the MMMs perform best when it is coated, the optimum concentration of zeolite is at 15 wt % and the optimum pressure was at 3 bar. The selectivity calculated was 3.3 while the permeability of  $O_2$  was 114.7 GPU.

## 5.2 **Recommendation**

From this study, there are several lacking that needs to be improved and new approach should be applied in order to get a better gas separation performance of the MMMs. Therefore, below are several recommendations for future works:

- a) The usage of silane coupling agent is an excellent approach to increase the compatibility of the polymer and zeolite. Therefore it is better to identify the right amount of silane coupling agent for different concentration of zeolite.
- b) Make a comparison on the morphology, structure and performance between MMMs with silane treated zeolite and MMMs with untreated zeolite.
- c) Use other approach such as Grignard reagent to increase the zeolite-polymer interaction and compare its performance with MMMs using silane treated zeolite.
- d) Use the mixture of gas instead of the usage of pure gases in order to judge the performance of the MMMs with condition similar to the real gas separation process in the industry.
- e) The MMMs has a limit for zeolite loading rate before its performance become unreliable. Therefore we need to increase the zeolite concentration to a higher boundary example 50 wt % in order to see its performance and limitation.
- f) Manual casting of MMMs effect the MMMs preparation since the velocity variable is not constant for each membrane produced. Better results can be obtained by using an automatic casting machine in the future.

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APPENDICES

## Constant operating variables for calculation of the separation properties of uncoated and coated membranes:

A= membrane surface area=  $12.57 \text{ cm}^2$ D_p= Pressure difference= 1 bar =75 cm Hg Polyethersulfone oxygen =  $0.51 \times 10^{-10} \text{ cm}^3$  (STP) cm/ cm². cm Hg permeability coefficient

## Calculation example for permeability and selectivity of $O_2 \mbox{ and } N_2 \mbox{ gases}$

This calculation is based on the data for the highest average selectivity in this study, 3.25 that was found at 3 bars with zeolite concentration of 15 wt%. It can be seen on Appendix B, Table B-3.

Pressure applied: 3 bar Volume Changes: 1 cm³ Membrane Area: 12.568 cm²

	Time(s)							
	$O_2$	$N_2$						
Membrane 1	4.1	13.6						
Membrane 2	3.4	9.6						
Membrane 3	2.3	8.3						

Three MMMs sample were tested for each pressure.

For Membrane 1:

Permeates flow rates for O₂ gas,

$$\frac{Volume \ changes}{Time} = \frac{1 \ cm^3}{4.1 \ s} \times \ 10^3 = 243.90 \ \times 10^{-3} \ \frac{cm^3}{s}$$

Permeates flow rates for N2 gas,

 $\frac{Volume \ changes}{Time} = \frac{1 \ cm^3}{13.6 \ s} \times \ 10^3 = 73.53 \ \times 10^{-3} \ \frac{cm^3}{s}$ 

The same calculations were done for Membrane 2 and 3. The calculations of pressure normalized flux in GPU for Membrane 1,

Volume Flowrate Membrane area × Pressure applied For O₂ gas,

$$\frac{243.90 \times 10^{-3} \frac{cm^3}{s}}{12.568 \, cm^2 \times 3 \, bar \, x \, \frac{75 \, cm \, Hg}{1 \, bar}} \times \frac{1 \, \times \, 10^6 \, GPU}{1 \, \frac{cm^3}{cm \, Hg. \, s. \, cm^2}} = 86.25 \, GPU$$

For N₂ gas,

$$\frac{73.53 \times 10^{-3} \frac{cm^3}{s}}{12.568 \ cm^2 \times 3 \ bar \ x} \frac{\frac{75 \ cm \ Hg}{1 \ bar}}{1 \ bar} \times \frac{1 \times 10^6 \ GPU}{1 \ \frac{cm^3}{cm \ Hg. \ s. \ cm^2}} = 26.00 \ GPU$$

The same calculations were done for Membrane 2 and 3. The calculation for selectivity,  $\alpha$  of Membrane 1,

$$\frac{Permeability of O_2}{Permeability of N_2} = \frac{86.25 \text{ GPU}}{26.00 \text{ GPU}} = 3.32$$

The same calculations were done to find the selectivity of Membrane 2 and 3. Therefore the average selectivity for Membrane 1, 2 and 3 is,

$$\frac{3.32 + 2.82 + 3.61}{3} = 3.25$$

APPENDIX A

Separation properties of uncoated MMMs at different Zeolite 4A concentration

Pressure (Bar)	Permeates Flowrates,		Pressure Normalized Flux		Selectivity, α	Average Pressure Normalized flux		Average Pressure Normalized flux		Average Selectivity,
	Q x(10 ⁻	$^{3} \text{ cm}^{3}/\text{s}$ )				Gl	PU	(Bai	α	
	O ₂	$N_2$	$Pl(O_2)$	$Pl(N_2)$		$Pl(O_2)$	$Pl(N_2)$	$Pl(O_2)$	$Pl(N_2)$	
	534.76	386.10	567.32	409.61	1.39					
1	549.45	518.13	582.91	549.69	1.06	488.35	415.60	0.55	0.47	1.18
	296.74	271.00	314.81	287.51	1.09					
	1162.79	1030.93	616.80	546.85	1.13				0.70	1.02
2	1492.54	1587.30	791.71	841.98	0.94	538.84	532.01	0.70		
	392.16	390.63	208.02	207.21	1.00					
	2173.91	2439.02	768.76	862.52	862.52 0.89		637.42	0.65	0.66	1.01
3	2380.95	2222.22	841.98	785.85	1.07	629.73				
	787.40	746.27	278.45	263.90	1.06					
	4166.67	4347.83	1105.10	1153.15	0.96					
4	2777.78	2777.78	736.73	736.73	1.00	707.01	739.11	0.70	0.73	0.94
	1052.63	1234.57	279.18	327.44	0.85					
	4545.45	6250.00	964.45	1326.12	0.73				0.72	
5	2941.18	2777.78	624.06	589.39	1.06	641.77	756.38	0.61		0.91
	1587.30	1666.67	336.79	353.63	0.95					

 Table A -1: Separation properties of uncoated membranes at 5 wt% zeolite concentration

Pressure (Bar)	Permeates Flowrates,		Pressure Normalized		Selectivity,	Average Pressure		Average Pressure		Average
	Q x(10 ⁻	$^{3} \text{ cm}^{3}/\text{s}$ )	Flux		α	Normali	zed flux	Normalized flux		Selectivity,
						GI	PU	(Barrer)		α
	O ₂	N ₂	$Pl(O_2)$	$Pl(N_2)$		$Pl(O_2)$	$Pl(N_2)$	P <i>l</i> (O ₂ )	$Pl(N_2)$	
1	1111.11	1123.60	1178.77	1192.02	0.99					
	714.29	602.41	757.78	639.09	1.19	865.17	814.78	0.54	0.51	1.08
	621.12	578.03	658.94	613.23	1.07					
2	3333.33	3125.00	1768.16	1657.65	1.07					
	5555.56	7692.31	2946.93	4080.37	0.72	2013.74	2716.38	0.57	0.77	0.78
	2500.00	4545.45	1326.12	2411.13	0.55	-				
3	3571.43	4166.67	1262.97	1473.47	0.86					
	14285.71	14285.71	5051.88	5051.88	1.00	2841.68	3017.10	0.70	0.74	0.91
	6250.00	7142.86	2210.20	2525.94	0.88					
4	5882.35	7142.86	1560.14	1894.46	0.82					
	14285.71	20000.00	3788.91	5304.48	0.71	2463.08	3079.71	0.58	0.73	0.85
	7692.31	7692.31	2040.18	2040.18	1.00					
5	10000.00	14285.71	2121.79	3031.13	0.70					
	16666.67	20000.00	3536.32	4243.58	0.83	2593.30	3132.17	0.54	0.65	0.84
	10000.00	10000.00	2121.79	2121.79	1.00					

 Table A -2: Separation properties of uncoated membranes at 10 wt% zeolite concentration

Pressure	Permeates Flowrates,		Pressure Normalized		Selectivity, a	Average Pressure		Average Pressure		Average
(Bar)	Q x( $10^{-3}$ cm ³ /s)		Flux			Normali	ized flux	Normalized flux		Selectivity, $\alpha$
						G	PU	(Barrer)		
	O ₂	N ₂	$Pl(O_2)$	$Pl(N_2)$		$Pl(O_2)$	$Pl(N_2)$	$Pl(O_2)$	$Pl(N_2)$	
1	2439.02	2500.00	2587.55	2652.24	0.98					
	2380.95	2631.58	2525.94	2791.83	0.90	2490.35	2583.45	0.51	0.53	0.97
	2222.22	2173.91	2357.55	2306.29	1.02					
2	8333.33	6666.67	4420.40	3536.32	1.25					
	6666.67	6250.00	3536.32	3315.30	1.07	3915.21	3323.97	0.51	0.44	1.18
	7142.86	5882.35	3788.91	3120.28	1.21					
3	9090.91	7692.31	3214.83	2720.24	1.18					
	10000.00	7142.86	3536.32	2525.94	1.40	3429.16	2731.04	0.51	0.41	1.26
	10000.00	8333.33	3536.32	2946.93	1.20					
4	10000.00	7692.31	2652.24	2040.18	1.30					
	11111.11	9090.91	2946.93	2411.13	1.22	2848.70	2466.08	0.51	0.44	1.17
	11111.11	11111.11	2946.93	2946.93	1.00					
5	11111.11	8333.33	2357.55	1768.16	1.33					
	12500.00	10000.00	2652.24	2121.79	1.25	2455.78	2180.73	0.51	0.45	1.16
	11111.11	12500.00	2357.55	2652.24	0.89					

 Table A -3: Separation properties of uncoated membranes at 15 wt% zeolite concentration

Pressure	Permeates Flowrates,		Pressure Normalized		Selectivity,	Average Pressure		Average Pressure		Average
(Bar)	Q x(10 ⁻	$-3 \text{ cm}^{3}/\text{s}$ )	Flux		α	Normali	zed flux	Normalized flux		Selectivity,
						Gl	PU	(Barrer)		α
	0.	Na	$Pl(O_2)$	$Pl(N_{a})$		$Pl(O_2)$	$Pl(N_{r})$	$Pl(\Omega_{r})$	$P_{l}(N_{a})$	
	02	112	11(02)	11(112)		11(02)	1 ((1)2)	11(02)	1 ((1)2)	
1	2857.14	2500.00	3031.13	2652.24	1.14					
	2127.66	2083.33	2257.22	2210.20	1.02	2718.55	2504.89	0.52	0.48	1.08
	2702.70	2500.00	2867.28	2652.24	1.08					
2	5555.56	6250.00	2946.93	3315.30	0.89					
	5263.16	5263.16	2791.83	2791.83	1.00	3091.69	3298.68	0.52	0.55	0.94
	6666.67	7142.86	3536.32	3788.91	0.93	-				
3	10000.00	6250.00	3536.32	2210.20	1.60					
	10000.00	7692.31	3536.32	2720.24	1.30	3264.29	2715.09	0.52	0.43	1.25
	7692.31	9090.91	2720.24	3214.83	0.85	-				
4	10000.00	10000.00	2652.24	2652.24	1.00					
	11111.11	8333.33	2946.93	2210.20	1.33	2848.70	2603.12	0.51	0.47	1.11
	11111.11	11111.11	2946.93	2946.93	1.00	-				
5	14285.71	12500.00	3031.13	2652.24	1.14					
	12500.00	11111.11	2652.24	2357.55	1.13	2904.83	2554.01	0.51	0.45	1.14
	14285.71	12500.00	3031.13	2652.24	1.14					
L	1	1	1	1		1	1		1	

 Table A -4: Separation properties of uncoated membranes at 20 wt% zeolite concentration

**APPENDIX B** 

Separation properties of coated MMMs at different Zeolite 4A concentration

Pressure (Bar)	Permeates		Pressure		Selectivity,	Average Pressure		Average Pressure		Average
	Flowrates,		Normalized Flux		α	Normal	ized flux	Normalized flux (Barrer)		Selectivity,
	Q x( $10^{-3}$ cm ³ /s)					G	PU		α)	
	O ₂	N ₂	$Pl(O_2)$	$Pl(N_2)$		P <i>l</i> (O ₂ )	$Pl(N_2)$	Pl(O ₂ )	$Pl(N_2)$	
	3.07	2.99	3.26	3.18	1.03					
1	5.07	4.26	5.38	4.51	1.19	4.73	4.32	0.54	0.49	1.09
	5.24	4.98	5.56	5.28	1.05					
	9.12	7.41	4.84	3.93	1.23				0.43	1.19
2	8.83	7.59	4.68	4.03	1.16	4.76	4.01	0.51		
	8.98	7.69	4.77	4.08	1.17					
	13.79	9.90	4.88	3.50	1.39				0.39	
3	12.77	10.00	4.52	3.54	1.28	4.75	3.59	0.51		1.33
	13.76	10.53	4.86	3.72	1.31					
	25.25	25.00	6.70	6.63	1.01					
4	20.00	18.52	5.30	4.91	1.08	6.11	5.73	0.52	0.48	1.07
	23.81	21.28	6.31	5.64	1.12					
	78.74	67.57	16.71	14.34	1.17				0.41	
5	58.82	43.48	12.48	9.23	1.35	14.44	11.39	0.52		1.28
	66.67	50.00	14.15	10.61	1.33					

**Table B -1:** Separation properties of coated membranes at 5 wt% zeolite concentration

Pressure	Permeates 1	Flowrates,	Pressure Normalized		Selectivity,	Average	Average Pressure		Average Pressure	
(Bar)	Q x( $10^{-3}$ cm ³ /s)		Flux		α	Normal	ized flux	Normalized flux		Selectivity,
						G	PU	(Barrer)		α)
	O ₂	N ₂	Pl(O ₂ )	$Pl(N_2)$		Pl(O ₂ )	$Pl(N_2)$	$Pl(O_2)$	$Pl(N_2)$	
1	8.26	6.65	8.77	7.06	1.24					
	7.99	6.54	8.48	6.94	1.22	8.20	6.66	0.51	0.42	1.23
	6.93	5.63	7.35	5.98	1.23					
2	22.68	19.19	12.03	10.18	1.18					
	22.12	21.74	11.74	11.53	1.02	10.01	9.20	0.56	0.51	1.09
	11.82	11.07	6.27	5.87	1.07					
3	71.43	58.82	25.26	20.80	1.21					
	47.62	38.46	16.84	13.60	1.24	17.92	13.98	0.56	0.44	1.33
	33.00	21.28	11.67	7.52	1.55					
4	500.00	344.83	132.61	91.46	1.45					
	125.00	90.91	33.15	24.11	1.38	128.93	97.46	0.93	0.70	1.36
	833.33	666.67	221.02	176.82	1.25					
5	1000.00	909.09	212.18	192.89	1.10					
	344.83	277.78	73.17	58.94	1.24	165.84	142.88	0.65	0.56	1.18
	1000.00	833.33	212.18	176.82	1.20					

**Table B -2:** Separation properties of coated membranes at 10 wt% zeolite concentration

Pressure	Permeates Flowrates,		Pressure Normalized		Selectivity,	Average	Average Pressure		Average Pressure	
(Bar)	$Q x(10^{-3} cm^{3}/s)$		Flux		α	Normali	zed flux	Normalized flux		Selectivity,
						GF	٧U	(Barrer)		α
	O ₂	N ₂	$Pl(O_2)$	$Pl(N_2)$		$Pl(O_2)$	$Pl(N_2)$	$Pl(O_2)$	$Pl(N_2)$	
1	6.67	4.06	7.07	4.30	1.64					
	9.62	9.44	10.21	10.02	1.02	10.01	8.70	0.54	0.47	1.25
	12.00	11.11	12.74	11.79	1.08					
2	24.69	14.25	13.10	7.56	1.73					
	49.50	22.03	26.26	11.68	2.25	30.63	15.17	0.69	0.34	1.99
	99.01	49.50	52.52	26.26	2.00					
3	243.90	73.53	86.25	26.00	3.32					
	294.12	104.17	104.01	36.84	2.82	114.67	35.15	0.54	0.17	3.25
	434.78	120.48	153.75	42.61	3.61					
4	153.85	68.03	40.80	18.04	2.26					
	625.00	270.27	165.76	71.68	2.31	110.96	41.54	0.73	0.27	2.73
	476.19	131.58	126.30	34.90	3.62					
5	333.33	212.77	70.73	45.14	1.57					
	1000.00	588.24	212.18	124.81	1.70	141.45	78.75	0.62	0.35	1.80
	666.67	312.50	141.45	66.31	2.13					

 Table B -3: Separation properties of coated membranes at 15 wt% zeolite concentration

Pressure	Permeates Flowrates,		Pressure Normalized		Selectivity,	Average	Average Pressure		Average Pressure	
(Bar)	Q x( $10^{-3}$ cm ³ /s)		Flux		α	Normali	ized flux	Normali	zed flux	Selectivity,
						Gl	PU	(Bai	rrer)	α
		1								
	$O_2$	$N_2$	$Pl(O_2)$	$Pl(N_2)$		$Pl(O_2)$	$Pl(N_2)$	$Pl(O_2)$	$Pl(N_2)$	
1	3.80	3.02	4.04	3.21	1.26					
	3.69	2.85	3.92	3.03	1.29	4.15	3.41	0.51	0.42	1.23
	4.25	3.76	4.51	3.99	1.13					
2	28.49	21.93	15.11	11.63	1.30					
	32.68	25.77	17.33	13.67	1.27	19.16	15.48	0.53	0.43	1.25
	47.17	39.84	25.02	21.13	1.18					
3	94.34	65.36	33.36	23.11	1.44					
	123.46	88.50	43.66	31.29	1.40	49.73	37.46	0.56	0.42	1.36
	204.08	163.93	72.17	57.97	1.24					
4	303.03	277.78	80.37	73.67	1.09					
	256.41	227.27	68.01	60.28	1.13	93.66	84.84	0.55	0.50	1.11
	500.00	454.55	132.61	120.56	1.10					
5	714.29	500.00	151.56	106.09	1.43					
	454.55	416.67	96.45	88.41	1.09	146.96	115.35	0.55	0.43	1.26
	909.09	714.29	192.89	151.56	1.27					

**Table B -4:** Separation properties of coated membranes at 20 wt% zeolite concentration