Development of Polyetherimide-Zeolite 4A Mixed Matrix Membrane for CO_2/CH_4 separation

By

A-ESAH MASOR

14194

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical)

SEPTEMBER 2014

University Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

ACKNOWLEDGEMENT

First and foremost, I would like to express my appreciation to all those who gave me the guidance and thanks for their kind assistance throughout my final year project.

I would like to express my deepest gratitude to Assoc. Prof. Dr. Hilmi Mukhtar, my supervisor, for his supervision and support until the end of this work. Thanks also for his valuable guidance, assistance, knowledge and experiences shared which contribute to my self- development.

I was so grateful and thankful to the Graduate Assistant, Mr. Rizwan Nasir, who has been trying all his afford to give me suggestion and guided me the way of doing my final project from the beginning till the end.

My thanks are also toward my dear lecturers in the chemical engineering department, colleagues and many people whom I could not mention all names here, for willingness to share the useful technical knowledge and large-hearted support from time to time during my project.

Last, the warmest thanks to my family and my friends for all of the great wishes and their continuous encouragement.

CERTIFICATION OF APPROVAL

DEVELOPMENT OF POLYETHERIMIDE-ZEOLITE 4A MIXED MATRIX MEMBRANE FOR CO_2/CH_4 SEPARATION

By

A-ESAH MASOR
14194

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons.)
(CHEMICAL ENGINEERING)

Approved by,

(AP. DR. HILMI BIN MUKHTAR)

Universiti Teknologi PETRONAS
TRONOH, PERAK
SEPTEMBER 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(A-ESAH MASOR)

ABSTRACT

The monetization of natural gas having high carbon dioxide content (>20mol %) post technological issues and challenges. Carbon Dioxide (CO_2) removal unit should be installed at offshore to reduce CO_2 content before sending to onshore. It has been found that membrane technology is the best technology for CO_2 removal at offshore due to its simplicity, small size and environmental friendly. However, selection of the suitable material for membrane fabrication still a big problem and Many previous research show that Polyetherimide and zeolite 4A have good properties that can be fabricated a membrane that have high efficiency for CO_2 removal.

The main objective of the current study was to develop Polyetherimide-zeolite 4A mixed matrix membrane. Mixed matrix membrane is the membrane which has polymer as a based and inorganic material as a filter. The membranes were casted using solution casting method. The physicochemical properties were evaluated using FESEM, FTIR, TGA and DSC.

FESEM results show that pure PEI membrane and MMMs are dense in structure. The thickness of membranes were in a good ranges (60-100μm). Zeolite particles created some physical attachment with PEI but still appeared some voids in between these two. Chemical properties were evaluate by FTIR. FTIR results confirmed that Zeolite 4A did not change chemical structure of PEI membrane. The thermal properties were evaluate using TGA and DSC. The result from TGA shows that pure PEI membrane has higher decomposition temperature compared to MMMs which corresponded to DSC result which show that the glass transition temperature of MMMs were lower than pure PEI.

The performances were evaluated by measuring the permeability and selectivity of pure CO_2 and CH_4 gases. The gas permeability result of MMMs show the increase in permeability of CO_2 more than 90 % compared to pure PEI membrane. The selectivity of CO_2/CH_4 in MMMs are also higher than pure PEI about 45%. Even though the magnitude for permeability and selectivity obtained in this study were small, the increase in MMM is obviously compared to pure PEI membrane. Therefore, it can be concluded that polyetheirmide-zeolite4A MMM can separate CO_2 from CH_4 better than pure PEI membrane.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

CO_2	Carbon Dioxide
CH_4	Methane
DEA	Diethanolamine
DSC	Differential Scanning Calorimeter
EUR	Estimated ultimate recovery
FESEM	Field emission scanning electron microscope
FTIR	Fourier Transform Infrared Spectroscopy
GPU	Gas permeation unit
MEA	Monoethanolamine
MMM	Mixed matrix membrane
NGV	Natural gas vehicle
NMP	N-Methylpyrrolidone
PEI	Polyetherimide
PI	Polyimide
PS	Polysulfone
Tg	Glass Transition Temperature
TGA	Thermal Gravimetric Analyzer
TSCF	Trillion Standard Cubic Feet

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Global warming has been recognized as one of the major environmental issues in the world. The emission of greenhouse gases is the root cause of global warming and one of the major gases is Carbon dioxide (CO_2) gas **.**CO_2 is produced and emitted to the atmosphere from several sources and mostly from energy production sectors such as in the production of natural gas from an underground reservoir[1].

Natural gas is a fossil fuel formed when layers of buried plants and animals which are organic matters are compressed under earth's crust at high pressure and temperature over thousands of years[2]. Natural gas is one of valuable alternative energy resources in the world. Although oil is the highest world's energy consumption, the demand of natural gas around the world is rapidly increasing year by year and it was expected to increase in the future. The usages of natural gas are covered in many areas. It is mostly used for electric power generation and industrial usage such as in Petrochemical, Oil and gas industry operation and Fertilizer industries, it is also used as a main fuel in residential and transportation such as Natural gas vehicle(NGV)[1].

1.1.1 Natural gas composition and impurities

One of the main issues for natural gas is its impurities. Natural gas consists primarily of methane (70-90% of the total component) and other light and heavier hydrocarbons. The impurities present in natural gas need to be removed to meet the pipeline quality standard[2]. The pipeline quality standard is an allowable amount of common impurities for delivery of natural gas to the pipeline. The pipeline quality standard for CO_2 in U.S.A is below 2 mole%[3]. Table1-1 shows the typical feed composition of natural gas well and its sale specifications.

CO_2 is one of the major contaminates in natural gas feeds and most of wellhead natural gas in the world contain exceed the standard limit, it has to be removed before further usage to meet the pipeline specifications as well as environment regulations. The natural gas that contains high concentration of impurity is considered as "acid gas".

The problem of acid gas has been discussed in many research studies. The acid gases create the environmental problem as well as operational problem. The examples of environmental effects of carbon dioxide are global warming, ocean acidification and anthropogenic climate change. Among the operation problem from acid gas are it causes corrosion of pipeline and equipment, lower the overall energy value of the natural gas and eventually lower the selling price of the gas [2, 4, 5].

Table 1-1: Typical feed composition of natural gas well and sale specification[2, 6]

Component	**Typical feed**	**Sale specifications**
CH_4	70-80%	90%
CO_2	5-45%	$< 2\%$
C_2H_6	3-4%	3-4%
C_3- C_5	$\sim 3\%$	$\sim 3\%$
N_2	$\sim 1-4\%$	$< 4\%$
H_2S	< 100ppm	< 4ppm
H_2O	saturated	< 100 ppm
C_6 and higher	0.5-1%	0.5-1%

The acid gas content is varied from well to well depend on its geographical location. By analyzing the natural gas reservoirs in Malaysia (Table 1-2), it noted that most of reservoirs in Malaysia contain very high CO_2 concentration with the range from 28% up to 85%. Moreover, the statistic of CO_2 content in natural gas in term of field location shows that the gas filed in Sarawak contain very high CO_2 content with 72% while the gas field in Peninsular Malaysia contain 46% of CO_2 as shows in Figure1-2[7].

The high content of CO_2 has been become an issue because the available CO_2 removal system is only capable to treat the natural gas with the maximum of CO_2 content up to 30 to 40%[8]. Therefore, it is very important to find the technology that able to treat natural gas with CO_2 content higher than 40%.

Table 1-2:CO_2 gas content in natural gas reservoirs in Malaysia[7]

Peninsular Malaysia				
Holder	**Field**	**Total EUR (TSCF)**	**CO_2 volume (TSCF)**	**CO_2 content (Volume %)**
PETRONAS	Bujang	1.47	0.97	66%
PETRONAS	Sepat	1.20	0.72	60%
PETRONAS	Noring	0.58	0.35	60%
PETRONAS	Inas	1.04	0.62	60%
PETRONAS	Tangga Barat	0.33	0.11	32%
PCSB	Ular	0.14	0.07	50%
PCSB	Gajah	0.12	0.06	50%
PCSB	Bergading	1.36	0.54	40%
PCSB	Beranang	0.08	0.02	28%
EMEPMI	Palas NAG	0.38	0.18	46%
Total		6.70	3.64	
Sarawak				
Holder	**Field**	**Total EUR (TSCF)**	**CO_2 volume (TSCF)**	**CO_2 content (Volume %)**
PETRONAS	K5	25.65	17.95	70%
PETRONAS	J5	5.37	4.67	87%
PETRONAS	J1	1.43	0.84	59%
PETRONAS	T3	1.04	0.65	62%
PETRONAS	Tenggiri Mrn.	0.33	0.15	46%
Total		33.82	24.26	

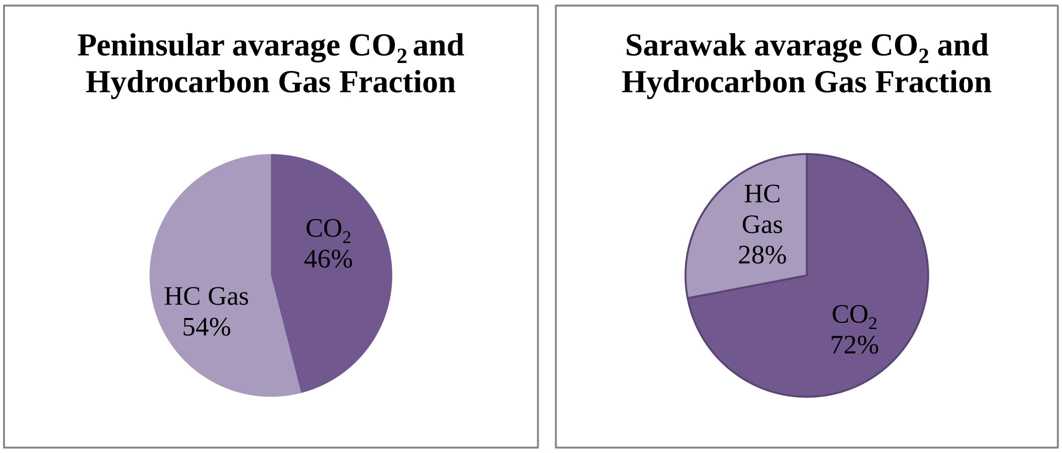


Figure 1-1: Average CO_2 and Hydrocarbon gas fraction in Peninsular and Sarawak, Malaysia

1.1.2 Conventional technologies for Natural Gas Purification

1.1.2.1 Amine Absorption

The most widely used technology for CO_2 removal from natural gas is absorption using amine solvents[9]. Amine absorption is accomplished by passing natural gas counter current with the selective solvent in column or plate where impurities are dissolved or captured by the solvent [5]. Amine absorption can be divided into two categories based on the interaction of the absorbed gas and the solvent. Physical Absorption capture the desired gas based on the solubility while chemical absorption capture desired gas based on the chemical reaction between solvent and gas component. Monoethanolamine (MEA) and Diethanolamine (DEA) are common amine based solvents used for the absorption process[1].

Even though amine absorption is the popular technology for CO_2 removal, it has limitations and challenges. In a single process, the amine absorption is only capable to purify the natural gas having acid gases from 5-15% down to pipeline quality[1].

Conventional amine absorption towers are heavy in weight and large in size. They pose many operational and environmental problems. Using amine absorption, the solvent can cause corrosion in the unit. Amine absorption also results in environmental hazards due to unrecyclable solvent which has difficulty in disposal. Moreover, it required high operation cost , longtime requirement for purifying acid gas because low partial pressure is needed while using chemical solvents as well as it required large area which is inconvenience for offshore application[2, 10].

1.1.2.2 Adsorption

The adsorption process is used in gas separation by using a solid surface called adsorbent to remove selective component from gas stream. These selective components adhere to the surface of adsorbent which has microporous structure. Zeolite, molecular sieves, silica gel, alumina and activated carbons are the typical adsorbents used for adsorption[1].

Even though adsorption process can be used for gas separation, it is more appropriate with the feed gas that has low concentration of CO_2 and moderate operating pressure Moreover, the design is complex and it is not suitable for continuous process due to attrition[11].

1.1.2.3 Membrane Technology

Due to the limitation of amine absorption and adsorption, membrane technology was developed. Membrane technology is separate gas mixture using thin barriers which only allow a certain molecule of gas to pass through. The first membrane system for CO_2 removal was installed in the early 1980s [5]. After that, membranes gas separation have been commercially used in a number of industrial processes and the use of membranes in natural gas processing has been known by CO_2 removal[5, 9].

Membrane technology has many advantages over others technologies. Membrane technology is chosen due to its simplicity, stability at high pressure, high recovery of products and required less area for installation. Separation using membrane has less environment impact due to it has no toxic solvents involved as well as no corrosion issues and inherent modularity (constant contact area). The most importantly, it is cost effective since it required lesser energy (no phase changes) and as the result low capital investment and operation[2, 5, 12].

In industrial applications, there are two important performance parameters which are the permeability and the selectivity. The selectivity is defined as the ratio of permeability between two components being separated, whereas permeability is defined as the transport flux per unit transport membrane driving force per unit membrane thickness. A high selectivity shows better separation while a high permeability reduces pressure drop losses associated with the membrane separation[13]. To date, the developing of a membrane material that has both characteristics remains a challenge.

Membranes are generally classified into two main types, inorganic and organic membranes. Inorganic membranes are classified based on the material used such as metals and ceramics. Organic membranes or known as polymeric membrane are generally divided into rubbery and glassy types. Most of industrial application selected glassy polymeric membranes for gas separation because of their high gas selectivity and good mechanical properties[13].

It has been reported that each type of membrane still has problems for gas separation application. Gas separation using polymeric membranes are simple, cost effective and environmentally friendly but they have a problem with the trade-off between selectivity and permeability. In contrast, inorganic membranes have good thermal and chemical stability with high selectivity and high gas flux, but their big scale applications are limited due to very high cost and difficulty of fabrication. Therefore mixed matrix membrane (MMM) which is the combination of polymeric membrane and inorganic membrane was developed to obtain the good transport properties of inorganic materials with the simplicity of preparing polymer based membrane.

1.2 PROBLEM STATEMENT

Currently the raw natural gas from well contain high carbon dioxide content up to 85 mole% which causes technological challenges for monetization. The conventional CO_2 removal using amine absorption has some gaps such as high operation cost and large area required and applicable only with the natural gas that has CO_2 content up to 15 mole %.

In order to remove CO_2 in natural gas that has higher concentration than 15%. The CO_2 removal unit should be installed at offshore to remove some CO_2 content from the raw natural gas before send it for further removal at onshore. Therefore membrane technology is the most suitable technology to install at offshore due to its simplicity, low capital cost and less environment impact.

However, in order to make CO_2 gas separation using membrane more applicable, high permeability and high selectivity are the two main parameters to be achieved because these two factors indicate the efficiency of the separation and up to now, researchers still cannot determine the best material for membrane fabrication that has high selectivity and high permeability.

Polyetherimide and Zeolite 4A has been proven to be good materials for membrane fabrication due to its properties. Therefore, in this study, mixed matrix membrane using Polyetherimide-Zeolite 4A combination will be fabricated, tested for separation performance and characterized to determine the morphology properties.

1.3 OBJECTIVES

The main objectives of this project are as follow:

1.3.1 To develop mixed matrix membranes using the combination of Polyetherimide and Zeolite 4A.

1.3.2 To characterize the physical, chemical and thermal properties of the developed mixed matrix membranes using FESEM, FTIR, TGA and DSC.

1.3.3 To evaluate the performance of the newly developed membranes in term of permeability and selectivity for pure CO_2 and CH_4 against variable feed pressure.

1.4 SCOPE OF STUDY

This project focused on the fabrication, characterization, and evaluation of mixed matrix membranes comprised of Polyetherimide (PEI) and Zeolite 4A. Details of the study is described in the following;

1.4.1 Fabrication of Polyetherimide -Zeolite 4A mixed matrix membranes.

Five (5) different type of membranes will be fabricated in this research study including the based PEI polymer and four (4) mixed matrix membranes with 5, 10, 15 and 20 wt%, respectively of zeolite 4A. N-Methylpyrrolidone (NMP) as the solvent will be selected for the solvent and the membranes will be casted via solution casting method. The prepared membrane will be dried at $90^{o}C$ for 12 hours and continue dry at $160^{o}C$ for 24 hours.

1.4.2 Characterization of Polyetherimide -Zeolite 4A mixed matrix membranes

The fabricated membranes will be characterized in term of its morphology and physical properties. Membrane morphologies will be carried out by using field emission scanning electron microscope (FESEM).The change in the chemical structure and the interaction between PEI and zeolite 4A will be carried out by using Fourier Transform Infrared Spectroscopy (FTIR). The thermal property will be investigated by using Thermal Gravimetric Analyzer (TGA) to observe the weight change of the fabricated membranes with temperature change and using Differential Scanning Calorimeter (DSC) to observe the glass transition temperature.

1.4.3 Performance evaluation of Polyetherimide -Zeolite 4A mixed matrix membranes.

The performance of the present developed pure membrane and mixed matrix membranes will be evaluated in term of $CO_2$and CH_4 permeability against operating pressure of 4, 6, 8 and 10 Bars. The ideal selectivity of fabricated membranes will be then calculated by dividing the permeability of CO_2 and CH_4.

1.5 RELEVANCY AND FEASIBILITY OF THE PROJECT

As the final year project comprises of two continues courses which are FYP1 in first semester and FYP2 in second semester. According to the scope of study, it can be seen that parameters of membrane to be studied have been carefully chosen to suit with the project timeline and in the same time, still represent their great effect on performance of membrane.

A feasible and details plan with specific time allocated for each part of the whole project were determined, challenges should be countered with guidance from supervisor, PhD students, and research officers while studying the matter through reading and self-learning. Other than that, all chemicals and equipment needed are available in the department and the characterization equipments are available at the university. Therefore, it was expected that the project can be completed during the time frame and can give a good outcome by the end of its completion.

CHAPTER 2
LITERATURE REVIEW

The development of membrane technology are discussed in Section 2.1. Past researches related to mixed matrix membrane are discussed in Section 2.2. Material for mixed membrane fabrication as well as membrane fabrication method are reviewed in Section 2.3and 2.4. Lastly, membrane characterization, transport theory in membrane and Gas separation performance are discussed in Section 2.5 to 2.7.

2.1 DEVELOPMENT OF MEMBRANE TECHNOLOGY

Membrane is defined as selective barrier between two phases that has ability to transport one component than the other[14]. It allows some molecules to pass through, called permeates and prevent the others called retentate as shown in Figure2-1. The separation occurs because of the appropriate driving force such as temperature, concentration, pressure or electrical gradients.

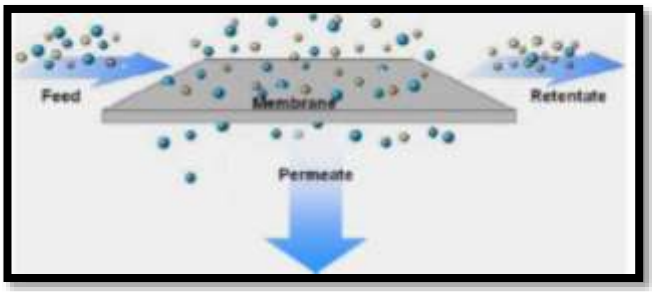


Figure 2-1: Schematic diagram of membrane process [16]

2.1.1 Polymeric membrane

Polymeric membranes are the membranes that made from polymer material such as Polyimide (PI), Polyetherimide (PEI), Polysulfone (PS) and etc. The separation mechanism in polymeric membranes are vary based on membrane properties such as chemical and physical structure), the nature of the gas (shape, size, and polarity), the interface between membrane and components[1]. Polymeric membranes have been developed for gas separation in the real industry due to many good properties including low cost, high mechanical stability and simplicity in processing. However, they also have disadvantages such as low thermal stability and cannot withstand with aggressive chemical environments [15].Moreover, many research studies shows that most of polymer materials have problem with the upper bound trade-off limitation between the permeability and selectivity which is shows in the Figure 2-2[16].

Polymers can be divided into two main types which are rubbery and glassy. In a rubbery polymer, segments of the polymer backbone can rotate freely around their axis. This type of structure makes the polymer soft and elastic. Thermal motion of these segments also leads to high permeant diffusion coefficients. In another hand, in glassy polymer, steric hindrance along the polymer backbone disallows rotation of polymer segments which result in a rigid and tough polymer. Thermal motion in this type of material is limited, therefore permeant diffusion coefficients are low. If the temperature of a glassy polymer is raised, a point is reached at which the increase in thermal energy is sufficient to overcome the steric hindrance restricting rotation of polymer backbone segments. At this temperature, called the glass transition temperature (Tg), the polymer changes from a glass to a rubber[17].

Sridhar et.al[18] mention that rubbery materials have high permeability, but poor selectivity due to they are lack of polar groups, have low degree of crosslinking and absence of crystallinity. While glassy polymers have higher perm selectivity and are therefore, more suitable in gas separation studies.

Basically, glassy polymer is a combination of amorphous and crystalline phases. The crystallites act as effective cross-links and therefore, decrease the area available for permeation. Crystallinity improves the mechanical properties such as stiffness and tensile strength as well as thermal property like Tg. Therefore, the final mechanical properties of polymeric membranes are related to the ratio of crystalline to amorphous which could be related to the performance characteristics such as permeability of polymer[18].

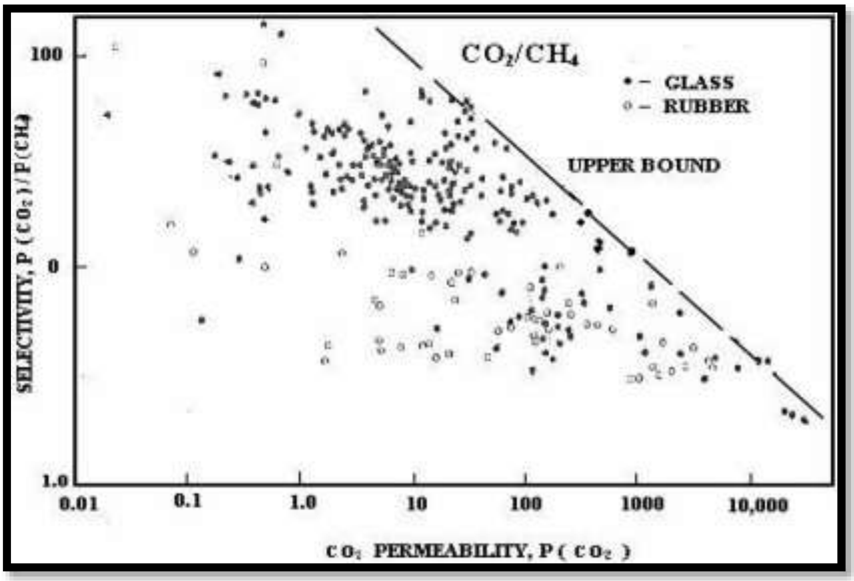


Figure 2-2: CO_2/CH_4 selectivity as a function of CO_2 permeability for all well-known membrane materials as of 1991[18].

2.1.2 Inorganic membrane

Inorganic membranes are the membranes that made from inorganic matter such as alumina, titanium, glass (silica), metal, and zeolite based membranes. Inorganic membranes have well-defined structure with pores which some gas molecules that have smaller molecule size compared to the pore can pass through while reject the large one. Inorganic membrane has separation rate and efficiency better than polymeric membrane and they also own high thermal and chemical stabilities.

Even though, inorganic membranes proven to have high separation efficiency, the fabrication in big scale is very difficult and high cost for large scale application. [15, 16, 19].

2.2.3 Mixed Matrix Membrane (MMM)

Mixed matrix membrane is an alternative approach to develop membranes that combine the best characteristics of both polymeric and inorganic materials by forming organic-inorganic hybrid membranes. Many combination of MMM have been proposed to enhance membrane performance. The main purpose is to overcome the drawback of polymeric and inorganic membrane and obtain the desired combination of the properties for good gas separation [4, 13, 16]. The schematic diagram of the mixed matrix membrane is shown in Figure 2-3.

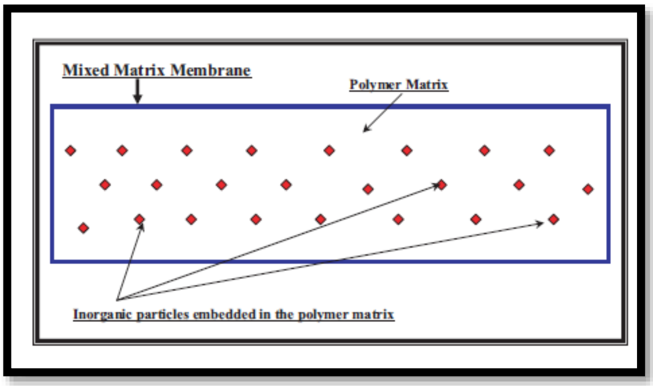


Figure 2-3: Schematic diagram of mixed matrix membrane [5].

One study stated that mixed matrix membranes have the potential to have high performance in selectivity and permeability and it can be applied to CO_2 separation from natural gas by developing a right kind of mixed matrix membrane[13].

Mahajan et al.[20] mentioned that one way to obtain a successful mixed matrix membrane is by choosing polymers that can maintain flexibility during membrane formation and have a favorable interaction with the inorganic filter. Aroon et al.[4] also agree that proper material selection for both the matrix and the inorganic phase is fundamentally important in the development of MMM. Because both polymer as well as inorganic properties can affect mixed matrix membranes morphology and separation performance[4].

However, the development of mixed matrix membranes remains challenging because there is no reliable and standard approach to identify suitable materials for the mixed matrix membrane and it has been proposed that the low performance of MMM may cause by improper interfacial contact between the solid phase and the bulk polymer phase. The concentration of the inorganic filler and its size also could affect the phase behavior. Therefore, it is important to find the maximum loading of inorganic filler that maintains the morphology of the membrane and does not cause phase separation between the membrane and the inorganic particles.

2.2 PAST RESEARCH STUDIES ABOUT MIXED MATRIX MEMBRANE

There are many research studies that has been developed many combination of mixed matrix membrane which can be summarized in the table below;

Table 2-1: Past research studies on mixed matrix membrane development

Year	Researcher	Polymer	Inorganic	Finding
1997	Zimmerman et al.[21]	PEI	Zeolite 4A	▪ Theoretically, the performance should be higher than upper bond under optimum conditions for O_2/N_2 separation but because of ▪ The defect lead to the performance still lying below the upper bound.
2005	Moore & Koros[22]	PEI	Zeolite 4A	▪ Different preparation conditions lead to different membrane morphologies ▪ Stress at the organic–inorganic interface should be minimized ▪ The method or solvent that can clog zeolite should be avoided.
2011	Basu et al. [23]	PI Matrimid	[Cu3(BTC)2] ,ZIF-8, MIL-53 (Al)	▪ Selectivity and permeance of CO_2/CH_4 increased with higher filler loading.
2011	Adams et al. [24]	PVAc	Zeolite 4A	▪ Significant transport enhancements MMMs' properties are surprisingly good.
2011	Moghadam et al. [25]	Matrimid ®-5218	Titanium dioxide (TiO2) nanoparticles	▪ TiO2 nanoparticles improved membrane performance in CO2/CH4 separation.
2011	Ismail et al.[26]	Polyethersulfone	MWCNT	▪ Selectivity increased as compared to unmodified MECNT. ▪ No interface voids present the membrane morphology.
2012	Karkhanechi et al.[27]	Polyimide (PI)/P84	Nano-zeolites 13X and 4A	▪ Interfacial void-free nanocomposite membranes were produced. ▪ Permeability is decreased and selectivity increased.

Table 2-1: Past research studies on MMM development (Continued)

Year	Researcher	Polymer	Inorganic	Finding
2012	Chen et al.[28]	Polyimide	FAU/EMT zeolite	▪ Increased permeability of CO2 due to amine loading.
2012	Liang et al.[29]	Polyethersulfone	(MMT) and TiO2	▪ Permeability were significantly higher with increasing MMT content
2012	Nik et al.[30]	6FDA-ODA polyimide	MOFs	▪ A rigidified polymer at the interface of the filler and polymer Matrix was occurred ▪ Therefore decrease the permeability while increasing the selectivity.
2013	Rostamizadeh et al. [31]	PDMS with cross- linker (polyhydrogen-methylsilane;	Zeolite nanoparticles	▪ Due to the nano-size of zeolite a homogeneous dispersion could be achieved in the resultant membrane. ▪ No formation of voids in the zeolite polymer interface.
2010	Simons et al.[32]	Polyether-imide(PEI)	Oxydiphthalic dianhydride (ODPA)	▪ High CO_2/CH_4 selectivity for the ODPA- PEI films at high pressure.
2013	Ozturk & Demirciyeva [33]	PEI & PI	Zeolite 4A	▪ CO_2/CH_4 (in biogas) permeability and selectivity of PEI was lower than fond in PI(Selectivity 26.62 for PI&18.42 for PEI at 483K
2010	Simons et al.[32]	Polyether-imide(PEI)	Oxydiphthalic dianhydride (ODPA)	▪ High CO_2/CH_4 selectivity for the ODPA- PEI films at high pressure.

Year	Researcher	Polymer	Inorganic	Finding
2013	Ozturk & Demirciyeva [33]	PEI & PI	Zeolite 4A	▪ CO_2/CH_4 (in biogas) permeability and selectivity of PEI was lower than fond in PI(Selectivity 26.62 for PI&18.42 for PEI at 483K

2.3 MATERIAL FOR MIXED MATRIX MEMBRANE FABRICATION

2.3.1 Polymer

Polymer is a main material for mixed matrix membrane as it is used as a base for membrane module. There are many types of polymer that has been used for membrane fabrication which can be summarized in the table below;

Table 2-2: Different type of Polymers that has been used for membrane fabrication. Adapted from [19]

No	Polymer	T_g (°C)	Operating Condition		Permeability		Selectivity
			T (°C)	P (Bar)	CO_2	CH_4	CO_2/CH_4
1.	Polyetherimide (PEI)+ Polyethylene glycol (PEG)	217	25	17	7.44E-4	0.12 E-4	62
2.	Polyimide(PI)	360-410	35	1	8.34	6.86	1.22
3.	Matrimid	325	35	10	7.26	0.23	31.6
4.	Polyphosphazene	-66	35	2	9.3	0.62	15
5.	Poly(p-phenylene oxide)	215	30	1	90	5.4	16.7
6.	Acrylonitrile Butadiene Styrene (ABS)	105	30	37	3.43	0.17	20.2

7.	Poly(vinyl trimethylsilane) (PVTMS)	105-144	30	1	190	22	8.6
8.	Poly(vinyl pyrrolidone)	150-180	50	26	0.02	1.69 E-24	48.1
9.	Polylactic acid	55-60	20	2	1.2	0.075	16
10.	Poly(aryleneether)s	138-158	35	1	30.3	1.9	16.13

From the table above, there are the tradeoff between selectivity and permeability. For example, first polymer which is Polyetherimide (PEI) has high selectivity compared to other polymers but it has very low permeability for CO_2 which also happened with Poly (vinyl pyrrolidone) in raw 8. In other hand, the polymers that has high permeability, they are having low selectivity such as Poly (p-phenylene oxide) in raw 5, Poly (vinyl trimethylsilane) (PVTMS) in raw 7 and Poly (aryleneether) s in last raw. These phenomena correspond to the plot by Robinson that is shown in Figure 2-2.

2.3.2 Inorganic

Mostly, inorganic filter or molecular sieve materials have uniform pores with diameters in the micro-size range (< 2 nm or 2–20 nm). Zeolite and carbon molecular sieves are among the most popular and commercially available molecular sieve materials. Molecular sieve materials can provide high selectivity because they have unique pore dimensions approaching the molecular dimensions of gases. There are three main factors that should be considered when selecting the inorganic filters. First, they should have the ability to achieve high perm-selectivity for the separation of the desired gas. Second, particle size due to the permeability of all gases increase as the pore size of the filter increase and lastly is filler loading percentage[19].

There are many types of inorganic filter that can be used for MMM fabrication can be summarized in the Table 2-3.

Table 2-3: Different inorganic filters and their properties[19].

Inorganic filter	Properties
Carbon molecular sieve (CMS)	▪ Effective for gas separation in adsorption application. ▪ Good absorptivity for some gases. ▪ Mean pore size around 3–6 Å.
Zeolite	▪ High diffusivity and selectivity as compared to polymer material but expensive. ▪ Difficult fabrication of non-defect-free membranes.
Silica nanoparticles	▪ Several shape and particle size in the range of 2–50 nm. ▪ Excellent mechanical and thermal stability and good adhesion. ▪ Limitations: the large pores may be blocked with polymer chains and chemical modification of pores is required.
Nonporous silica	▪ Can change gas separation properties. ▪ Can affect the polymer chain packing in glassy polymers. ▪ Can modify the molecular packing of polymer chains; ▪ Can improve permeability and selectivity of membrane
Metal organic framework (MOF)	▪ High surface area, controlled porosity, good affinity with particular gases. ▪ Strong chemical bonding, rigid framework, finite pore size. ▪ High permeability, but low selectivity
Zeolitic imidazolate framework (ZIF)	▪ Similar sieving property to zeolite ▪ thermal and chemically stable and hydrophobic surface
Carbon nanotubes (CNTs)	▪ Able to meet the Robeson upper bound ▪ Limitation: hazardous, expensive and Uniform dispersion difficult
Metal oxide	▪ Nano-scale diameter, high specific area. ▪ The particle distribution can be improved and ▪ The chance of nonselective void formation is reduced

2.3.3 Solvent

There are many solvents have been used for membrane preparation. The first type of solvent is Methyl-pyrrolidone (NMP) with the molecular formula aC_5H_9NO. It is a chemically stable and powerful polar solvent. It has been used as a solvent together with alcohol and water for carbon dioxide, carbon, hydrogen sulfide and organic sulfur compound removal. Moreover, it is considered as green solvent because its toxicity is very low[19].

The second solvent is *N*- Dimethyl-acetamide (DMAc) with the molecular formula C_4H_9NO. It is a polar and aprotic solvent. It is an excellent solvent for high molecular weight polymers and synthetic resins. The third one is Dichloromethane (DCM) with the molecular formula CH_2Cl_2. It has low boiling point and therefore has shorter evaporation time. Using this solvent can prevent from the sedimentation of zeolite particles in MMM. However, it has high volatility which can lead the membrane to exhibit a wavy structure[19].

The forth one is Chloroform with molecular formula CHCl3. It is a commonly laboratory solvent due to it relatively unreactive, appropriately volatile and miscible with most of organic liquid. The fifth one is Tetrahydrofuran (THF) with molecular formula C_4H_8O. It has been used as evaporative solvent to help skin formation and in membrane fabrication because it is high volatility which help the formation for a skin layer. However, it is hazards if inhalation and ingestion and also flammable[19].

The last solvent is N- Dimethylformamide(DMF) with molecular formula C_3H_7NO. It is also a polar solvent. It is suitable for salt compounds with a high molecular weight. It is high dielectric constant, electron donor properties, and can form complexes. It has high boiling point and miscible in water and can be recycle easily. It has been used for the production of elastomers, spandex fibber and synthetic leather[19].

In order to choose the suitable solvent for membrane fabrication, there are some factors that need to be considered such as the type of selected polymer and inorganic material should be able to dissolve in the solvent. Moreover, the simplicity for handling and its hazards also the important factors that should be emphasized.

The properties of different solvents are summarized in the table 2-3;

Table 2-4: Different solvent properties[19].

Solvent	MW [gmol^{-1}]	Density [g cm^{-3}]	BP. [°C]	V. P. [kPa]	Solubility in water	Solubility parameter [J$^{1/2}$cm$^{-3/2}$]
1-Methyl-2-pyrrolidone (NMP)	99.13	1.028	202	0	Soluble	22.9
N,N- Dimethylacetamide (DMA)	87.12	0.937	166	0.2	Soluble	22.1/22.8
Dichloromethane (DCM)	84.94	1.336	39.8–40	46.5	Not soluble	19.9
Chloroform	119.39	1.499	58–62	21.1	Not soluble	18.9–19.0
Tetrahydrofuran(THF)	72.10	0.888	64–66	19.3	Soluble	18.62
N,N- Dimethylformamide (DMF)	73.09	0.949	153	0.3	soluble	24.9

2.4 MEMBRANE FABRICATION TECHNIQUES

Basically, there are two different techniques for membrane fabrication which are Phase-Inversion and solution casting.

2.4.1 Phase-Inversion Method

Phase inversion also knows as phase separation. The basic concept is changing a one-phase casting solution into two separate phases[34]. Phase inversion is used to fabricate any membrane that polymer and solvent mixture form a homogeneous solution under specific condition of pressure and temperature but separates into two phases when these conditions are changed. For instance, phase inversion can be induced by vaporization of a volatile solvent from a homogeneous polymer solution, or by freezing a casting solution which is homogeneous only at high temperatures[19].

The phase transformation can be done in many ways. First method is by immerse the polymer solution in a non-solvent coagulation bath (typically water) called “Immersion precipitation”. Demixing and precipitation occur because the exchange of solvent (from polymer solution) and non-solvent (from coagulation bath). Therefore, the solvent and non-solvent that will be used in this technique must be miscible. Second method is thermally induced phase separation. After demixing is made, the solvent is removed by extraction, evaporation or freeze drying. This is based on the fact that the solvent quality usually decreases when the temperature is decreased[35].

Next method Vapor-induced phase separation. The polymer solution is opened to an atmosphere containing a non-solvent (typically water); absorption of non-solvent causes demixing/precipitation. Among these techniques, thermally induced phase separation and immersion precipitation are the most commonly used method in the fabrication of polymeric membranes with different morphologies[35].

2.4.2 Solution Casting Method

This method is normally used to prepare small samples of membrane for laboratory experiment scale. The prepared solution containing polymer, inorganic filter and solvent is spread on a flat glass plate with a casting knife. The casting knife comprises of a steel blade, resting on two runners, arranged to form a precise gap between the blade and the plate onto which the film is cast. After casting, the solution is left for solvent to evaporate and leave a thin, uniform membrane film[34]. The membrane solution used for solution casting should be viscous enough to avoid it from running over the casting plate, therefore typical polymer concentrations are in the range 15–20 wt.%.

The advantages of this method are the simplicity in operation, low cost and obtain the final membrane in crystalline and isotopic form[19]. In the other hand, the problem that might occur is void creation between polymer and inorganic filter. Mahajan et al.[20] tried to solve this problem by developed the membrane in two steps under high temperature. Other studies also has been done for making casting solution of MMM by adding inorganic filter in the solvent first to get a slurry and homogenous solution and then a polymer was mixed into this solution[20, 22].

2.5 MEMBRANE CHARACTERIZATION

Since the vital aim of the research is to give a rational guideline for membrane manufacture condition to achieved the desired membrane morphology. Therefore, membrane characterization is one of the essential components of membrane research. It is the tool to determine the desired properties of membrane in structural level.

2.5.1 Membrane Morphology

Several devices were used to characterize the morphology of the composite membrane but the commonly use are field emission scanning electron microscope (FESEM). FESEM produces an image by using a microscope that uses electrons instead of light[36].

Kwak et. al [37] used FESEM to study the surface morphology of TiO2 Nanoparticle on Polyimide based membrane. He mentioned that the morphology image from FESEM showed the well adsorbed of TiO2 nanoparticles on the surface of Polyimide based membrane.

From the literature, a good mixed matrix membrane should have the inorganic filters that disperse though out the based polymer and should have no defect such as void near the filter or the poor interaction between the polymer and inorganic filter.

2.5.2 Glass transition temperature

Glass transition temperature is defined as a point of temperature which the increase in thermal energy is adequate to overcome the steric prevention restricting rotation of polymer backbone segments and at this temperature, the glassy polymer changes to a rubbery polymer [34]. The glass transition temperature indicates a qualitative measure of the flexibility of polymers. It is a useful tool for comparisons of the polymer chain rigidity of mixed matrix membranes and pure polymeric membrane[38]

In membrane, Differential Scanning Calorimetry (DSC) is used to find the glass transition temperature[39]. Ozturk and Demirciyeva[33] determined the Glass transition temperature of their membrane (PI or PEI with zeolite)using DSC. The result showed that zeolite loadings (10–30 wt. %) increased the Tg values of PI and PEI about 1.2 K. The change in Tg might be because the hydrogen bond between the polymer and zeolite which restrict the movement of the polymer chain and therefore increase glass transition temperature.

Another study also determined glass transition temperature using DSC. The result showed that the glass transition temperature of the matrix polymers increased with the incorporation of the CMS particles[38].

Sen [40] also mentioned in his research study that the analysis result from DSC showed the increase in the glass transition temperatures, Tg, due to the incorporation of zeolite 4A particles into the polycarbonate(PC) based mixed matrix membrane. Bakhtiari et. al[41] also found that the addition of zeolite 4A in Matrimid polymeric membranes increases the gas transition of Matrimid based membrane.

2.4.1 Thermal stability of membrane

There are many types of thermal analysis techniques. Thermogravimetric analysis (TGA) is one of the common thermal analysis techniques that is used to characterize a wide variety of materials. The TGA is used to measure the mass loss of a polymer as a function of temperature to determine the thermal stability of membrane.

Lai et. al [42] tested their membrane which was the combination of poly(vinylidene fluoride) and nanoclay nanocomposite samples using TGA and They mentioned that all the membrane showed a two-step mass loss or thermal decomposition and the first temperature that the first stage of decomposition took place decrease as the nano-clay loading increases. The result was explained by Li and Kim [43] that the weakening in thermal stability in PVDF/modified clay nanocomposite membranes occurs due to they have lower activation energy compared to pure PVDF membrane.

In another study which was done by Bakhtiari et. al [41], he found that the mass lose in Matrimid 5218 - zeolite 4A MMM was lower than the one found in pure Matrimid polymeric membranes which indicated that the addition of zeolite 4A in Matrimid polymeric membranes can increase the thermal stability of Matrimid based membrane.

From the literature, it can be concluded that if the membrane has high thermal stability, it should has low mass lose or no any mass lose during the testing.

2.6 Transport mechanism in membrane

2.6.1 The transport mechanism in dense membrane

In gas separation application, most of the research focuses on the dense membrane using glassy polymer as material because it has capability to control the permeation of different gas components. In dens membrane, solution-diffusion is the mechanism that transports the selective gas. The mechanism can be explained in three step. First, the gas molecules are adsorbed into the surface of membrane in the feed side and then diffuses across the membrane, and finally desorbed in the permeate phase of the membrane as shows in Figure2-4.

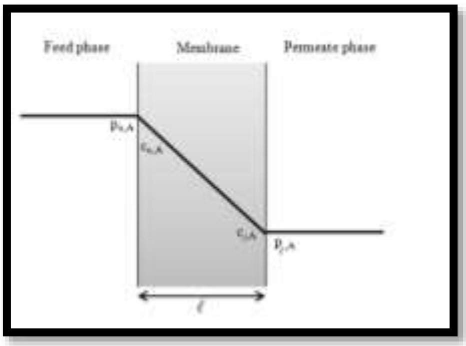


Figure 2-4: Solution diffusion mechanism

2.6.2 The transport mechanism in Porous membrane

The separation mechanism in porous membranes can be summarized as below;

- If the membranes have relatively large pore size, in the range between 0.1-10 μm, gas molecules will collide absolutely with other molecules and go through the membrane by convective flow and no separation occur.
- If the pores are smaller than 0.1 μm, the pore size is similar or smaller than the mean free path of the gas molecules. Therefore, the gas molecules are transported via Knudsen flow. For this type of flow, the ideal separation factor for binary gas mixtures can be determined from the square root of the proportion of the molecular weights.
- If the membrane has very small pores around 5-20 Å, then gases are separated via molecular sieving mechanism which the gas that want to be separated must has smaller size than pore size.

The transportation through porous membrane includes both diffusion in the gas phase and diffusion of adsorbed component on the pore surface (surface diffusion) as shows in Figure 2-5

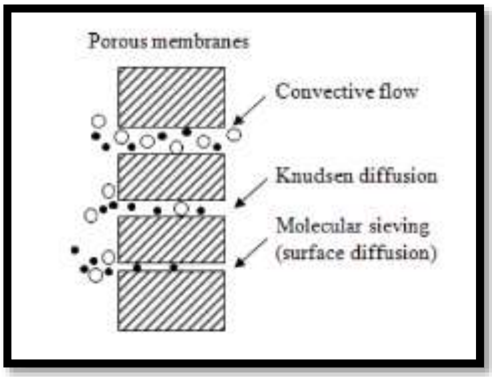


Figure 2-5: Transport mechanism in porous membrane

2.7 Gas separation performance

There are many factors that contribute to the successful fabrication of a high-performance membrane module[34]. One of important factor is membrane materials should have good chemical and mechanical properties. In another hand, permeation properties are very crucial to ensure that the membrane can separate gas mixture efficiently.

Gas separation in membranes is driven by applying a pressure difference across the membrane. In order to obtain a desired pure stream of CO_2, the selectivity for CO_2 must be high. Moreover, to attain the compact membrane unit, a high permeability is also required[44].

In gas separation, the separation properties can be measured by applied a gas mixture at a pressure P_O to the feed side of the membrane, the permeate gas (the gas that can pass through membrane) will be removed from the downstream side at pressure P_L[45]. The flux of component A through the gas separation membrane is given by:

$$\boxed{J_A = \frac{P_A}{l_M}(p_{AO} - p_{AL})} \qquad 2\text{-}1$$

$P_A = K_A D_A$, gas-phase permeability coefficient
p_{AO} =Partial vapour pressure of A on the feed side
p_{AL} = Partial vapour pressure of A on the permeate side
l_M= The membrane thickness

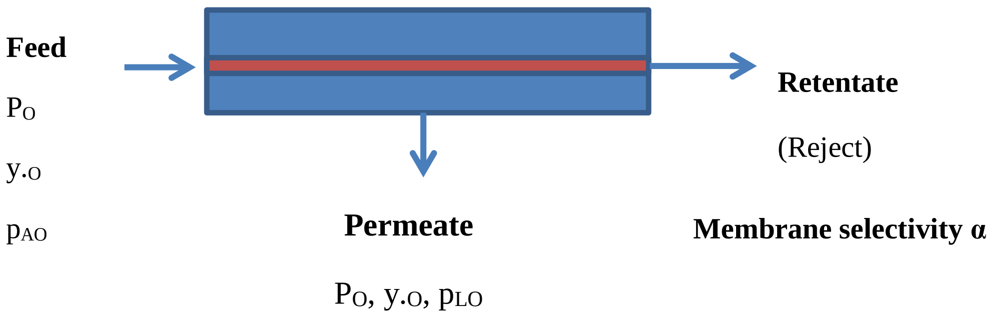


Figure 2-6: Membrane gas separation factors

The membrane permeability is defined as the transport flux per unit transport membrane per unit membrane thickness. It is a function of the solubility (K) and diffusivity of the compound in the membrane material (D) as shown in equation 2. The membrane selectivity is referred as a measure of the ability of the membrane to separate two different gases A and B. It can be calculated by divide the permeability value of gas A over permeability value of gas B and expressed as a separation factor (∝). Permeability is reported in units of Barrer (1 Barrer = 1×10-10 cm3·(STP) ·cm/(cm2·sec·cmHg)).[39].

$$\boxed{\text{Permeability } (P_A) = \text{Solubility } (K_A) \text{x Diffusivity} (D_A)} \quad \ldots\ldots 2\text{-}2$$

$$\boxed{\propto_{AB} = \frac{P_A}{P_B}} \quad \ldots.\ 2\text{-}3$$

Where;

$\propto_{AB}$ is selectivity of gas A form gas B

P_A, P_B are the permeability of gas A and gas B respectively.

CHAPTER 3

MATERIAL AND METHOD

In this project, the effect of zeolite 4A loading on PEI-Zeolite 4A mixed matrix membrane was studied. The material selection was discussed in Section 3.1. The project methodology and mixed matrix membrane preparation method were discussed in Section 3.2. The characterization of PEI-Zeolite 4A mixed matrix membrane and evaluation of gas separation performance at different pressure were presented were discussed in Section 3.5-3.6. Lastly, the project activity, project key milestones and Gantt chart were shown in Section 3.7-3.9.

3.1 MATERIAL SELECTION

The proper material selection for matrix and inorganic phase is very important. This is because the polymer and inorganic phase properties can affect the membrane morphology.

3.1.1 Polyetherimide (PEI)

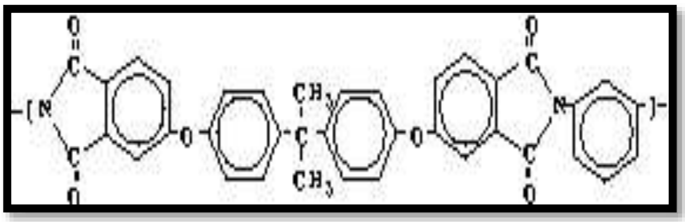


Figure 3-1: Molecule structure of Polyetherimide

Figure3-1 shows the molecule structure of Polyetherimide. PEIs are an amorphous glassy polymer [46]. PEIs are selected for membrane fabrication due to it has relatively high CO_2/CH_4 selectivity with high chemical and thermal stability and the potential to prepare asymmetric fibers as high flux membranes [32]. The properties and quality of PEI that used in this study are shown in Table 3-1.

Table 3-1: Properties of PEI

Properties	**Detail**
Supplier	Sigma Aldrich
Type of polymer	Amorphous glassy polymer
Molecular formula	$C_{37}H_{24}O_6N_2$
Molecular weight of repeat unit	592.61 g/mol.
Glass transition temperature, Tg	216°C.
Amorphous density at 25°C	1.27 g/cm^3.
Shape	Pellet
Color	Gold

3.1.2 Zeolite 4A

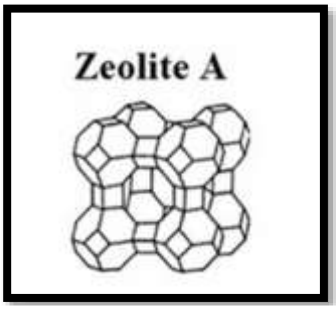


Figure 3-2: Molecule structure of Zeolite 4A

Zeolite 4A was used as filter in mixed matrix membrane. The properties and quality of zeolite 4A used in this study are shown in Table 3-2.

Table 3-2: Properties of Zeolite 4A

Properties	**Detail**
Supplier	Sigma Aldrich
Molecular formula	$Na_{12}[AlO_2.SiO_2]_{12}.27H_2O$ [47].

Molecular weight of repeat unit	592.61 g/mol.
effective aperture size	4 $^{\circ}A$
Amorphous density at 25^{o}C	720. 83 kg / m^3
Particle size	8-12 mesh (2380-1680 micron).
Moisture content	1.5 wt.%
Shape	Bead
Color	White

Zeolite are crystalline, hydrated alumino-silicates of group I and II elements, in particular, sodium, potassium, magnesium, calcium, barium and strontium. One study stated that structurally, zeolites are framework alumino-silicate which are based on infinitely extending three dimensional AlO_4 and SiO_4 tetrahedral linked to each other by sharing all the oxygen[47].

Zeolites 4A are chosen for mixed matrix membrane fabrication as the filter because their properties that have open crystal structure and relatively small pores size could induce a resistant to the diffusion of the gas penetrant through the zeolite pore. Moreover, due to its small pore size, zeolite can separate gas penetrant on the basis of the differences in molecular size and shape.[16]. Zeolite 4A with an effective aperture size of 3.8-4 ˚A should be able to distinguish the two molecules due to entropic factors. Therefore, the molecular sieving phase must accurately correspond to the size and shape differences of the gas molecules [4]. The diameter of gas molecules used in this study is in the range 3.3Å for CO_2 and 3.8 Å for CH_4, therefore gas molecules can be easily transported through zeolite and it is expected that CO_2 with smaller size than zeolite 4A should be passed through pores of zeolite 4A while CH_4 does not do so.

Zeolites 4A has been proved to be an effective inorganic filter that can increase the performance of gas separation. Kusworo et al. [16] developed the mixed matrix membrane using zeolite 4A on polyimide-polyethersulfone (PI/PES) based polymer. His study shown that the PI/PES-zeolite 4A mixed matrix membrane with 25 wt. % zeolite loading showed the best performance for O_2 /N_2 and CO_2/CH_4 gas separation. Ahmad and Hagg[48]also fabricated mixed matrix membrane using Zeolite 4A as the filter and used Poly vinyl acetate (PVAc) as based polymer. His result corresponded to the study of Korworo that the addition of zeolite 4A up to 25wt. % increased the selectivity of gas separation. Moreover, Rezakazemi who fubricated mixed matrix membrane using Zeolite 4A on Polydimethylsiloxane (PDMS*)* based polymer also supported that zeolite 4A can significantly improve the separation properties of membrane.

3.1.3 N-Methylpyrrolidone (NMP)

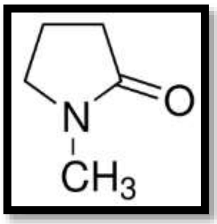


Figure 3-3: Functional group of NMP

NMP is the lactam of 4-methylaminobutyric acid and a very weak base. It is a clear to slightly yellow liquid miscible with water and solvents like ethyl acetate, chloroform, benzene and lower alcohols or ketones. It is one of dipolar aprotic solvents which include dimethylformamide, dimethylacetamide and dimethyl sulfoxide. These characteristics are highly useful in a variety of chemical reactions where an inert medium is of concern [22].

NMP is chosen to use as a solvent in membrane formation because it is a chemically stable and powerful polar solvent[19] which has a lower volatility than most of the solvents used in membrane formation[5]. In fact, it can replace hazardous solvents because of its low toxicity. The properties and quality of NMP that used in this study are shown in Table 3-3. [19].

Table 3-3: Properties of NMP

Properties	Detail
Supplier	Sigma Aldrich
Grade	anhydrous grade with 99.5% pure
MW [g mole–1]	99.13
Density [g cm–3]	1.028
B. P. [°C]	202
V. P. [kPa]	0
pH	7.7-8
Solubility in water	soluble

NMP is a most suitable solvent for Polyetherimide(PEI) since it has been used as the solvent for membrane fabrication using Polyetherimide in many research studies such as in the study of Saleh and Ismail [9] to produce Polyetherimide/ polyvinylpyrrolidone-based carbon hollow fiber membrane, the study of Simon[32] for film preparation of ODPA-based Polyetherimide polymer and the work of Bakeri [12] For fabrication of Polyetherimide hollow fiber membrane for gas–liquid contacting processes.

3.2 PROJECT METHODOLOGY

3.2.1 Project flow chart

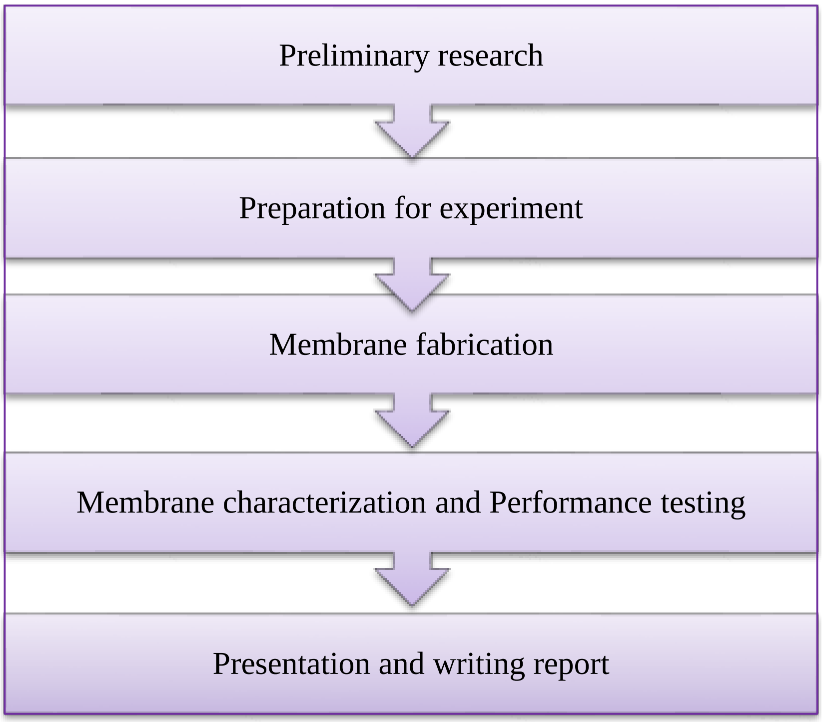


Figure 3-4: Project Flowchart

3.2.2 Project Design

The experimental work involved in this study is shown in a flowchart as shown in Figure 3-5.

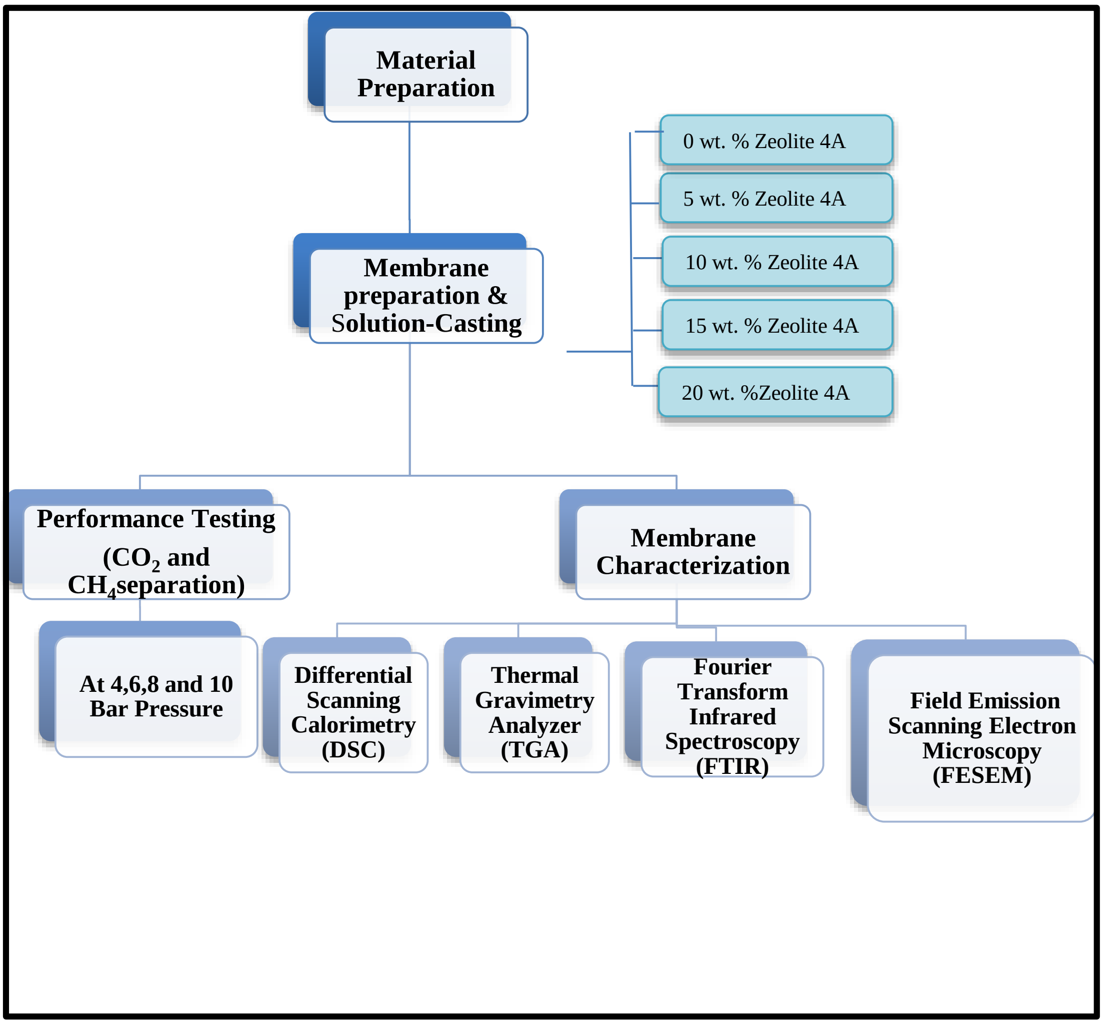


Figure 3-5: The experimental workflow of project

3.2.3 Composition of materials

There were 7 samples prepared and the compositions were listed as the following:

Table 3-3: Pure and MM M name code and composition

Membrane	Name code	NMP solvent(g)	PEI polymer(g)	Zeolite 4A powder(g)
Pure PEI-10%	PEI10	50	5	-
Pure PEI-15%	PEI15	50	7.5	-
Pure PEI-18%	PEI18	50	9	-
PEI-15%+zeolite-5%	MMM5	30	4.5	0.225
PEI-15%+zeolite-10%	MMM10	30	4.5	0.45
PEI-15%+zeolite-15%	MMM15	30	4.5	0.675
PEI-15%+zeolite-20%	MMM20	30	4.5	0.9

3.2.4 PREPARATION OF PURE PEI AND PEI-ZEOLITE 4A MIXED MATRIX MEMBRANE

a. **PEI polymeric membranes**

i. PEI was first dried in vacuum oven at 110 °C for overnight time to remove all moisture content.
ii. 30 g of NMP solvent was added in glass bottle.
iii. Weight amount of PEI pellet was gradually added in the prepared solvent.
iv. The prepared solution with PEI was stirred for 3 days.
v. Before casting, the solution was degas for 2 hours to remove air bubble that might occur during stirring.
vi. The solution was poured onto a flat and smooth glass plate and placed in casting machine to spread the solution to a uniform thickness by using a pneumatic force.
vii. The flat sheet membrane was pre- dried in an oven for 12 hours at 90 °C and continue dried at 160°C for 24 hours to remove the solvent[49].

b. Mixed matrix membranes

i. PEI and Zeolite were first dried in vacuum oven at 110 °C for overnight time to remove all moisture content.
ii. 30 g of NMP solvent was added in glass bottle.
iii. Weight amount of zeolite 4A particles were added in prepared solvent and
iv. The prepared solution with zeolite 4A was stirred for 1 days.
v. Before adding PEI, the solution was sonicated at 60 amplitude for 60 second.
vi. Weight amount of PEI pellet was gradually add in the prepare solvent.
vii. The prepared solution with PEI was stirred for 3 days.
viii. Before casting, the solution was degas for 2 hours to remove air bubble that might occur during stirring.
ix. The solution was poured onto a flat and smooth glass plate and placed in casting machine to spread the solution to a uniform thickness by using a pneumatic force.
x. The flat sheet membrane was pre- dried in an oven for 12 hours at 90 °C and continue dried at 160°C for 24 hours to remove the solvent[49].

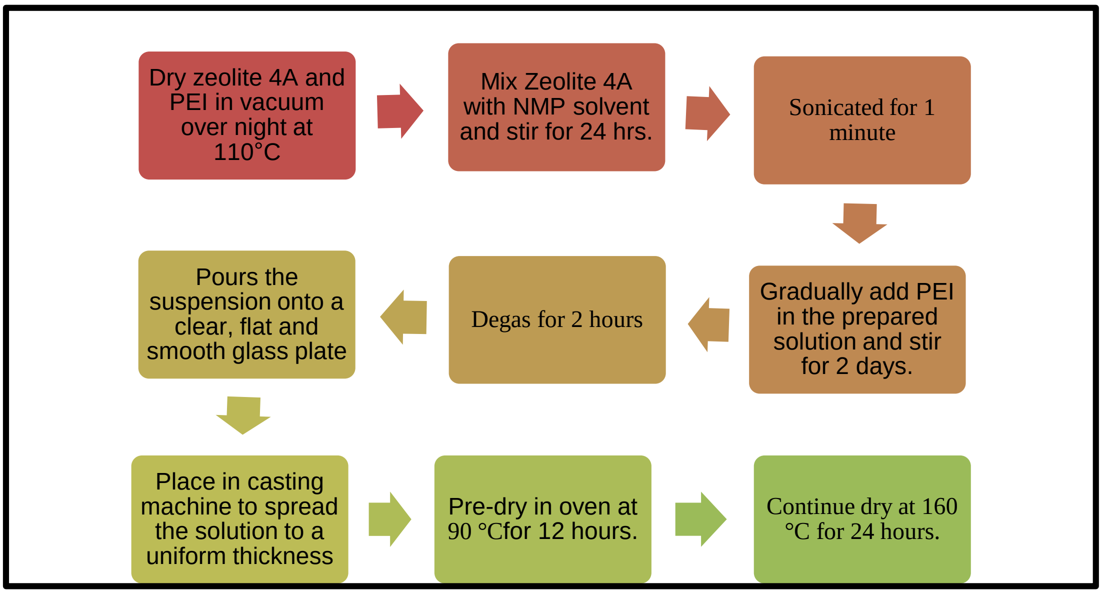


Figure 3-6: Steps in MMM membrane fabrication

In addition to standard lab apparatus (glassware, stirrer set, etc.), important equipment for the completion of the study includes oven, transonic digital, membrane fabrication unit and gas permeability unit as shows in the Table 3-3.

Table 3-4: Tools required

Device	Purpose
1. Oven	To dry the sample.
2. Stirrer	To mix the materials.
3. Transonic Digitals	To remove air bubbles that might be formed during mixing and stirring.
4. Membrane fabrication unit	To prepare the flat sheet membrane.
5. Gas permeability unit	To evaluate the performance in gas separation.

3.3 MEMBRANE CHARACTERIZATION

The fabricated mixed matrix membrane of PIE-Zeolite 4A and pure membrane were characterized using different types of analytical equipments. The objectives are summarized in the Table3-6.

Table 3-5: Membrane characterization and objective

Type of characterization	Objective
Membrane morphology- FESEM,	To study the physical properties by observing the morphology of the membranes[16].
Membrane Functional group- Fourier Transform Infrared Spectroscopy (FTIR)	To study the chemical properties by determining the composition and certain functional groups in membranes [16].
Membrane thermal stability- Thermal Gravimetric Analyzer (TGA)	To study thermal property by determining the weight change of the fabricated membrane with temperature change [16].
Membrane glass transition temperature- Differential scanning calorimetry (DSC)	To study the thermal property and flexibility of membranes by finding the glass transition temperature (Tg)[16].

3.3.1 Field Emission Scanning Electron Microscope (FESEM)

The fabricated membranes were characterized using Field Emission Scanning Electron Microscope (FESEM) to study the physical properties by observing the morphology of the membranes[16]. FESEM gives the surface and cross-section image, the thickness of the membrane, void existence, filler size, and defect on surfaces.

The samples were cut in dimension of 0.5-1cm width and 3-5cm length. Before analysed using FESEM, the membranes were prepared by immersing into the nitrogen gas liquid. Membrane cross-section was attached on the side of the sample holder using double-sided tape and labelled accordingly as three samples were attached at the same time. The shorter part of membrane was again cut into smaller size to fit the sample holder and attached on the top surface of the sample holder. Next, the sample holder was put into a coating machine and was gold-coated in an inert gas filler container. The membrane pieces were scanned for the morphology studies.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR test was required to study the chemical properties by determining the composition and certain functional groups that present in membranes [16]. The method used was KBr pellet method by preparing 13 mm-diameter pellets. Roughly 0.1 to 1.0 % sample was well mixed into 200 to 250 mg fine KBr powder and then finely pulverized and put into a pellet-forming die under pressurized pellet casing. For the prepared membrane, the results should produce the peak of related main functional group in PEI, NMP (if there is residue solvent) and zeolite 4A.

3.3.3 Thermogravimetric Analysis (TGA)

All fabricated membranes were analysed using TGA to study thermal property by determining the weight change of the fabricated membrane with temperature change [16]. Seven (7) samples were tested with the amount of membrane samples about 10-20 mg each. The heating temperature range was 30°C to 800°C with 10°C/minute and nitrogen gas purge.

3.3.4 Differential scanning calorimetry (DSC)

DSC analysis were conducted to study the thermal property and flexibility of membranes by finding the glass transition temperature (Tg)[16]. The procedure are follow Vu et al.[38] by heating the sample from 50 ◦C to about 50 ◦C above the normal glass transition temperature of the pure polymer at a rate of 20 ◦C/min in two cycle. The first cycle is aimed to remove thermal history and the glass transition temperature of the sample was determined in the second heat cycle.

3.4 MEMBRANE PERFORMANCE TESTING

3.4.1 Testing procedures

The fabricated mixed matrix membrane and pure membrane are tested by using the gas permeability testing unit as shown in Figure 3-8 to evaluate the performance in gas separation by using pure CO_2 and CH_4 and test at vary pressure in the rage of 4-10 Bar.

a) The fabricated membrane was cut into round shapes around 5.7 diameter, placed into gas permeability unit (shown by red arrow in Figure 3-9).
b) The fabricated membrane was closed with screws to make sure that no gas leak around the membrane.
c) The testing started by opening the inlet gas as shows in Figure 3-10. Then turn the gas selection valve to the desired gas.
d) After that turn on the open gas valve. The feed gas will pass from top to the surface of the membrane.

e) The flow of gas can be measured by recording time that the bubble flow at constant volume which shows in Figure 3-8.

In this project, the 5 flat sheet membranes were fed with CH_4 and CO_2 each at 4, 6, 8 and 10 bar pressure. For each type of gas, pressure and sample used, the permeation was left for 10 minutes for conditioning the flow. The readings were taken about 5 times and calculated for average. The testing equipment was also represented by the schematic diagram in Figure 3-7 for better understanding.

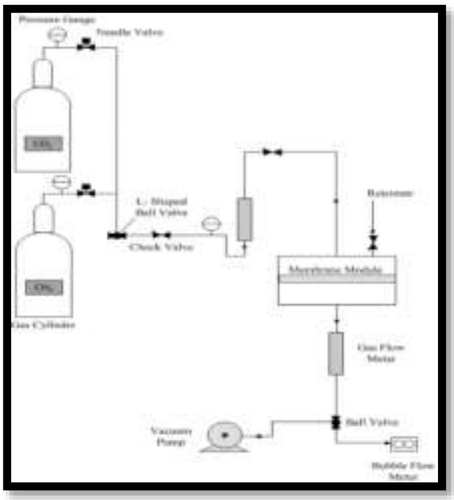


Figure 3-7 Diagram of Gas Permeability Testing unit

Figure 3-8: Back Side of Gas permeability Testing Unit (Bubble flow measurement)

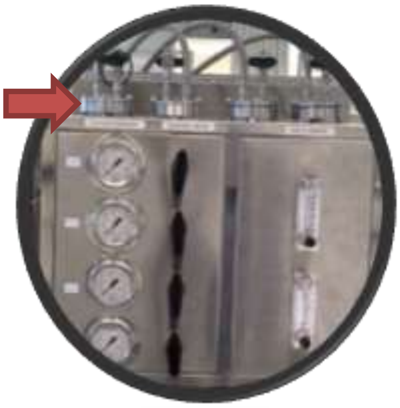


Figure 3-9: Front side of gas permeability Testing Unit

Figure 3-10: Gas permeability Unit at Block 3, UTP

3.7.2 Permeability result analysis

Due to the limitation of equipment, it is very difficult the get the actual uniform thickness of membrane. Therefore, gas permeance with GPU unit is calculated to measure the permeability of gas across membrane. Permeance is the permeability over the thickness.The permeance of gases were calculated using Fick's Law. Permeation rate was plotted again feed pressure. The selectivity was obtained by dividing the permeability of CO_2 gas over permeability of CH_4 gas. The plot of selectivity also done again feed pressure. The detail calculation is attached in appendix

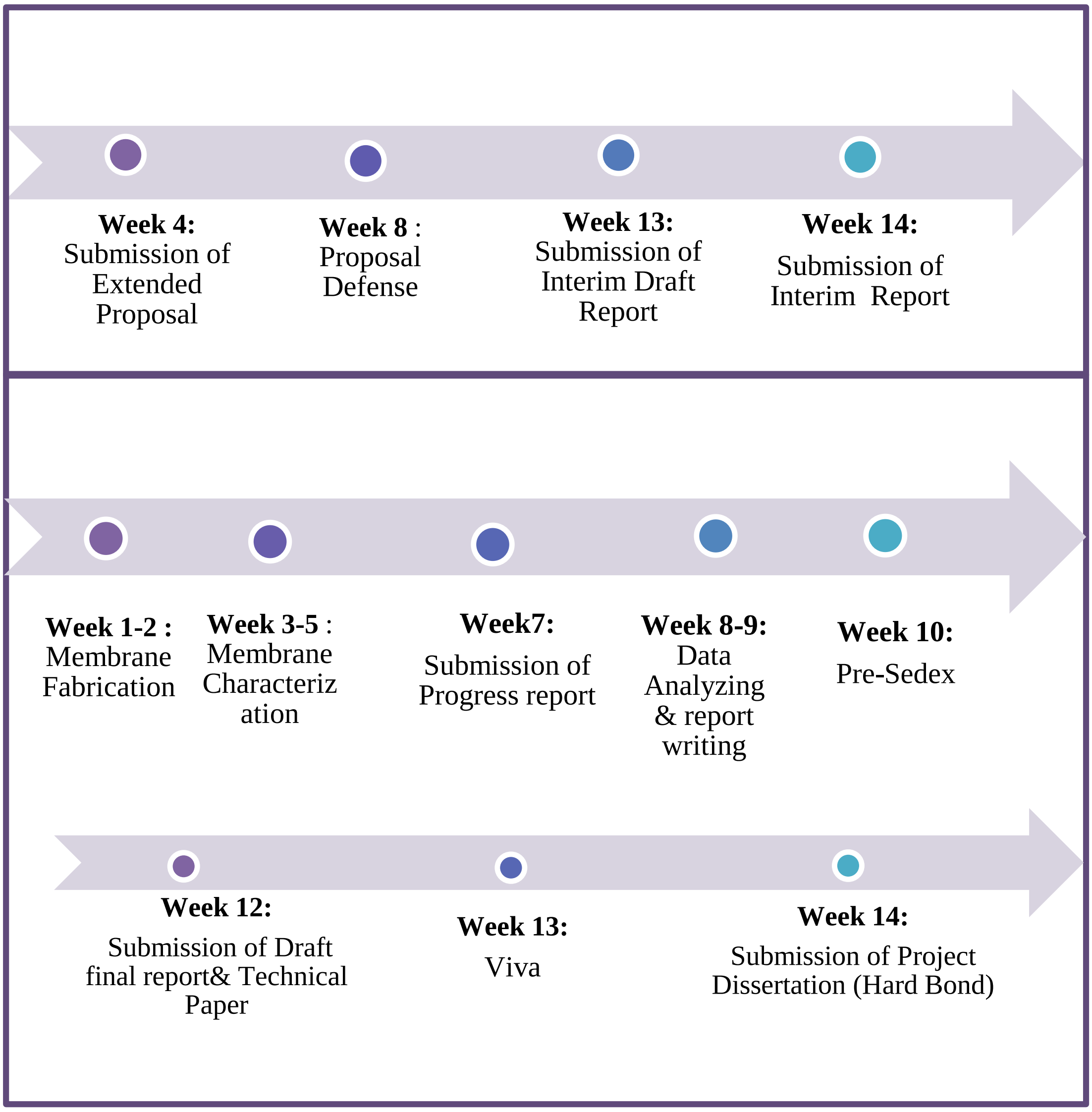
3.8 PROJECT ACTIVITIES

Table 3-6: Project Activities for FYP2

Task	Week	Action
Fabrication of pure membrane	1-2	Fabricate the pure membrane and identify the suitable concentration of polymer for MMM fabrication.
Fabrication of MMM	3-4	Fabrication of MMM with different filter loading.
Membrane Characterization	5-6	Characterized the fabricated membrane using TGA, DSC, FESEM and FTIR
Performance testing	7	Test the membrane using gas permeability testing to see the performance in gas separation.
Progress report submission	8	Analyzing the result and prepare the progress report.
Data analyzing and preparation of dissertation	9	Future analyze the result and prepare for dissertation
Checking the material and equipments	9	Contact the person in charge for the lab to check all material and equipments that need to be used for experiment.
Pre-sedex	10	Prepare the presentation slide and present during pre-sedex.
Preparation of Technical paper	11	Prepare the technical paper

Submission of Draft final report& Technical Paper	12	Submit the draft final report and technical paper
Viva and Submission of Project Dissertation (Hard Bond)	13-14	Prepare for viva and submit the Dissertation

3.9 PROJECT KEY MILESTONES



3.10 GANTT CHART

Table 3-8 and 3-9 below shows the planning for this project in Gantt chart form.

Table 3-7: Gantt chart for the project for FYP1

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Confirmation of Project Topic and Supervisor	■	■												
2	Preliminary Research work		■	■	■	■									
3	Submission of Extended Proposal						■								
4	Proposal Defense								■						
5	Project work continue									■	■	■	■		
6	Submission of Interim Draft report													■	
7	Submission of Interim report														■

Table 3-8: Gantt chart for the project for FYP2

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project work continues	■	■	■	■	■	■	■							
2	Submission of Progress Report								■						
3	Project Work Continue									■	■	■	■		
4	Pre-Sedex										■				
5	Submission of Draft final report											■			
6	Submission of dissertation(Soft bound)												■		
7	Submission of Technical Paper												■		
8	Viva													■	
9	Submission of Project Dissertation (Hard Bond)														■

CHAPTER 4

RESULT AND DISCUSSION

In this study, mixed matrix membranes were fabricated using polyetherimide (PEI) and zeolite 4A particles as the filler. The physical characterization of zeolite 4A particles are discussed in section 4.1. The fabricated pure membranes and MMMs are shown in section 4.2. The membrane characterization are discussed in Section 4.3, whereas the separation performance of each membrane were discussed in 4.4.

4.1 CHARACTERIZATION OF ZEOLITE 4A

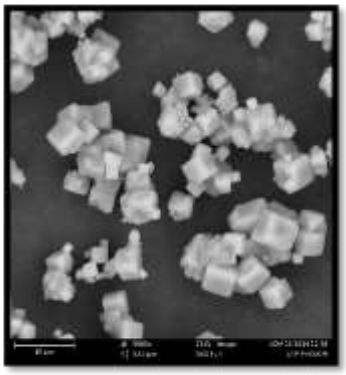


Figure 4-1: Scan Electron Microscopy (FESEM) image of Zeolite 4A powder (5000X)

Figure 4-1 shows the Field Electron Scan Electron Microscopy (FESEM) image of zeolite 4A power. The micrograph confirmed that zeolite 4A power has a different particle size distribution in the rage of 1.7-3.0 µm. All particles show white color. Most of particles have cube shape. Non-uniform shape of some particles was due to the grinding process and agglomeration of zeolite 4A particles were also observed.

4.2 FABRICATION OF MEMBRANES

The first objective of this project is to fabricate the mixed matrix membrane with the combination of Polyetherimide (PEI) and zeolite 4A. Three (3) pure Polyetherimide membranes with the polymer concentration of 18, 15 and 10 wt. % and four (4) mixed matrix membranes with different of zeolite loading of 5, 10, 15 and 20 wt. % of polymer based.

4.2.1 Pure PEI membrane

In order to choose the suitable concentration of polymer for subsequent fabrication process, 5 solution with pure polymer concentrations of 10, 15, 18, 20 and 25 wt. % were prepared. However, the polymer solution with 20 and 25wt. % could not proceed with the fabrication step due to polymer beads saturated and could not dissolve all in NMP solvent at room temperature. The duration that pure PEI with the concentration of 10, 15 and 18 wt. % were dissolved in NMP solvent at room temperature were 2, 3 and 4 days respectively. The fabricated membranes are shown in the picture below. From the fabricated membrane on white paper support as shows in Figure 4-2, pure PEI with 15% shows the best homogeneous thickness throughout the membrane while the PEI with 10 and 18% shows non-smooth surface with different thickness.

The thermal stability result from TGA analysis of pure membrane which will be explained more details in Section 4.2 shows similar result for all three pure membranes. However, when these three membranes were tested for gas separation performance using gas permeation testing unit, both PEI with 10 and 18% were cracked and unable to be tested for the performance which indicate low mechanical properties. Therefore, 15% concentration of PEI were selected as the polymer based for mixed matric membrane

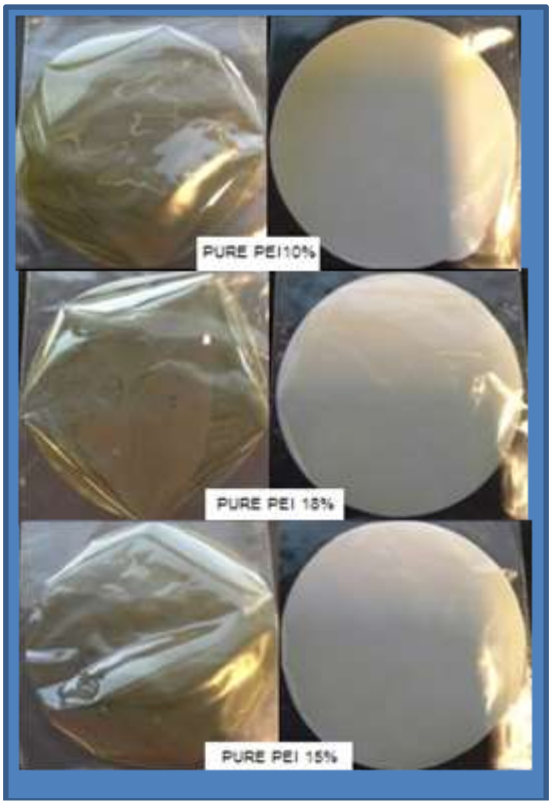


Figure 4-2: Fabricated Pure PEI membranes

4.1.2 Mixed Matrix membrane

Four (4) mixed matrix membranes were fabricated using constant 15% concentration of PEI and different loading of zeolite 4A with 5, 10, 15 and 20wt. %. The result mixed matrix membranes are shown in Figure 4-3 below.

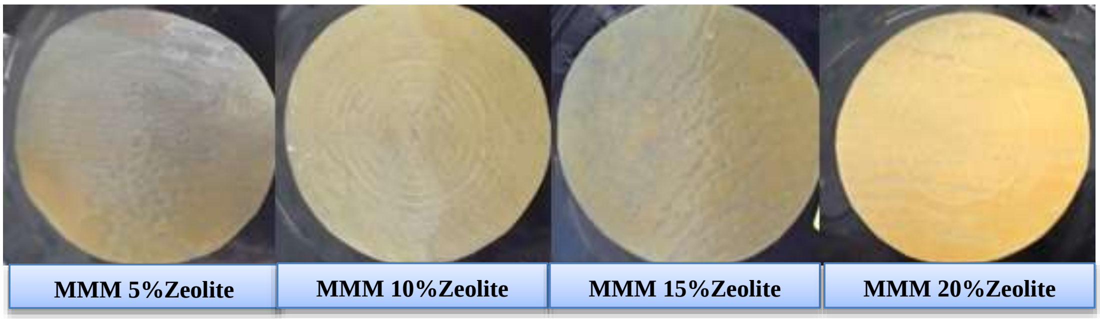


Figure 4-3: The fabricated mixed matrix membranes

The mixed matrix membranes were fabricated successfully with non-cracked. The yellow color of membranes are darker as the zeolite4A loading increase. All fabricated mixed matrix membranes show non-smooth surface at the top and smooth surface at the bottom.

4.2 MEMBRANE CHARACTERIZATION

4.2.1 Field Emission Scanning Electron Microscopy (FESEM)

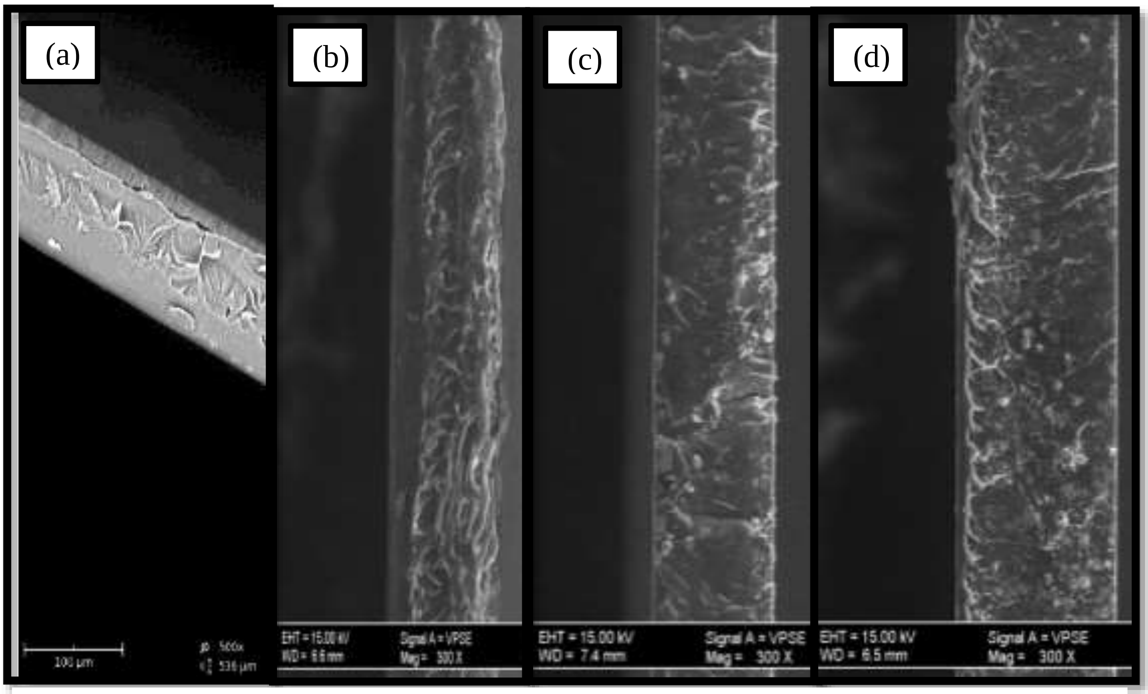


Figure 4-4: Cross-sectional image of (a) pure PEI membrane at 500x , (b)MMM5, (c) MMM15 and (d) MMM 20 at 300 x

Figure 4-4(a-d) show FESME micrographs of pure PEI , MMM5, MMM15 and MMM15 membranes. Pure PEI membrane (Figure 4-4 (a)) is dense membrane in structure. With addition of zeolite 4A in MMM (Figure 4-4(b-d)), the membrane morphology structure remain dense type but less compact area.

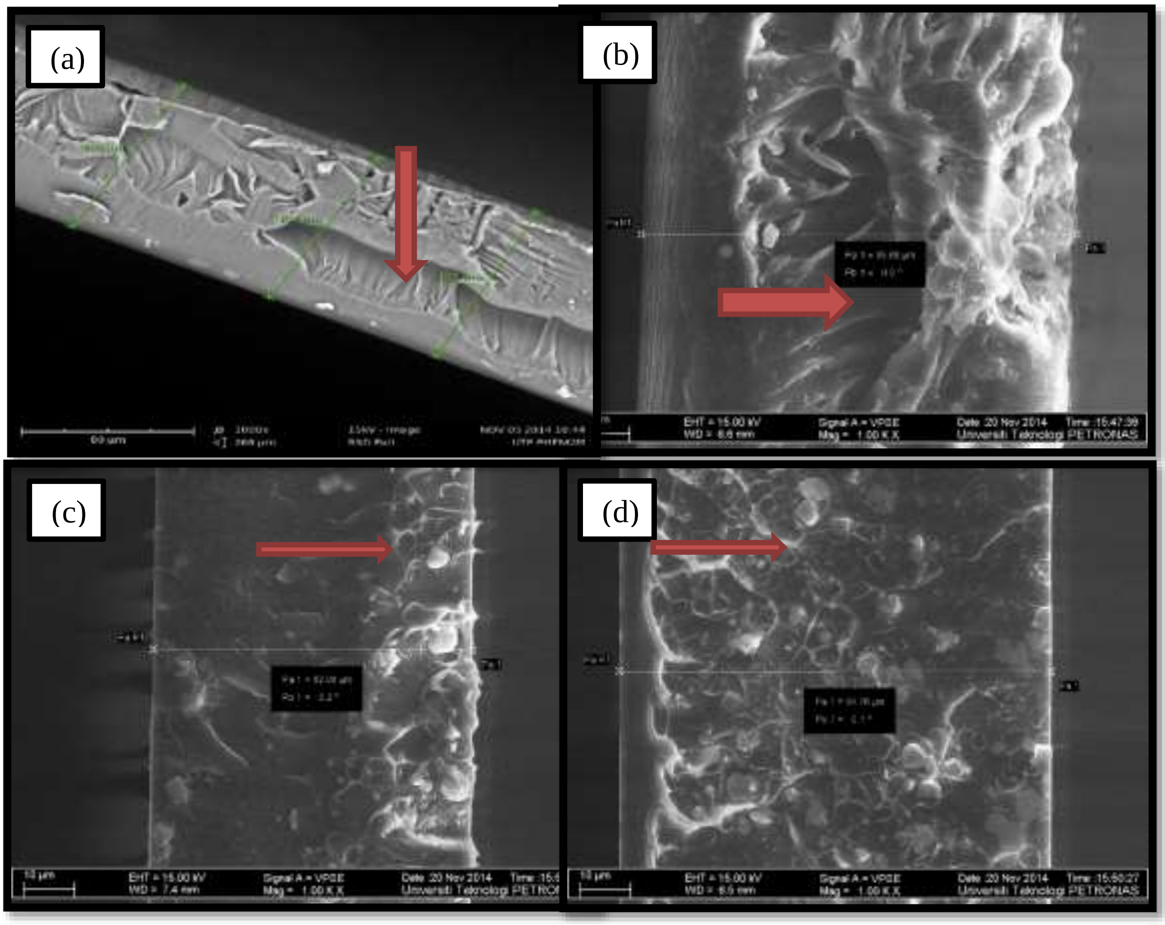


Figure 4-5: Cross-sectional image of (a) pure PEI membrane, (b)MMM5, (c) MMM15 and (d) MMM 20 at 1000 x

FESEM image at 1000x show give the actual thickness of fabricated membranes. Pure PEI membrane has an average thickness of 107 µm while MMM5, MMM15 and MMM20 show the thickness of 86, 63 and 84 µm respectively.

From Figure 4-5(a), pure PEI membrane has a big void inside structure as shows in red arrow and the void seemed to be smaller as the zeolite loading increase. Moreover, it can be obviously seen that there is a significant difference between the structures of pure PEI membrane and mixed matrix membrane. The zeolite particles fill in large voids in pure membrane. The dispersion of these particles improve the permeability for both gas which will be explained more in Section 4.3. These are two possible reason for the void occurrence in this study. The air bubbles which might create during stirring process cause the void structure inside the membrane. Another reason might due to the drying process, if the solvent leave the membrane very fast, voids will occur.

Therefore, in order to prevent from voids structure, air bubble should be eliminated by sufficient degas time and the proper drying rate should be considered.

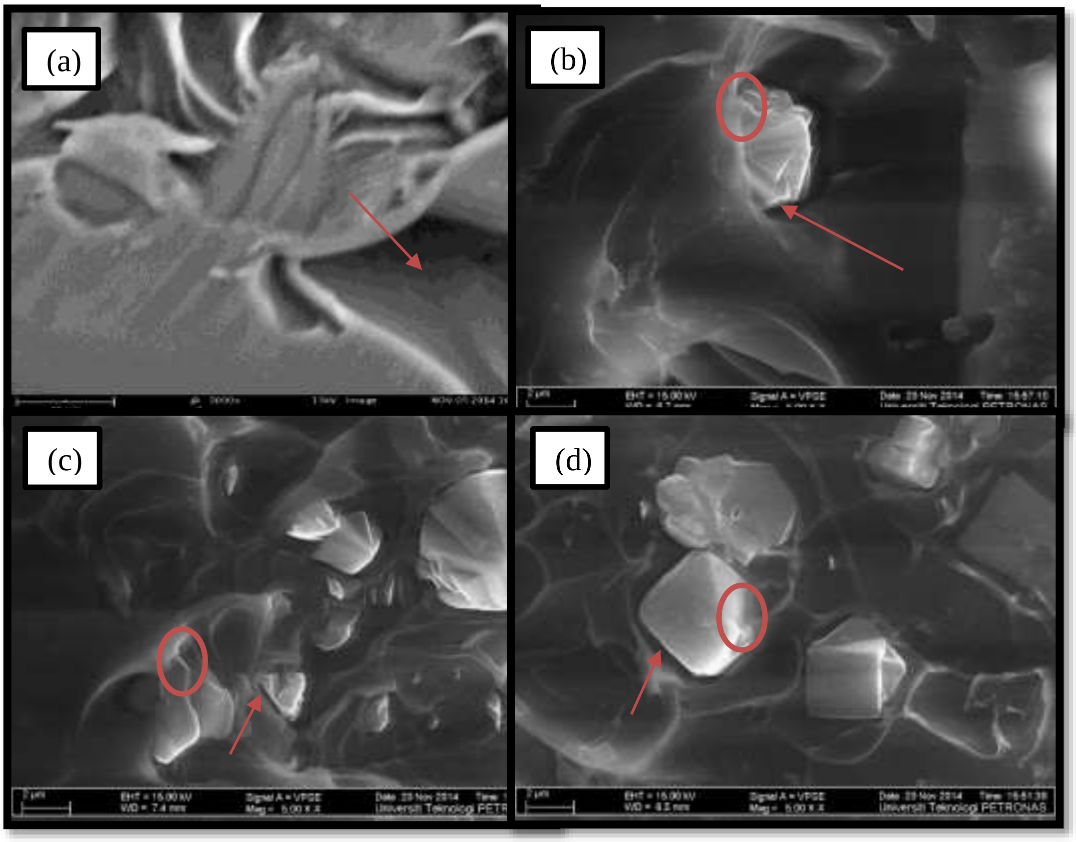


Figure 4-6: Cross-sectional image of (a) pure PEI membrane , (b)MMM5, (c) MMM15 and (d) MMM 20 at 5000 x

Figure 4-6(a-d) show the membranes morphology in very small scale up to 5000x. One of the common problems in MMM fabrication is the void between polymer based and inorganic filter. In this study, this problem was observed. The red arrow in Figure4-6 shows voids between polymer and zeolite particles indicate less interaction between these two materials which is common occurrence in glassy membrane. However, in some point, that the zeolite particles also have physical attachment with PEI based which shows in Figure 4-6 by red circle.

When compared to the most recent experimental research of these MMM for gas seperation by Ozturk and Demirciyeva [33], the morphology of PEI-Zeolite 4A MMM was also dense structure with some agglomeration of zeolite particles. However, the agglomeration and void appeared in this study are lesser compared to their study.

4.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

From literature, the structure of Polyetherimide as followed:

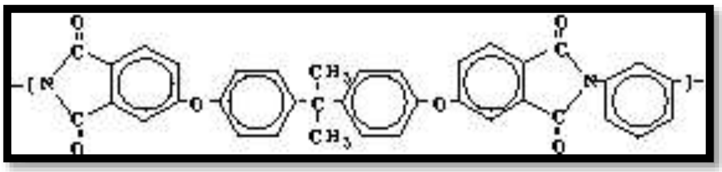


Figure 4-7: Polyetherimide molecule structure

The chemical structure of repeating PEI monomer was illustrated in Figure 4-7 and FTIR test is required to determine the functional groups that present in the membrane. FTIR results for pure PEI membranes are shown in Figure 4-8.

Basically, there are five (6) main functional groups in PEI; benzene, aldehyde, ketone, amine, amide and ether group.

First, the benzene group which is dominant in PEI structure shows C-H bond at 3000-3100 $\mathrm{cm}^{-1}$and the C=C bond at 1465, 1465 and 1473 $\mathrm{cm}^{-1}$for PEI10, 15 and 18wt. % respectively. For aldehydes and ketones, FTIR results for pure PEI shows these functional group at 1714, 1716 and 1712 $\mathrm{cm}^{-1}$for PEI10, 15 and 18wt/% respectively.

For amine group, the most characteristic band is due to the N-H bond stretch. For PEI, this bond appear at 3484, 3484 and 3484 $\mathrm{cm}^{-1}$for PEI10, 15 and 18wt/% respectively. For amide functional group, it combines the characteristic of amines and ketones due to it consists of both the N-H bond and the C=O bond. Therefore amides show a very strong, at broad band around the left end of the spectrum, in the range between 3100 and 3500 $\mathrm{cm}^{-1}$for the N-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around 1710 $\mathrm{cm}^{-1}$for the C=O stretch.

Lastly, the ether group spectrum of PEI10, 15 and 18% are shown at 1077, 1077 and 1712 cm^{-1} respectively.

From the FTIR spectra of pure PEI, it can be seen clearly that PEI consists of all functional groups stated in literature. Moreover, the result shows that all pure membrane samples with different concentration of PEI showed a similar peak, only differ on its intensity which confirmed that all sample went through a similar process.

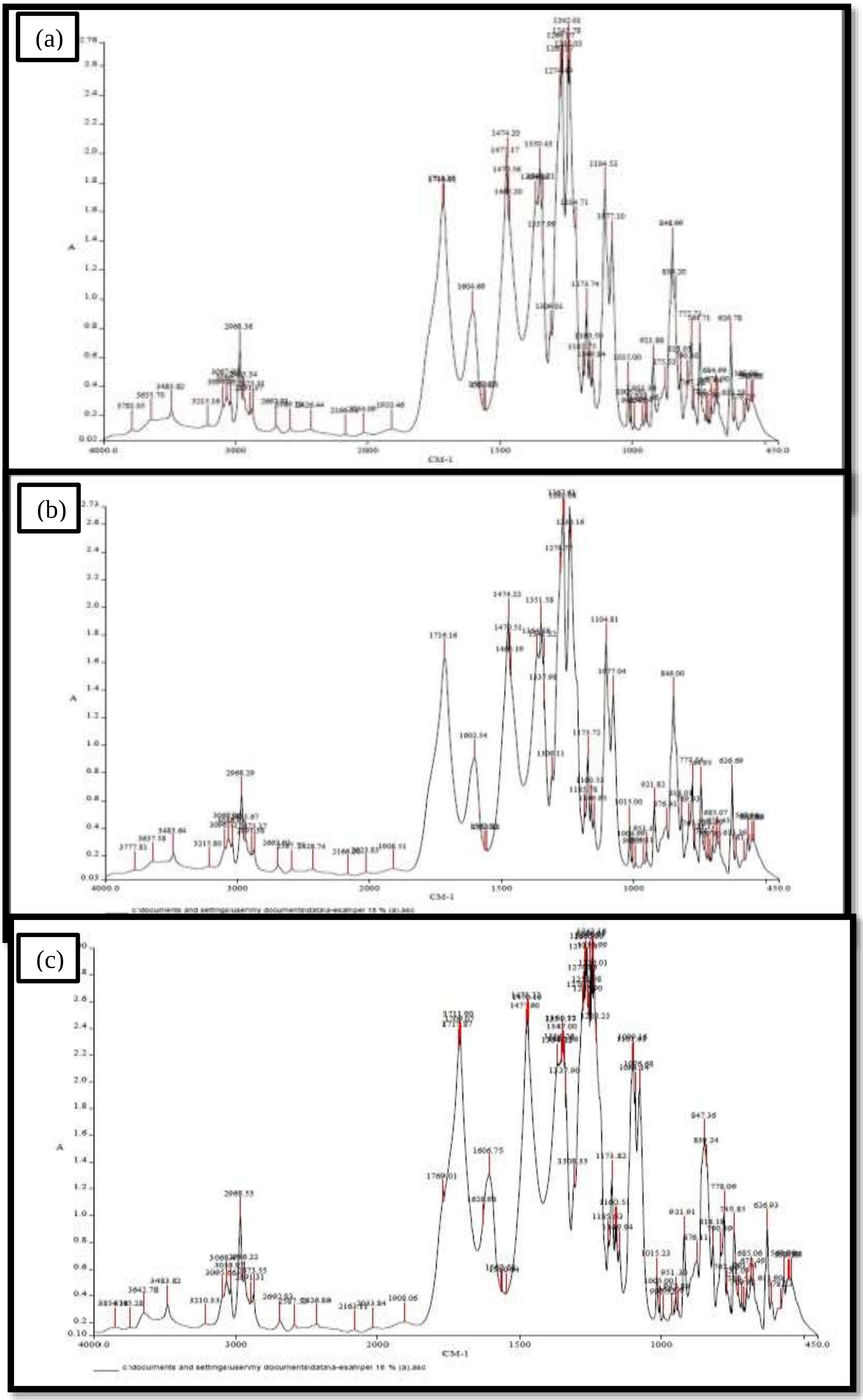


Figure 4-8: FTIR spectrum of Pure Polyetherimide membrane (a) PEI 10, (b) PEI 15and (c) PEI 18

a) FTIR spectrum for MMMs

The zeolite molecule structure is Na_{12} $[AlO_2.SiO_2]_{12}.27H_2O$. The FTIR spectrum for MMM are shown in Figure4-9. From the spectrum, it is observed that there are additional spectrum for MMM compared to pure PEI. One peak appears at 1773.18-1775.04cm^{-1} for all MMM which indicate the C=O in y-lactone. There are more number of aldehydes and ketones group which show a strong, prominent, stake-shaped band around 1710 - 1720 cm^{-1} (right in the middle of the spectrum). These additional peak may result from the interference of solvent residue which is high in MMMs.

The existing of zeolite4A particles can be seen at the peak of 1093-1100 cm^{-1}which shows the siloxane class with Si-O-Si bond. Moreover, silicon molecule of zeolite also make bonds with CH_3 at the peak around 850-810cm^{-1} which shows the interaction between zeolite particles with PEI.

In addition, the peak of 430-520 cm^{-1} do not appear in pure PEI but appear in MMM. This peak indicates the C-O-C bond of ether with bending type while ether group that appears in pure membrane shows stretching type. Since the main functional groups of PEI remain in MMM, it can be concluded that the zeolite loading in PEI based membrane does not change the chemical structure but changes some physical arrangement inside the membrane.

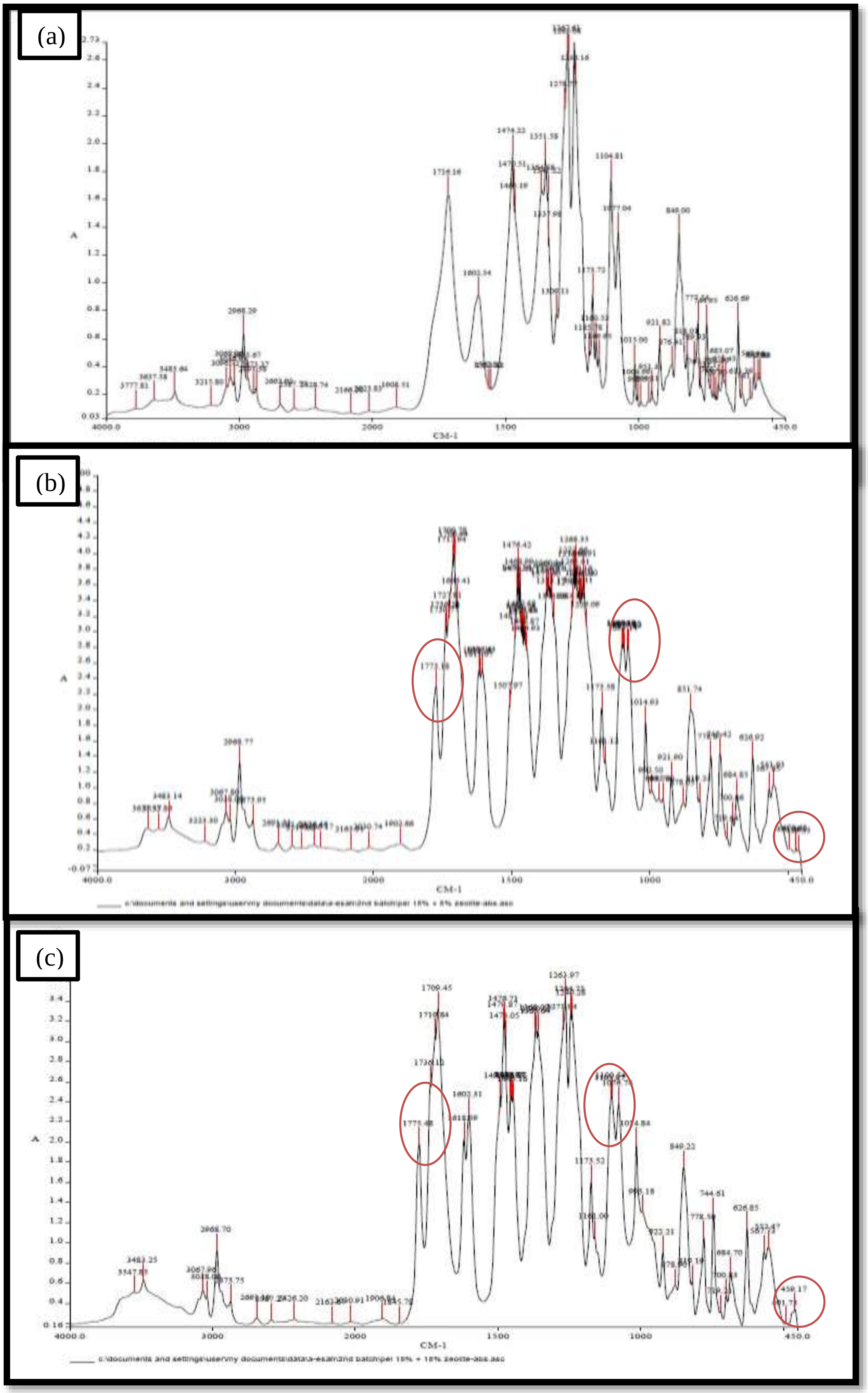


Figure 4-9: Comparison of FTIR spectrum of Pure PEI membrane (a), MMM5(b)and MMM15(c)

4.2.3 Membrane Thermal Characterization

Table 4-1: Decomposition temperature of membrane samples

Membrane	**Weight loss at 0°C -100°C (%)**	**Weight loss at 200°C -300°C (%)**	**Weight loss at 400°C -800°C (%)**	**Weight loss at 450°C -800°C (%)**
PEI 10%	-	4.6	-	59.2
PEI 15%	-	4.5	-	59.6
PEI 18%	-	4.4	-	51.7
MMM5	0.6	3.0	43.90	-
MMM10	1.4	5.0	44.69	-
MMM15	1.4	5.7	43.91	-
MMM20	2.1	5.5	38.97	-

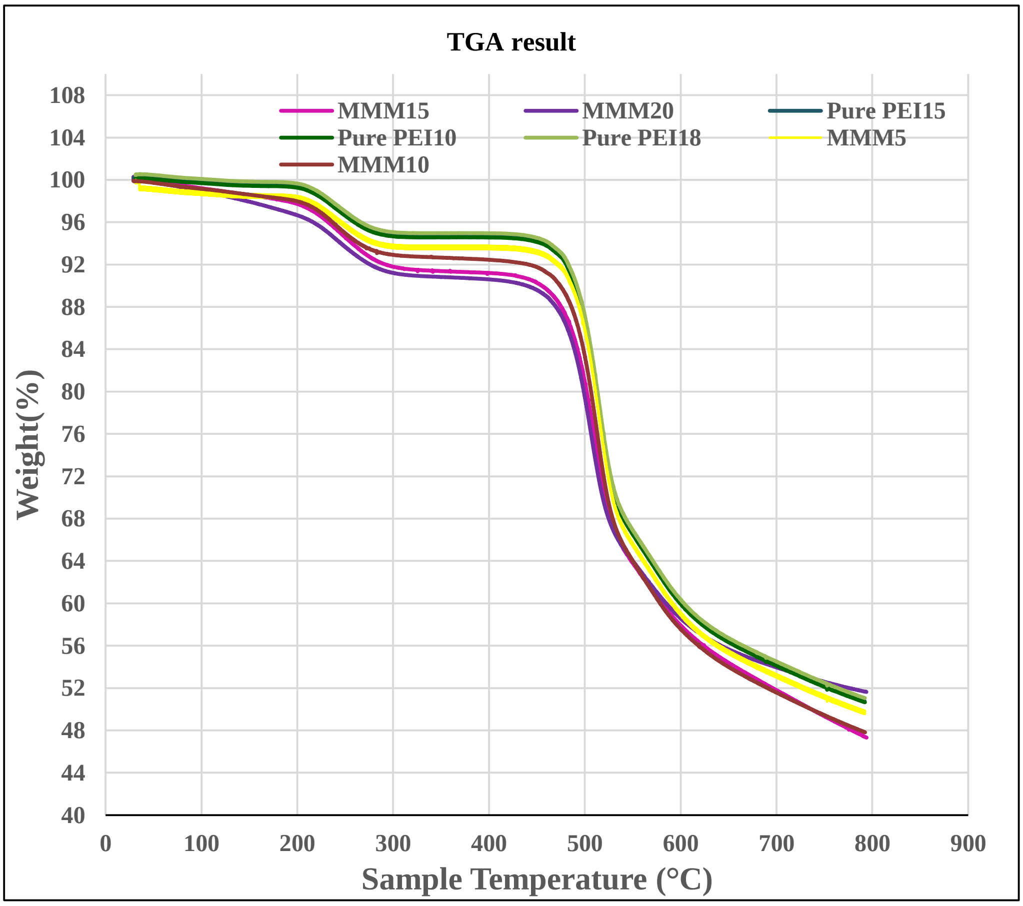


Figure 4-10: Weight loss (%) of fabricated membranes vs. temperature

The thermal stability of all fabricated membranes were analyzed using Thermogravimetric Analysis (TGA). TGA is used to measure the mass loss of a polymer as a function of temperature. During TGA analysis, membranes were subjected to the same experimental conditions where membrane samples were heated from 30 °C to 800 °C at a rate of 10 °C/min under air at 20 mL/min. The weight loss of the fabricated membranes over the temperature range are shown in Figure4-10.

From the graph in Figure 4-10, all pure PEI membranes looked to be free from moisture as there is no weight loss up to 100 °C while all MMMs shows some weight loss up to 100 °C about 0.6-2%. Figure 4-10 also shows that the weight loss of pure PEI membrane experienced two weight loss curves; first at 200 °C and second at 450 °C. The first weight loss is 2-4 % which might be due to residue solvent in the membrane even after drying. This can be eliminated by extending the drying time of the membrane as reported in literature[49]. The second weight loss of pure PEI about 50% at 450 °C is due to the degradation of PEI[49].

Regardless of small weight loss due to moisture content, MMMs also showed a two-stage mass loss, the first stage weight loss occurred around 200°C which shows the residue amount of NMP solvent left in membrane film while the second stage shows the decomposition temperature of MMM membrane which started at about 400°C with the weight average weight loss of 40%.

MMMs show second weight loss (around 400°C) faster compared to pure PEI membranes (450°C). This observation shows that the addition of zeolite 4A into PEI based membrane reduce the polymer degradation temperature. However, the quantity of zeolite loading does not have much effect on the thermal stability among the MMMs as all fabricated MMMs experienced polymer degradation at almost the same temperature range from 400°C to 800°C with similar percentage of weight loss. Table 4-1 summarizes the weight loss experienced by fabricated membranes as determined by TGA.

When compared with literatures, most of research study shows that Zeolite loading increase decomposition temperature of membrane due to the restriction to the polymer. The decrease of decomposition temperature of MMM in this study might due to due to the less interaction between PEI and Zeolite 4A which create small voids in between and hence reduce the decomposition temperature

In conclusion, TGA analysis in this study shows that the zeolite loading in PEI based membrane reduce the thermal stability of pure membrane because pure membrane started to decompose at higher temperature than MMM. Moreover, all membranes have remaining solvent which indicate insufficient drying time during membrane fabrication.

4.2.4 Membrane Glass Transition Temperature (Tg)

Table 4-2: Glass transition temperature from DSC analysis

Membrane	**Polymer composition (w/w% solvent)**	**Zeolite 4A composition (w/w% polymer)**	**Tg (°C)**
Pure membrane	15	0	210
MMM5	15	5	206
MMM10	15	10	208
MMM15	15	15	206
MMM20	15	20	206

All membrane samples were analyzed using Differential scanning calorimetry (DSC) to determine the glass transition temperature. The glass transition temperature provided a qualitative measure of the flexibility of polymers. The material which has lower Tg, that material will be more flexible [23].

In this project, the Tg of membranes were determined in order to understand the effect of zeolite loading on chain flexibility of polymer[49].

The DSC result of all membranes are shown in Figure 4-11 and Table 4-2The glass transition temperature (Tg) of pure PEI as stated in literature is 216◦C[50]. As shows in Table4-2, The DSC result of pure PEI membrane is 210 ◦C which is 6 ◦C lower than reported in literature. The decrease in glass transition temperature may result from plasticization by having NMP solvent residue as plasticize agent.

Tg result in all MMMs show similar result which is 206 ◦C. This indicates that the percentage of zeolite loading was not significant effect. However, it was 4◦C lower compared to pure PEI. The decrease in glass transition temperature might be because of the percentage solvent residue in MMMs were higher than in pure PEI.

When compared to the literatures in Section 2.6.3, the glass transition temperature of MMM was increase as zeolite loading increase. The increase of Tg was due to the restrictions of zeolite to the movement of the polymer chains by the formation of hydrogen bonding between zeolite particles and polymer.

There are many factors that affecting the glass transition temperature in polymer ; chemical structure, molecular weight, plasticizers, co-polymer and melting point[51]. The factors that might affect the reduction of glass transition temperature in this study are the chemical structure and plasticizer.

As mention in Section 3.1, in one mono structure of PEI, there are two methyl group (CH_3) and this functional group also contain in NMP solvent. When NMP solvent remains in membranes film, the number of methyl group will be increase. And as reported in literature, the number of successive CH_2 or CH_3group in the side chain will reduce the glass transition temperature[51].

Another factor is plasticizer. Plasticizers are low molecular weight and non-volatile substances (mostly in liquid phase) that are added into the polymer to improve its flexibility, utility as well as process ability. Plasticizers depress Tg by reduction of cohesive force between the polymer chains. When the plasticizer molecule enter the polymer matrix, it will produce polar attractive between its molecule and polymer chain. These attractive force decrease the cohesive forces between the polymer chains and therefore increase the chain motion, hence decrease Tg[51]. In fact, it was reported in literature that the water and other low molecular weight solvent exert a plasticizing effect on many polymer and reduce the glass transition temperature[52].

From the above statement, water and NMP solvent can be plasticizers which reduce the glass transition temperature of membranes. Because the result from TGA analysis shows the moisture content and the residue solvent in membranes. Water (Mw=18 g/mol.) and NMP solvent (Mw= 99.13g/mol.) have much lower molecular weight as compared to PEI (Mw= 592.61 g/mol.). The low molecular weight of water and NMP solvent corresponded to the properties of plasticizer as mentioned before.

Therefore, from DSC result it can be concluded that the pure PEI membrane has 6◦C lower glass transition temperature compared to literature due to plasticizer which are water and NMP solvent residue. Moreover, Tg of MMMs decrease about 4◦C compared to Pure PEI because the solvent residue in MMMs were higher than in pure PEI.

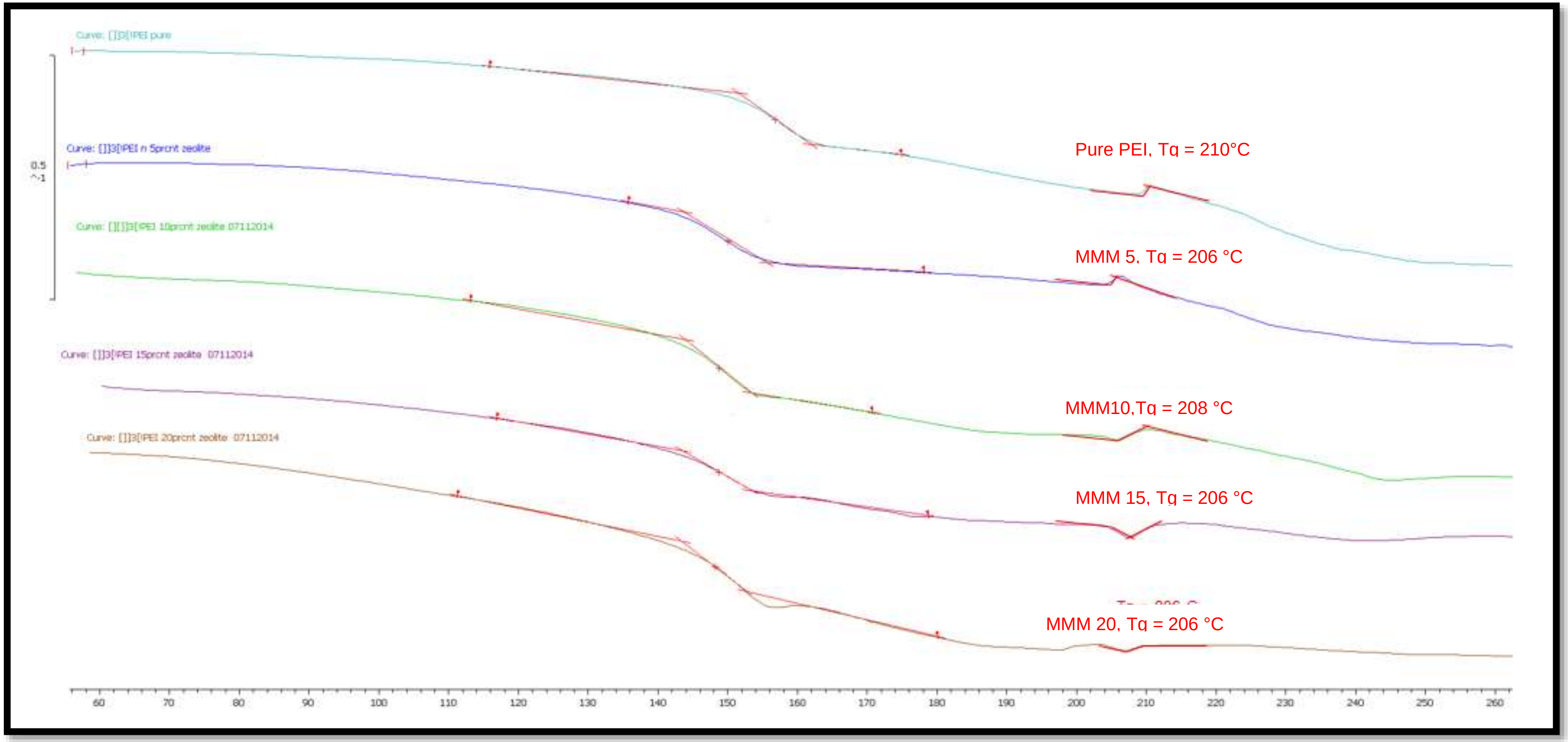


Figure 4-11: DSC analysis result

4.3 MEMBRANE GAS SEPARATION PERFORMANCE

Gas permeability studies of the membrane samples were evaluated by using pure gas of CO_2 and CH_4 to determine the separation factor in gas separation. All membranes were tested at room temperature with the pressure of 4, 8, 6 and 10 Bar. The permeation properties of pure Polyetherimide and MMM are summarized in table 4-4, 4-5 and 4-6 and the graph of these results were plot in Figure 4-12.

Table 4-4: CO_2 Permeance (GPU) at different feed pressure

Pressure (Bar)	**CO_2 Permeance (GPU) Membranes**		
	Pure PEI	**MMM 15**	**MMM20**
4	0.0775	2.3753	2.9206
6	0.0576	2.4639	3.1990
8	0.0667	2.5877	3.2169
10	0.0801	2.6786	3.8990

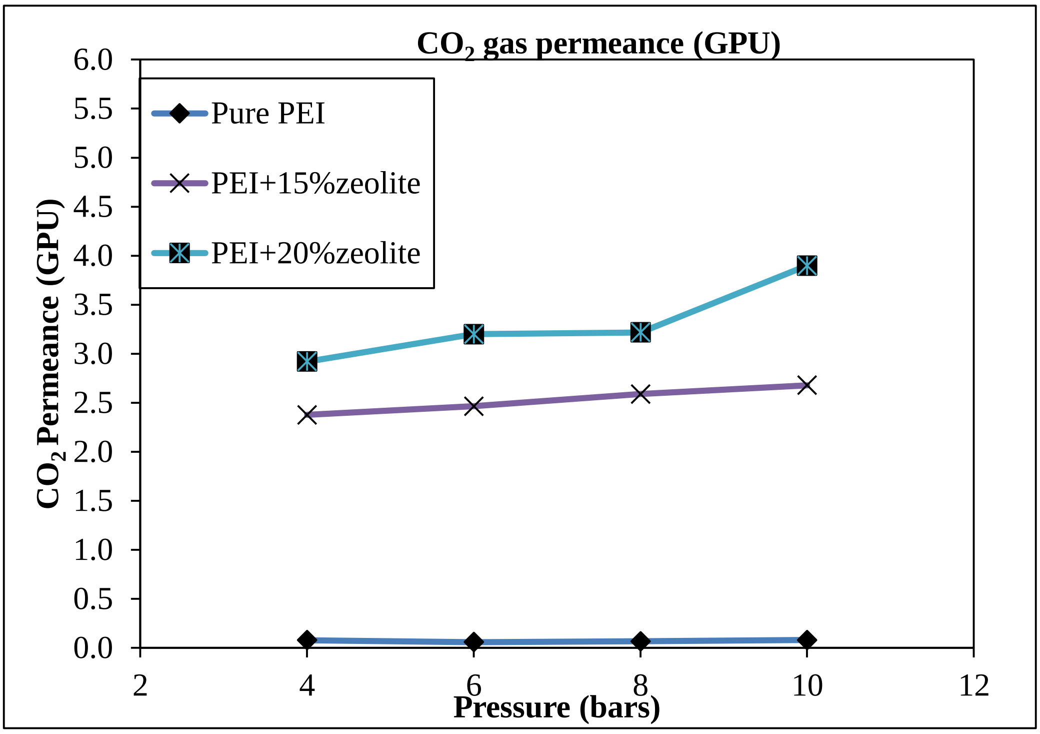


Figure 4-12: CO_2 Permeance (GPU)

Table 4-4 and the Figure 4.12 shows the permeability of carbon dioxide versus the operating pressure. It is observed that the permeability of carbon dioxide across all membranes are very less and slightly increase as the operating pressure increasing from. However, the permeability of carbon dioxide across MMMs are obviously increase more than 90% compared to pure PEI membrane. Therefore, addition of zeolite in PEI polymer based membrane has significantly improve the CO_2 permeability in membrane.

Table 4-5: CH_4 Permeance (GPU)

Pressure (Bar)	**CH_4 Permeance (GPU)**		
	Membranes		
	Pure PEI	**MMM 15**	**MMM 20**
4	0.0475	0.8082	0.8986
6	0.0433	0.9836	0.9626
8	0.0520	1.5030	1.1474
10	0.0539	2.1920	1.5118

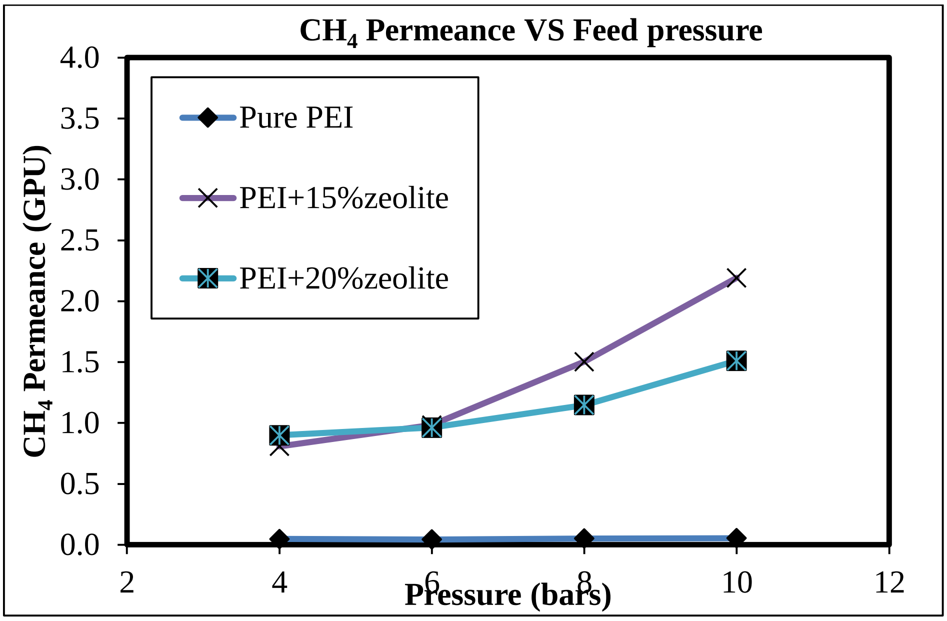


Figure 4-13: CH_4 Permeance (GPU)

Table 4-5 and Figure 4.13 shows that the permeability of CH4 across the membrane versus the operating pressure. The permeability of CH_4 is also increases with the increasing of pressure. However, it is much slower compared to CO_2.

Table 4-6: Selectivity of CO_2/CH_4

Pressure	Selectivity (GPU_{CO2}/GPU_{CH4})		
	Membrane		
	Pure PEI	MMM15	MMM 20
4	1.63	2.94	3.25
6	1.33	2.51	3.32
8	1.28	1.72	2.80
10	1.49	1.22	2.58

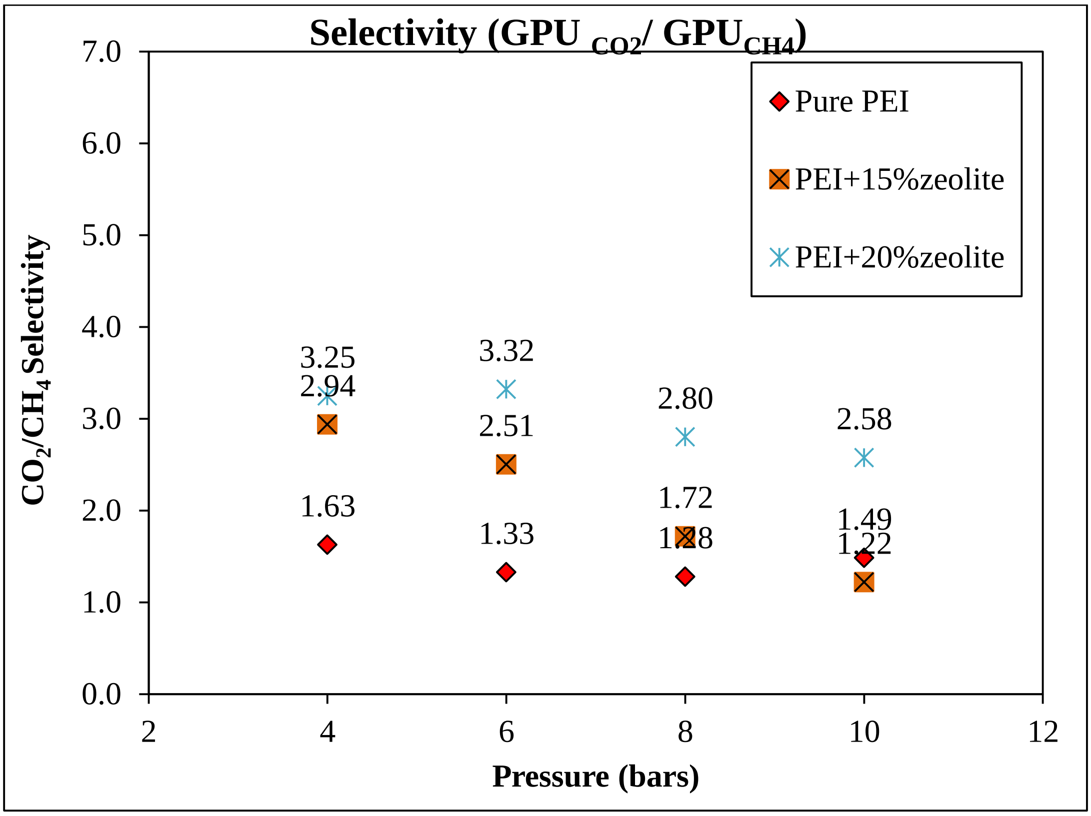


Figure 4-14: CO_2/CH_4 Selectivity

Table4-6 and Figure 4.14 shows the membrane selectivity versus the operating pressure. The selectivity is calculated by dividing CO_2 permeance with CH_4 permeance. From the result obtained, it is observed that the membrane selectivity across the prepared membrane are around 1.28 to 3.32.

In overall, the selectivity is decrease as the operating pressure increase which correspond to the theory of glassy membrane, the selectivity of glassy membrane decrease as increase feed pressure[53]. Due to some defect in membrane, the selectivity of pure PEI as well as MMMs were not high as in literatures [21, 33]. However, the trend still similar and MMMs show higher selectivity about 45% compared to pure PEI membrane. In conclusion, from gas permeability result, MMMs transport CO_2 faster and show higher selectivity than pure PEI.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

CO_2 content in natural gas is a global issue which needs to be solved. From literatures, mixed matrix membrane has been proven to be a good membrane material for gas separation due to its advantages over others technologies. Even though there are many research studies have been done to fabricate the mixed matrix membrane, the material selection still a big challenge for membrane to be applicable in the real industry.

At the end of this course, the objectives of study were achieved. Pure PEI membrane and PEI-zeolite4A MMMs were successfully fabricated. All membrane samples were tested for gas separation performance and characterized using Field Electron Scanning Electron Microscopy (FESEM), Fourier Transform Infrared Spectroscopy (FTIR), Thermal Gravimetric Analyzer (TGA) and differential scanning calorimetry (DSC).

Physical properties were evaluate using FESEM. FESEM images show big void in pure PEI. After addition zeolite particles in PEI based membrane, big voids were disappeared. Zeolite particles also have some physical attachment with PEI but still appeared some very small voids in between these two.

Chemical properties were evaluate by FTIR. The additional spectrum that occurred in MMMs compared to pure PEI membrane indicate the effect of zeolite loading and the interference of solvent residue in membrane. However, the zeolite 4A did not change the chemical structure of PEI based membrane but change some physical arrangement were changed.

The thermal properties were evaluate using TGA and DSC. The result from TGA shows that pure PEI membrane has higher decomposition temperature than MMMs and also show that there are solvent residue in membrane about 5%. The DSC result shows that all fabricated membrane has lower glass transition temperature about6-10 ◦C compared to as stated in literature. The reduction of glass transitions temperature was due to the plasticization cause by solvent residue.

The gas permeability result of MMMs show the increase in permeability of CO_2 more than 90 % compared to pure PEI membrane. Even though, the selectivity results are not much different, the selectivity in MMMs are higher than pure PEI about 45%.

Even though the magnitude for permeability and selectivity obtained in this study were small, the increase in MMM was obviously compared to PEI. Therefore, it can be concluded that the addition of zeolite4A in PEI based membrane improve the separation of CO_2 from CH_4 and these two material should be developed more for membrane gas separation.

5.2 RECOMMENDATION

Even though the result of permeability and selectivity in this project were not high as expected, the addition of zeolite 4A in PEI based membrane showed a positive trend for both separation factors. The future studies should be done to improve the performance of these membranes. Drying time should be carefully determined when fabricating membrane because if the solvent remains in membrane film, it will cause plasticization which affect the glass transition temperature as well as gas separation performance and also membrane morphology. Moreover, always ensure that the membranes are free from moisture content by drying the fabricated membrane at low temperature before every testing or characterization. In addition, the interaction between zeolite particles and polymer can be increase by adding a suitable substance that can prevent from the formation of void between these two materials.

REFERENCES

1. Amelia Suyono Wiryoatmojo, h.M., *Development Of Mixed Matrix Membranes For Separation Of CO_2 From CH_4*, in *Chemical engineering*. 2010, University Teknology PETRONAS.

2. Shimekit, B. and H. Mukhtar, *Natural Gas Purification Technologies–Major Advances for CO_2 Separation and Future Directions*, in *Advances in Natural Gas Technology*. 2012, InTech. p. 235-270.

3. Zhang, Y., et al., *Current status and development of membranes for CO_2/CH_4 separation: A review.* International Journal of Greenhouse Gas Control, 2013. **12**(0): p. 84-107.

4. Aroon, M.A., et al., *Performance studies of mixed matrix membranes for gas separation: A review.* Separation and Purification Technology, 2010. **75**(3): p. 229-242.

5. Hillock, A.M.W., *Crosslinkable Polyimide Mixed Matrixmembranes For Natural Gas Purification*, in *Doctor of Philosophy in Chemical Engineering*. 2005, Georgia Institute of Technology.

6. Asim Mushtaq, h.M., azmi Mohd Shariff, Hafiz Abdul Manna,, *A Review: Development of Polymeric Blend Membrane for Removal of CO_2 from Natural Gas.* International Journal of Engineering& Technology, 2013. **13**(02).

7. Nasir Haji Darman, A.R.B.H. *Technical Challenges and Solutions on Natural Gas Development in Malaysia*. in *The petroleum Policy and Management (PPM) Project 4th Workshop of the China – Sichuan Basin Case Study*. 2006. Beijing, China: PETRONAS.

8. Ahmed, T.Y. and M.M. Ahmada, *Flowsheet Development and Simulation of Off-Shore Carbon Dioxide Removal System at Natural Gas Reserves.* International Journal, 2011. **2**(1).

9. Ismail, W.N.W.S.a.A.F., *Gas permeation properties and characterization of polyetherimide/polyvinylpyrrolidone-based carbon hollow fiber membrane for CO_2/CH_4 separation.* International Journal of Chemical and Environmental Engineering, 2011. **2**(1).

10. Zhou, J., *Hybrid Membrane/Absorption Process For Acid Gas Removalin Flng Applications.*

11. Ebenezer, S.A. and J. Gudmunsson, *Removal of Carbon dioxide from natural gas for LPG production.* Semester project work, 2005.

12. Bakeri, G., et al., *A novel surface modified polyetherimide hollow fiber membrane for gas–liquid contacting processes.* Separation and Purification Technology, 2012. **89**(0): p. 160-170.

13. Hung, H.L., *Synthesis and Characterization of 6FDA-Durene Polymer Based Mixed Matrix Membrane*. 2012, University Teknology PETRONAS: Tronoh,peral.

14. Ghazali, N.A.S.b.M., *Carbon Dioxide Removal from Natural Gas Stream Using Polycarbonate Membrane*. 2009, University Teknologi PETRONAS.

15. ÇAKALIN, Ü., *Natural Gas Purification By Zeolite Filled Polyethersulfone Based Mixed Matrix Membranes*, in *Chemical Engineering*. 2009, Middle East Technical University.

16. Tutuk Djoko Kusworo, A.F.I., Azeman Mustafa, and Kang Li, *The Effect Of Type Zeolite On The Gas Transport Properties Of Polyimide-Based Mixed Matrix Membranes*. 2008. **12**(2).

17. Baker, R.W., *Membrane technology and applications*. Membrane Technology and Applications, Third Edition. 2004. 325-378.

18. Sridhar, S., B. Smitha, and T. Aminabhavi, *Separation of carbon dioxide from natural gas mixtures through polymeric membranes—a review.* Separation & Purification Reviews, 2007. **36**(2): p. 113-174.

19. Nasir, R., et al., *Review Material Advancements in Fabrication of Mixed-Matrix Membranes.* Chemical Engineering & Technology, 2013. **36**(5): p. 717-727.

20. Mahajan, R., et al., *Challenges in forming successful mixed matrix membranes with rigid polymeric materials.* Journal of Applied Polymer Science, 2002. **86**(4): p. 881-890.

21. Zimmerman, C.M., A. Singh, and W.J. Koros, *Tailoring mixed matrix composite membranes for gas separations.* Journal of membrane science, 1997. **137**(1): p. 145-154.

22. Moore, T.T. and W.J. Koros, *Non-ideal effects in organic–inorganic materials for gas separation membranes.* Journal of Molecular Structure, 2005. **739**(1–3): p. 87-98.

23. Basu, S., A. Cano-Odena, and I.F.J. Vankelecom, *MOF-containing mixed-matrix membranes for CO_2/CH_4 and CO_2/N_2 binary gas mixture separations.* Separation and Purification Technology, 2011. **81**(1): p. 31-40.

24. Adams, R.T., et al., *CO_2/CH_4 permeation in high zeolite 4A loading mixed matrix membranes.* Journal of Membrane Science, 2011. **367**(1–2): p. 197-203.

25. Moghadam, F., et al., *The effect of TiO_2 nanoparticles on gas transport properties of Matrimid5218-based mixed matrix membranes.* Separation and Purification Technology, 2011. **77**(1): p. 128-136.

26. Ismail, A.F., et al., *Gas separation performance of polyethersulfone/multi-walled carbon nanotubes mixed matrix membranes.* Separation and Purification Technology, 2011. **80**(1): p. 20-31.

27. Karkhanechi, H., et al., *Fabrication of Homogenous Polymer-Zeolite Nanocomposites as Mixed-Matrix Membranes for Gas Separation.* Chemical Engineering & Technology, 2012. **35**(5): p. 885-892.

28. Chen, X.Y., et al., *Mixed matrix membranes of aminosilanes grafted FAU/EMT zeolite and cross-linked polyimide for CO_2/CH_4 separation.* Polymer, 2012. **53**(15): p. 3269-3280.

29. Liang, C.-Y., et al., *A comparison on gas separation between PES (polyethersulfone)/MMT (Na-montmorillonite) and PES/TiO_2 mixed matrix membranes.* Separation and Purification Technology, 2012. **92**: p. 57-63.

30. Nik, O.G., X.Y. Chen, and S. Kaliaguine, *Functionalized metal organic framework-polyimide mixed matrix membranes for CO_2/CH_4separation.* Journal of Membrane Science, 2012. **413**: p. 48-61.

31. Rezakazemi, M., K. Shahidi, and T. Mohammadi, *Synthetic PDMS composite membranes for pervaporation dehydration of ethanol.* Desalination and Water Treatment, 2014(ahead-of-print): p. 1-8.

32. Simons, K., et al., *CO_2 sorption and transport behavior of ODPA-based polyetherimide polymer films.* Polymer, 2010. **51**(17): p. 3907-3917.

33. Ozturk, B. and F. Demirciyeva, *Comparison of biogas upgrading performances of different mixed matrix membranes.* Chemical Engineering Journal, 2013. **222**(0): p. 209-217.

34. Baker, R.W., *Overview of membrane science and technology.* Membrane Technology and Applications, Second Edition, 2004: p. 1-14.

35. Lalia, B.S., et al., *A review on membrane fabrication: Structure, properties and performance relationship.* Desalination, 2013. **326**: p. 77-95.

36. *Radiological and Environmental Management*. Radiological and Environmental Management 2014 [cited 2014 22 October].

37. Kwak, S.-Y., S.H. Kim, and S.S. Kim, *Hybrid organic/inorganic reverse osmosis (RO) membrane for bactericidal anti-fouling. 1. Preparation and characterization of TiO_2 nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane.* Environmental science & technology, 2001. **35**(11): p. 2388-2394.

38. Vu, D.Q., W.J. Koros, and S.J. Miller, *Mixed matrix membranes using carbon molecular sieves: I. Preparation and experimental results.* Journal of Membrane Science, 2003. **211**(2): p. 311-334.

39. Kim, S., *High permeability/high diffusivity mixed matrix membranes for gas separations*. 2007, Virginia Polytechnic Institute and State University.

40. ŞEN, D., *Polycarbonate based Zeolite 4A filled mixed matrix membranes: Preparation, Characterization and gas separation performances*. 2008, MIDDLE EAST TECHNICAL UNIVERSITY.

41. Bakhtiari, O., et al., *Preparation, characterization and gas permeation of polyimide mixed matrix membranes.* J Membra Sci Technol, 2011. **1**(101): p. 2.

42. Lai, C.Y., et al., *Preparation and characterization of poly(vinylidene fluoride)/nanoclay nanocomposite flat sheet membranes for abrasion resistance.* Water Research, 2014. **57**(0): p. 56-66.

43. Li, H. and H. Kim, *Thermal degradation and kinetic analysis of PVDF/modified MMT nanocomposite membranes.* Desalination, 2008. **234**(1–3): p. 9-15.

44. Fujioka, Y., et al. *Development of Innovative gas separation membranes through sub-nanoscale materials control*. in *Research symposium presentation. Research Institute of Innovative Technology for the Earth (RITE)*. 2007.

45. *Gas separation Principles & Operation*. Process design 10 July 2014]; Available from: http://www.separationprocesses.com/Membrane/MT_ChpGS-3.htm.

46. Baker, R.W., *MEMBRANES FOR VAPOR/GAS SEPARATION*. Membrane Technology and Research, Inc.

47. Ugal, J.R., K.H. Hassan, and I.H. Ali, *Preparation of type 4A zeolite from Iraqi kaolin: Characterization and properties measurements.* Journal of the Association of Arab Universities for Basic and Applied Sciences, 2010. **9**(1): p. 2-5.

48. Ahmad, J. and M.-B. Hägg, *Preparation and characterization of polyvinyl acetate/zeolite 4A mixed matrix membrane for gas separation.* Journal of Membrane Science, 2013. **427**(0): p. 73-84.

49. Mohshim, D.F., H. Mukhtar, and Z. Man, *The effect of incorporating ionic liquid into polyethersulfone-SAPO34 based mixed matrix membrane on* CO_2 *gas separation performance.* Separation and Purification Technology, 2014. **135**(0): p. 252-258.

50. Scott, C.E. *Polyetherimide*. 2008 [cited 2014 15 June]; Available from: http://www.polymerprocessing.com/polymers/PEI.html.

51. Iqbal, M.Z. *Physical Properties of Polymer*. 2008 22 May 2008; Available from: http://www.slideshare.net/guest824336/ppp8-2-factors-affecting-tg.

52. Zeleznak, K. and R. HOSENEY, *The Glass Transition in Starch1*. Cereal Chem, 1987. **64**(2): p. 121-124.

53. Simons, K., *Membrane technologies for CO_2 capture*. 2010: University of Twente.

APPENDIX A: GAS PERMEABILITY CALCULATION

Example of calculation:

Data record: constant volume v= 1 ml,

Time= 54.10 second

Area of membrane= 24.63cm^2

1) Volumetric flow rate (Q)

$$Q = \frac{\Delta V}{\Delta t} \text{.......................... ....Equation B-1}$$

$$= \frac{1}{54.10} = 0.0185\ cm^3$$

2) Volumetric flow rate (Q) at standard condition

$$Q_{STP} = Q\ x\ \frac{T_{STP}}{T_i} \text{..................Equation B-2}$$

$$= 0.0185 \frac{cm^3}{s} x\ \frac{273\ K}{293\ K}$$

$$= 0.016934\ cm^3(STP)/s$$

3) Flux,

$$J = \frac{Q_{STP}}{A} \text{...........................Equation B-3}$$

$$= \frac{0.016934 \frac{cm^3(STP)}{s}}{24.63 cm^2}$$

$$= 0.00688\ \frac{cm^3(STP)}{cm^2.s}$$

4) Permeability, P

$$P\ = \frac{J.l}{\Delta P} \text{..........................Equation B-4}$$

where l= membrane thickness

$\Delta\text{P} = \text{Pressure across membrane}$

5) Permeance,

$$\frac{\text{P}}{\text{l}} = \ \frac{\text{J}}{\Delta\text{P}}\ \ldots\ldots\ldots\ldots\ldots..\ldots\ldots\ \text{Equation B} - 5$$

1 bar= 75.006

Absolute Feed pressure = 4 bar = 300.02 cmHg + 76.0002 cmHg

= 376.002 cmHg

Permeate Pressure= 76.002 cmHg

Therefore, $\Delta P = 376.002 - 76.002 = 300.002\ cmHg$

Substitute all values in equation B-4

$$\frac{P}{l} = \frac{J}{\Delta P} = \frac{0.0068}{300.002} \frac{cm^3(STP)}{cm^2 .s\ cmHg} = 2.29154\text{E-}06\ \frac{cm^3(STP)}{cm^2 .s\ cmHg}$$

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

Therefore, Permeance = 2. 29 GPU