

**DEVELOPMENT OF BLEND IONIC LIQUID GLASSY  
MEMBRANE FOR CO<sub>2</sub>/CH<sub>4</sub> GAS SEPARATION**

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UNIVERSITI TEKNOLOGI PETRONAS  
SEPTEMBER 2015**

**Development of Blend Ionic Liquid Glassy Membrane for  
CO<sub>2</sub>/CH<sub>4</sub> Gas Separation**

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

SEPTEMBER 2015

Universiti Teknologi PETRONAS,  
32610, Bandar Seri Iskandar,  
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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BANDAR SERI ISKANDAR, PERAK  
September 2015

## 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.

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HANNANEH MILANI KALKHORAN

## ABSTRACT

Natural gas generally contains large amount of methane along with heavier hydrocarbons. Also it often consists of non-hydrocarbon, such as carbon dioxide which need to be removed due to its effect on pipeline quality. There are different technologies that has been used for natural gas treatment which are adsorption process, absorption process, cryogenic condensation but because of some limitation there is a new method has been developed known as membrane. Polymeric membrane is the most use membrane in industry but Because of existence of some limitation, blend ionic liquid glassy membrane has been introduced. This blend membrane has been developed by adding ionic liquid (IL): 1-Ethyl-3- Methylimidazolium Trifluoromethanesulfonate ([emim][CF<sub>3</sub>SO<sub>3</sub>]) in three different concentration into the polymer. The blend ionic liquid glassy membrane was casted manually and fabricated by using dry-phase inversion. The membranes were characterized by SEM, FTIR and DSC in terms of morphology, composition and glass transition temperature which in this study the membranes were dense and nonporous in terms of morphology, in terms of composition it can be observed that by adding IL there is a significant change in wave number which showed the addition of IL. In terms of glass transition temperature, the analysis showed an increase. In regards to gas performance in terms of permeability and selectivity, from the analysis it can be observed the selectivity in 10 bar is increasing from 1.143 to 12.669, same changes can be seen for 12 and 14 bar. In terms of permeability for CO<sub>2</sub> in 10 bar it can be observed that it is increasing from  $4 \times 10^{-7}$  to  $1 \times 10^{-6}$  although for CH<sub>4</sub> it can be seen that in 10 bar it is decreasing from  $3.5 \times 10^{-7}$  to  $1 \times 10^{-7}$ .also the same changes can be seen in higher pressure of 12 and 14 bar.it also can be seen by increasing the pressure the permeability for CO<sub>2</sub> in 10 bar was decreasing from  $4 \times 10^{-7}$  to  $1.24 \times 10^{-7}$ . Same changes can be seen for CH<sub>4</sub>.

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# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

#### 1.1.1 Natural Gas

As we go forward, the global need for energy is increasing and also the environmental effect of using the energy sources increase like greenhouse gas emissions. Consequently, it is important to find a replacement energy source which produce appropriate amount energy with high quality and environmental friendly. One of the source of energies that satisfied mentioned requirement is Natural Gas. Moreover, it is a source of hydrocarbons for petrochemicals. Although natural gas is considered as a clean fuel compared to other fossil fuels, it is not essentially clean and free of impurities. Pure natural gas cannot be used directly due to its unwanted impurities like carbon dioxide CO<sub>2</sub>, thus the impurities should be removed to avoid pipeline and equipment corrosion and to enhance the energy of natural gas (Shimekit & Mukhtar, 2012).

As a fossil fuel, natural gas is formed from the decaying remains of pre-historic plant and animal life which have lived more than million years ago. Despite the fact that there are different hypotheses about the starting point of fossil powers, the most generally acknowledged hypothesis expresses that fossil fuels are normally formed when natural matters are decomposed and packed under the earth's coating at high pressure and for quite a while. This kind of natural gas is shaped by the decay procedure of compacted natural matters that are secured in mud, residue and trash at high temperature underneath the outside layer of the earth. Natural gas can also be made by the action of small methane-producing bacteria. For this situation, methane formation occurs close to the earth's surface and the methane produced is generally

scattered into the environment. In the other hand, this methane also can be caught underground and recovered as natural gas(Shimekit & Mukhtar, 2012).

The process of NG purification is divided into two which are gas dehydration and gas sweetening(Younger, 2004).In Dehydration of NG the purpose is to remove water. In regards to gas sweetening, the purpose is mainly removing CO<sub>2</sub> because it is highly acidic in the presence of water. Furthermore, the existence of CO<sub>2</sub> may waste the pipeline capacity and reduce the energy content of natural gas which eventually lowers the calorific value of natural gas also it has the higher composition in the raw NG(Adewole, Ahmada, Ismail, & Leo, 2013).

There are several techniques to remove CO<sub>2</sub> that generally had been used for instance cryogenic distillation, absorption, adsorption and membrane separation(Zhang, Sunarso, Liu, & Wang, 2013). The cryogenic distillation, absorption, adsorption methods involve high treatment cost, large equipment. However membrane separation technology shows a rapid growth during a past few decade(A.F. Ismail, Norida, & Sunarti, 2003).

Capability of membrane gas separation to reach higher efficiency of separation, be more capital efficient, yield faster separation coupled with the simplicity of operation in modern compact modules and high space economy are some of the economic advantages of which makes it attractive for industrial application.

### **1.1.2 Composition of Natural Gas**

The natural gas composition at wells are different base on type, depth, and location of the underground reservoirs and the geology of area. Most often oil and natural gas that are found together from reservoir. The gas composition produced from a reservoir might change. In addition to methane that existed in a gaseous state at underground pressures will become liquid at normal atmospheric pressure in the reservoir. Generally, they are called natural gas liquids (NGLs). Carbon dioxide has to be removed as one of the major toxic compositions in natural gas because it decrease the energy content. Also it become acidic in contact with water which damage the pipeline. Furthermore in case of transportation of natural gas by using pipeline due to it expenses liquefied natural gas (LNG) is considered as a good choice.by decreasing

the temperature of natural gas in LNG processing plant, existing CO<sub>2</sub> can be frozen and block the pipeline. Also, Separation CO<sub>2</sub>/CH<sub>4</sub> is a challenging process. Hence, the CO<sub>2</sub> removal through the purification processes is important for an improvement in the quality of the product(Dortmundt & Doshi, 1999). In comparison with other hydrocarbon energy sources, natural gas has higher energy conversion efficiencies(Economides & Wood, 2009).

In general it contains a large amount of methane (Epa.gov, 2013) along with heavier hydrocarbons such as ethane, propane, iso-butane, normal butane, etc. it also contains non-hydrocarbons, such as nitrogen, hydrogen sulphide and carbon dioxide(Shimekit & Mukhtar, 2012).

TABLE 1.1 Typical Composition Of Natural Gas in Vol% (Natural Gas.Org 2010).

Methane	CH <sub>4</sub>	70-90%
Methane	C <sub>2</sub> H <sub>6</sub>	0-20%
Propane	C <sub>3</sub> H <sub>8</sub>	
Butane	C <sub>4</sub> H <sub>10</sub>	
Carbon Dioxide	CO <sub>2</sub>	0-8%
Oxygen	O <sub>2</sub>	0-0.2%
Nitrogen	N <sub>2</sub>	0-5%
Hydrogen sulphide	H <sub>2</sub> S	0-5%
Rare gases	A, He, Ne, Xe	trace

### 1.1.3 CO<sub>2</sub> Removal Technologies for Natural Gas Purification

There are a couple innovation created keeping in mind the end goal to refine the natural gas, for example, cryogenic refining, absorption process, adsorption procedure and membrane separation. The advancements had been enhanced from year to year so as to minimize capital and working expense, follow gas specifications and environmental purpose(Shimekit & Mukhtar, 2012). Since there is no phase change in membrane separation, it can be considered as energy saving gas separation technology(Crespo & Bøddeker, 1994). There are different technologies for CO<sub>2</sub> removal which each of them has their own strengths and weaknesses(Shimekit & Mukhtar, 2012)

TABLE 1.2 Pros and Cons for Different Technologies to Remove (SHIMEKIT & MUKHTAR, 2012)

<b>Process</b>	<b>Advantages</b>	<b>Disadvantages</b>
<b>Absorption</b>	<ul style="list-style-type: none"> <li>• Commonly used for efficient (&gt;50%) removal of acid gases.</li> </ul>	<ul style="list-style-type: none"> <li>• Purifying acid gas as low partial pressure is needed while using chemical solvents required long time.</li> <li>• Not economical due to its need for high partial pressure during using physical solvents.</li> </ul>
<b>Adsorption</b>	<ul style="list-style-type: none"> <li>• Highly pure products</li> </ul>	<ul style="list-style-type: none"> <li>• lower product recovery</li> <li>• single pure product</li> </ul>
<b>Cryogenic</b>	<ul style="list-style-type: none"> <li>• higher recovery compared to other techniques</li> <li>• high purity products</li> </ul>	<ul style="list-style-type: none"> <li>• Highly energy intensive</li> <li>• Not economical</li> <li>• Difficult operation process because of different feed stream.</li> </ul>
<b>Membrane separation</b>	<ul style="list-style-type: none"> <li>• Simplicity, low capital investment and operation.</li> <li>• Stability at high pressure</li> <li>• products High recovery</li> <li>• Good space efficiency</li> <li>• friendly to environment</li> </ul>	<ul style="list-style-type: none"> <li>• Recompression of permeate</li> <li>• Moderate purity</li> </ul>

## **1.2 Problem Statement**

Base on reservoir sources, raw natural gas has different compositions, but it is generally composed of methane (30% – 90%), with other light and heavy hydrocarbons. Besides, it also contains some impurities such as carbon dioxide. It is necessary to remove Carbon dioxide in order to avoid pipelines and equipment corrosion. There are some methods for natural gas treatment which are absorption, adsorption, and cryogenic distillation. But due to some limitation, there have been a considerable research on membrane gas separation as a new technology which has some advantages compare to other methods such as its lower capital cost, easy operation process, and high CO<sub>2</sub> removal percentage.

Polymeric membranes are known because of their excellent basic transport properties, high ability of process and their low cost. Though due to their limit in the trade-off between permeability and selectivity(Robeson, Burgoyne, Langsam, Savoca, & Tien, 1994), they have been studies to develop and overcome this weakness.

This study has been done to develop a membrane and overcome its limitation. In this project enhancing polymeric membrane has been done by adding ionic liquid in three different concentration to improve the selectivity and permeability as to important parameters which shows the efficiency of membrane.

## **1.3 Objectives**

- i.** To synthesize the flat sheet dense polymeric membrane and ionic liquid polymeric membrane.
- ii.** To characterize the developed membranes to investigate the physicochemical properties of membranes.
- iii.** To evaluate the gas separation performance of developed membranes by using pure CO<sub>2</sub> and CH<sub>4</sub> gases in term of permeability and selectivity.

#### 1.4 Scope of Study

- i. to develop blend glassy membrane by using Polysulfone (PSU) dissolved in NMP as solvent and addition of different composition of 1-Ethyl-3-Methylimidazolium Trifluoromethanesulfonate ([emim][CF<sub>3</sub>SO<sub>3</sub>]) for separation of Carbon Dioxide (CO<sub>2</sub>) from Methane (CH<sub>4</sub>). The composition of NMP will be fixed which is 20gr while the addition of ionic liquid ([emim][CF<sub>3</sub>SO<sub>3</sub>]) will be different in concentration 10 wt%, 15 wt% and 20 wt%.
- ii. to characterize the membrane three different techniques will be used which are SEM (scanning electron microscopy) to find information about chemical composition, and crystalline structure and orientation of materials making up the sample, FTIR (Fourier Transform Infrared Radiation) to identify unknown materials and determine the quality of a sample and also determine the amount of components in a mixture, DSC (Differential Scanning Calorimetry) to study the changes that take place in a polymer when you heat it which is known as the thermal transitions of a polymer.
- iii. Finally, the performance of membrane will be evaluated in term of permeability and selectivity. In this step CO<sub>2</sub> and CH<sub>4</sub> will be passed through membrane separately in three different pressures.

## CHAPTER 2

### LITRATURE REVIEW

#### 2.1 Introduction

In the last few decades, membrane technology has been a great attention for gas separation technology especially for natural gas sweetening(Pandey & Chauhan, 2001). Membrane technology has been started as early as in 1850 when Graham introduced the Graham's Law of Diffusion. Then, gas separation utilization in membrane technology has been commercialized in late 1900's. Nowadays, several hundreds of plants use membrane technology for the separation of gases. Most plants use cellulose-acetate membranes. According to Baker, the competitiveness of membranes for the separation of CO<sub>2</sub>/CH<sub>4</sub> would strongly increase if stable membranes with higher selectivity during operation would become available. Separation processes account for 40 % to 70 % of capital and operating cost in the chemicals industry(Pais, Loureiro, & Rodrigues, 1997)

Membrane-based separation technologies have a broad range of applications, including process water treatment and reuse, metal and catalyst recovery, solvent recovery, gas separation, and concentration of heat-sensitive biological macromolecules and protein separation among others(Nunes & Peinemann, 2001).

A membrane is a semipermeable, or selectivity permeable, barrier that allows some molecules or ions cross it while hindering the passage of others. In membrane separation, a portion of fluid known as permeate (or filtrate) passes through the membrane, while other components are rejected by the membrane and retained in the retentate (or concentrate) stream(Wijmans & Baker, 1995). The transport of materials across a membrane requires a driving force. Using membrane separation for natural

gas treatment has some advantages like low capital cost, easy operation process and high CO<sub>2</sub> removal percentage(Mohshim, Mukhtar, Man, & Nasir, 2012).

Synthetic Membranes can be classified as microporous membranes or nonporous (dense) membranes according to their structure and mechanism of separation(Merkel, Bondar, Nagai, Freeman, & Pinnau, 2000) Synthetic membranes are made-up from different materials, including both organic and inorganic materials such as metal and ceramics. Ceramic and metal membranes can be used in separations where aggressive media (e.g., acids, strong solvents) are present. They also have excellent thermal stability, which makes them suitable for high-temperature operations (gwater.com, 2001).

Polymeric membranes take over the market because they are less expensive and more useful than inorganic membranes. They are naturally formed by coating a thin polymer layer on a porous backing or support to create a combination that provides high permeability, selectivity, mechanical strength, and chemical stability operations(Mellada & Menendez, 2008).

Solution-diffusion mechanism type has been used for gas separation membrane. For gas separation, permeability and selectivity are the major component in determining the most efficiency of the gas separation(Mohshim et al., 2012). Base on the solution diffusion model, two major parameters are controlling the permeability of molecules through membranes which are Diffusivity (D) and solubility (S). Diffusivity (D) is how fast the molecules transport through membrane and solubility (s) is an amount of gas sorbed by membrane at given temperature and pressure(Adewole et al., 2013). The permeability (P) is the ability of molecules to pass through a membrane. The membrane can its best performance when it has high selectivity and also permeability although it can only achieve high permeability and low selectivity and vice versa (Mohshim et al., 2012).

### 2.1.1 Polymeric Membrane

Polymeric membranes advanced for different industrial applications including gas separation. In regards to gas separation, the selectivity and permeability of the membrane material defines the efficiency of the gas separation process. The Most common classes that membrane has been categorised is based on their materials which are organic (polymers) and inorganic (ceramic, glass, metals, carbon molecular sieve and clay)(Li, Fane, Ho, & Matsuura, 2011).It can also be categorised into three groups according to flux density and selectivity: i) porous, ii) non-porous and iii) asymmetric.

Porous membrane is a rigid, highly voided structure with randomly distributed inter connected pores. It is known to have high flux but low selectivity, meanwhile non-porous membrane or dense membrane have high selectivity properties although the permeability is usually low. The main property of this kind of membrane is that even molecules with similar sizes can be separated if their solubility in the membrane varies significantly(Pandey & Chauhan, 2001)

A dense membrane can be made by melt extrusion, where a melt is intended as a solution in which the polymer in both solute and solvent. In the casting method, dense membranes which has been made from dissolution of a polymer in a solvent are cast that is followed by evaporation of the solvent after casting(Pandey & Chauhan, 2001)

Polymeric membranes can be classified into two categories base on polymeric materials which are i) Glassy, ii) Rubbery.

#### i. Glassy

This kind of membrane are rigid, has glass like structure and operate below glass transition temperature(Basu, Akhtar, Rahman, & Islam, 2004). Glassy polymer has been used mostly in industry due to its high selectivity and good mechanical properties(Shimekit & Mukhtar, 2012)

## ii. Rubbery

This type of membrane is soft, flexible and operate above glass transition temperature. It is an example of elastomer type polymer where the polymer has the ability to return to its original shape after being stretched or deformed(Linares & Acosta, 2004).

Polymer blending as a property modification technique is an approach that is widely used to obtain cheap materials with improved properties. At first sight, polymer blends may be classed into homogeneous, or miscible, and heterogeneous, or immiscible, blends(Hachisuka & K. Ikeda, 1999).

One of the most studied glassy polymer membrane materials for CO<sub>2</sub>/ CH<sub>4</sub> separation is polysulfone (PSU). Because of its low price, chemical stability, and mechanical strength, its gas permeation properties have been broadly discovered for gas separation (Mulder, 1996). PSU has low CO<sub>2</sub> permeability and CO<sub>2</sub>/ CH<sub>4</sub> selectivity(Bos, Punt, Wessling, & Strathmann, 1998) but it has high plasticization pressure which is important due to its effect on membrane selectivity(Lozano et al., 2011).

### **2.1.2 Separation of Carbon Dioxide (CO<sub>2</sub>) from Methane (CH<sub>4</sub>)**

Methane is the largest composition in natural gas composition and carbon dioxide is the highest toxic existed in natural gas. Due to acidic properties of Carbon dioxide in contact with water, it cause corrosion in pipeline. It is important to remove acid gas such as carbon dioxide before it is compressed and transportation. CO<sub>2</sub>/ CH<sub>4</sub> separation is important in industries like natural gas treatment. There are different methods such as absorption, adsorption and cryogenic distillation have been used for natural gas treatment. All of these technologies are consists of phase changes which cause flooding, excessive loading, foaming and so on (Shimekit & Mukhtar, 2012). Also these methods requires complex equipment, high energy consumption and capital cost. As a result, a new method presented known as membrane separation technology which has some benefits like energy efficiency, utilization of non-toxic chemical and also operating procedure is simple(Ahmad, Jawad, S.C.Low, & S.H.Zein, 2012). Membrane can be categorized in three group base on materials which include Polymeric membranes, inorganic membranes and mixed matrix membranes.

### 2.1.3 Ionic Liquid

Ionic liquids are ionic compounds that exist as liquids at low temperatures. They consist of organic cations and (mostly) inorganic anions. There is no formal definition of the minimum melting point for a compound to be described as an ionic liquid; many researchers use 80°C, although some compounds with melting points as high as 100°C are referred to as ionic liquids. The low melting point of these compounds is due primarily to the bulky and cumbersome structure of the corresponding ions, which inhibits the formation of a crystalline solid. One of the advantages of ionic liquids are that they are non-volatile, and in fact have no measurable vapour pressure, meaning that they will not be lost to evaporation. Also, they are able to dissolve a wide range of organic and inorganic compounds, including some polymers and minerals, are non-flammable, have a high thermal stability, and have a high electrochemical stability. These compounds can also be tailored to give properties desirable for specific applications. Many researchers believe that the use of ionic liquids could drastically reduce the chemical industry's reliance on flammable, volatile, environmentally damaging organic solvents and lead to new processes that allow for recycling of solvents and catalysts and are more friendly to the environment(Bennett & Leo, 2004).

The use of room temperature ionic liquids (RTILs) in combination with polymer membranes for gas separation, in the form of supported ionic liquid membranes (SILMs), has been studied for several years(Scovazzo et al., 2004). Conventional supported liquid membranes (SLMs) are composed of porous membranes coated in organic liquids, which often leads to higher permeability due to the favourable diffusivities of gasses in liquids compared to solids. The major problem with SLMs is the loss of the liquid via evaporation during operation. The replacement of organic solvents with non-volatile ionic liquids has overcome this problem, and SILMs have exhibited high selectivity for some industrially important gas pairs, such as CO<sub>2</sub>/CH<sub>4</sub>(Dai, Noble, Gin, Zhang, & Deng, 2016; Park et al., 2009) with higher permeability than polymer membranes. Typically, SLMs can resist pressures of only a few bar, which is much lower than the pressures under which many industrial gas separation occur. Several methods have been developed to overcome these problems,

such as mixed-matrix membranes, composite ionic liquid and polymer membranes (CILPMs) and so on(Cho et al., 2009).

In CILPMs, ionic liquid and the polymer are dissolved in a solvent and the solution is cast and dried on flat glass surface to fabricate CILPMs. In contrast to SILMs, the ionic liquid is trapped within the polymer membrane and, therefore, is not liable to liquid loss at higher pressures. However, a drawback is the lower gas permeability that are typical of CILPMs compared with SILMs. To overcome the problem of low permeability, higher temperatures can be employed but this requires the use of thermally stable materials in membrane preparation(Pesiri, Jorgensen, & Dye, 2003).

The choice of polymer for CILPMs is based on physical and chemical properties, such as good stability and durability at operating conditions, high solubility of RTILs and ability to form dense membranes. In this research, Ethyl-3-MethylimidazoliumTrifluoromethanesulfonate ([emim][CF<sub>3</sub>SO<sub>3</sub>]) with three different concentrations of 10 wt%, 15 wt% and 20 wt% were combined in fix composition of PSU and NMP, in order to study their effect on the permeability of carbon dioxide and methane and CO<sub>2</sub>/CH<sub>4</sub> separation.

## CHAPTER 3

### METHODOLOGY

In this chapter the general procedure of the project and methodology of the project has been explained. Also the equipment, the materials and their properties have been clarified.

#### 3.1 Materials

##### i. Polymer : Polysulfone (PSU)

Polysulfone is a semi-transparent, heat-resistant, thermoplastic offering excellent mechanical, electrical and chemical resistance. These polymers are known for their toughness and stability at high temperatures.

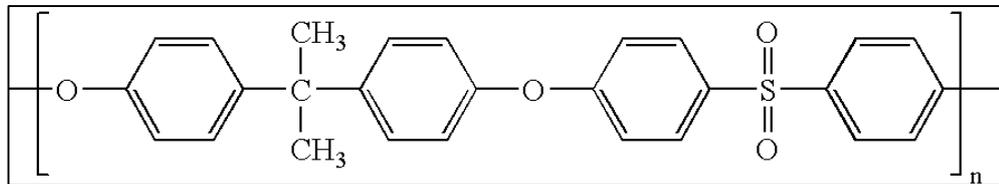


FIGURE 3.1 PSU Chemical Structure.

TABLE 3.1 PSU Properties.

PROPERTIES	POLYSULFONE
Chemical Formula	C <sub>27</sub> H <sub>22</sub> O <sub>4</sub> S
Appearance (at room temperature)	Powder
Molecular Weight of Repeat Unit	442.52 g/mol
Melting Point	180-190 °C
Glass Transition Temperature	185°C

ii. Solvent : N-methyl 2-pyrrolidone(NMP)

This solvent has been used Because of the lower volatility compare to other solvents and also it releases fewer organic emissions to the atmosphere. It is also chemically stable.

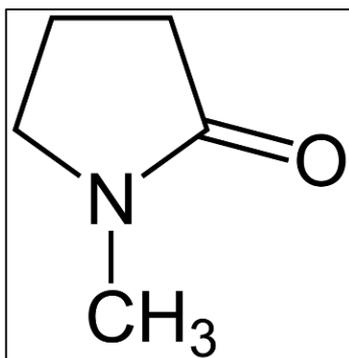


FIGURE 3.2 NMP Chemical Structure.

TABLE 3.2 NMP Properties.

PROPERTIES	NMP
Chemical Formula	C <sub>5</sub> H <sub>9</sub> NO
Appearance (at room temperature)	Liquid
Molecular Weight	99.13 g/mol
Melting Point	-24 °C
Boiling Point	202 °C

iii. Ionic Liquid : 1-Ethyl-3-Methylimidazolium Trifluoromethanesulfonate  
([emim][CF<sub>3</sub>SO<sub>3</sub>])

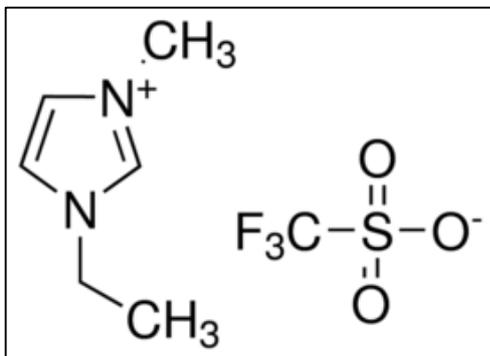


FIGURE 3.3 ([emim][CF<sub>3</sub>SO<sub>3</sub>])Chemical Structure.

TABLE 3.3 ([emim][CF<sub>3</sub>SO<sub>3</sub>])Properties.

PROPERTIES	([emim][CF <sub>3</sub> SO <sub>3</sub> ])
Chemical Formula	C <sub>7</sub> H <sub>11</sub> F <sub>3</sub> N <sub>2</sub> O <sub>3</sub> S
Appearance (at room temperature)	Liquid
Molecular Weight	260.24 g/mol
Melting Point	-12 °C
Boiling Point	>350 °C

## 3.2 Equipment

### i. Magnetic stirrer



FIGURE 3.4 Digital Hotplate Magnetic Stirrer.

### ii. Oven



FIGURE 3.5 Oven.

iii. Doctor Blade

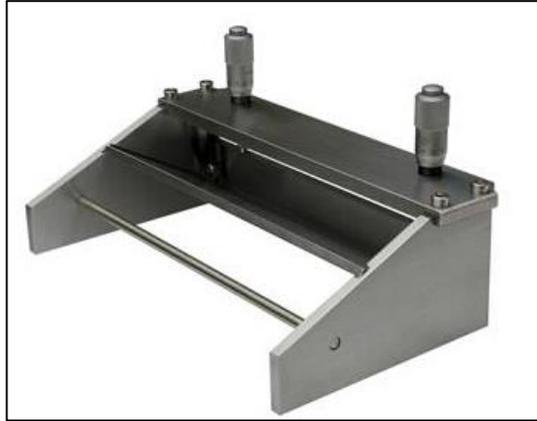


FIGURE 3.6 Doctor Blade.

iv. Scanning electron microscopy (SEM)

To find information about chemical composition, and crystalline structure and orientation of materials making up the sample.

v. Differential Scanning Calorimetry(DSC)

To identify unknown materials and determine the quality of a sample and also determine the amount of components in a mixture.

vi. Fourier Transform Infrared Radiation (FTIR)

To study the changes that take place in a polymer when you heat it which is known as the thermal transitions of a polymer.

### 3.3 Procedure

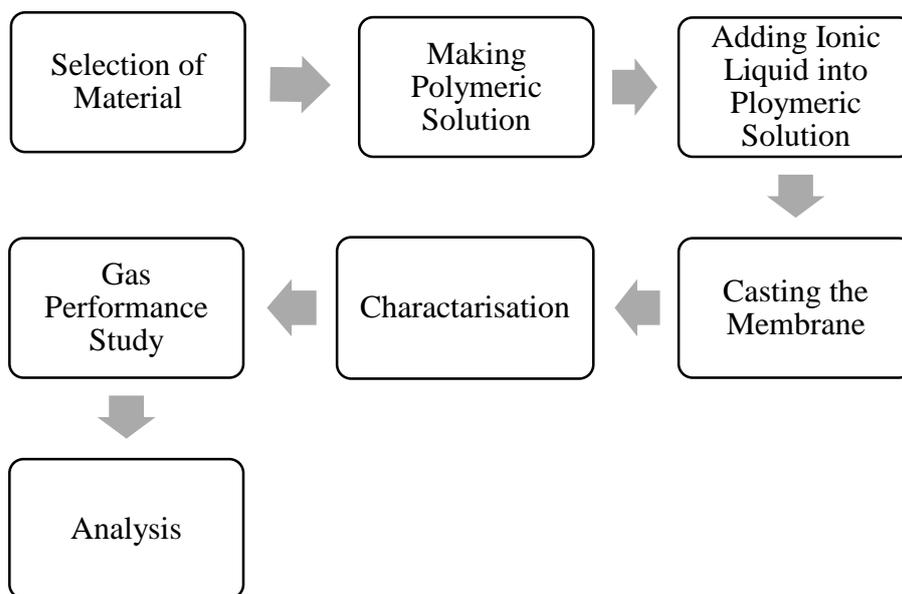


FIGURE 3.7 Methodology of Project.

The samples are listed as below:

TABLE 3.4 Number of Samples

NMP(gr)	PSU(wt%)	[emim][CF <sub>3</sub> SO <sub>3</sub> ]( wt %)
20	20	–
20	20	10
20	20	15
20	20	20

#### 1. Material Selection

In this step N-methyl 2-pyrrolidone (NMP) has been chosen as a green solvent, Polysulfone(PSU) has been chosen as polymer and 1-Ethyl-3-Methylimidazolium Trifluoromethanesulfonate ([emim][CF<sub>3</sub>SO<sub>3</sub>]) as ionic liquid.

## 2. Synthesis of Polymeric Membranes

First the polymeric membrane has been prepared by adding the glassy polymer (PSU) in the solvent (NMP). In this step 20 wt% of PSU has been added o 20gr solvent. Polymer was dissolved in a solvent at room temperature under continuous stirring to obtain a homogeneous mixture.

To be more accurate micropipette (Figure 3.8) has been used to measure 20 gr of solvent which is NMP with analytical balance (Figure 3.9) and added 20 wt% of polymer (PSU) into it which base on below equation was 4gr.

$$\frac{\text{amount of polymer [PSU]}(\text{gr})}{\text{amount of sovent[NMP]}(\text{gr})} \times 100 = \text{concentration} \quad (1)$$



FIGURE 3.8 Micropipette.



FIGURE 3.9 Analytical Balance.

The polymer has been used is powder (Figure 3.10) before it has been measured it has been in the oven at 100°C for 1 hour to remove the moisture from the powder. Then it has been added to the solvent.

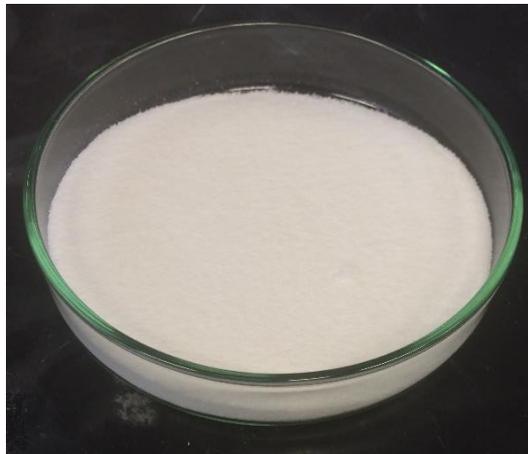


FIGURE 3.10 Polysulfone (PSU)

Since a miscible solution was required, the mixture of PSU and NMP has to be stirred continuously which to have a perfect solution digital hot plate magnetic stirrer (figure 3.4) has been used.

In this step the solution has to be stirred for 24 hours continuously at room temperature and the equipment speed has been set at 110 RPM (Figure 3.11).



FIGURE 3.11 Miscible Sample.

After making the solution it has been casted manually into glass plate by using doctor blade with thickness of 100  $\mu\text{m}$ . Since the oven was no stable at the time, the casted samples has been kept in room temperature for 2 hours till the colour turn to white which shows the solvent has been evaporated or separated. After 2 hours the samples has been placed in the oven for 24 hours a 130°C for complete evaporation of solvent.

### 3. Synthesis of Blend Ionic Liquid Polymeric Membranes

The same procedure is done to measure 20wt% of PSU which is 4gr to add to 20gr solvent. Then we add the ionic liquid with three different concentration of 10 wt%, 15 wt% and 20 wt% to our PSU+NMP solution which base on the equation below is 0.4gr,0.6gr,0.8gr. The solution will be continuously stirred at room temperature to obtain a homogeneous mixture.

$$\frac{\text{amount of Ionic liquid (gr)}}{\text{amount of sovent[PSU](gr)}} \times 100 = \text{concentration} \quad (2)$$

Same procedure goes for casting the enhanced polymeric membrane.

### 4. Characterization of membranes

The resultant polymeric membrane and polymeric ionic liquid membranes were characterized. Characterization of the developed membrane was done by different analytical equipment which are as below:

- i. SEM (scanning electron microscopy) which expose information about the sample such as chemical composition, and crystalline structure and orientation of materials making up the sample.
- ii. FTIR (Fourier Transform Infrared Radiation) to identify unknown materials and determine the quality of a sample and also determine the amount of components in a mixture.

- iii. DSC (Differential Scanning Calorimetry) to study the changes that take place in a polymer when you heat it which is known as the thermal transitions of a polymer.

## 5. Gas Permeability Study

The performance of developed membranes will be studied in a gas permeation unit in terms of selectivity and permeability with pure compositions of CO<sub>2</sub> and CH<sub>4</sub> at different pressures 10, 12, 14 bar. The permeability and ideal CO<sub>2</sub>/CH<sub>4</sub> selectivity has been calculated by using the following Equation 3 and 4.

## 6. Analysis

In this step the permeability and selectivity of the membrane will be calculated by using following equations:

$$\frac{P_{\text{CO}_2}}{l} = \frac{J}{\Delta P}$$
$$\frac{P_{\text{CH}_4}}{l} = \frac{J}{\Delta P} \tag{3}$$

$$\alpha = \frac{P_{\text{CO}_2/l}}{P_{\text{CH}_4/l}} \tag{4}$$

Where:

$$J = \text{flux} \left( \frac{\text{cm}^3}{\text{cm}^2 \times \text{s}} \right)$$

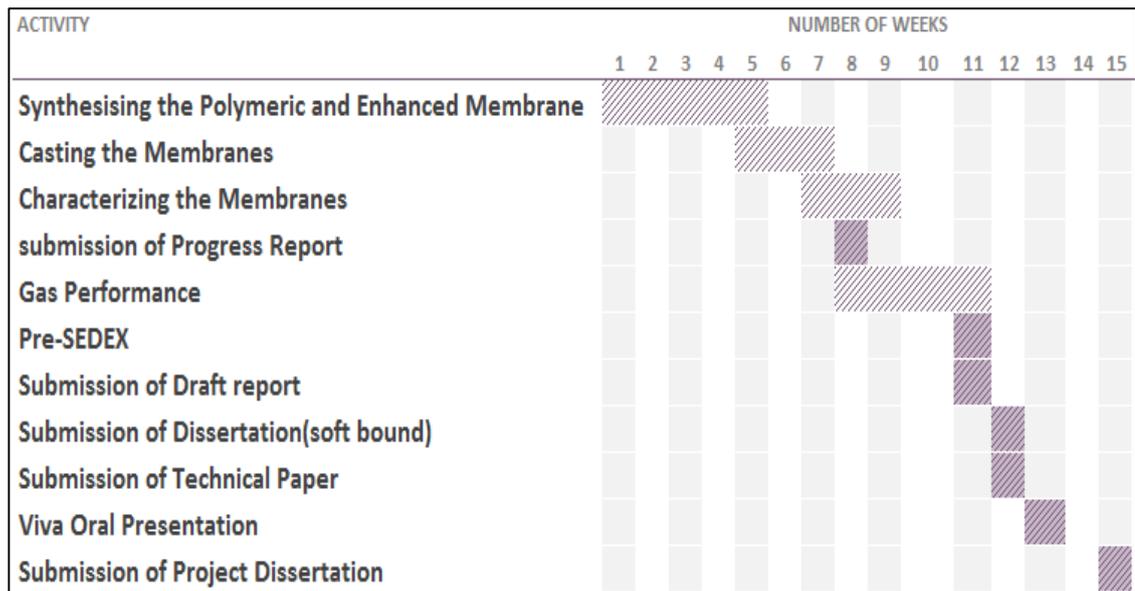
$$\Delta P = \text{pressure drop (cm-Hg)}$$

$$l = \text{mebrane thickness (cm)}$$

$$P = \text{permeability} \left( \frac{\text{cm}^3 \times \text{cm}}{\text{cm}^2 \times \text{s} \times \text{cm} - \text{Hg}} \right)$$

$$\alpha = \text{selectivity}$$

TABLE 3.5 Gantt Chart



 Activities
  Important Dates

## CHAPTER 4

### RESULTS AND DISCUSSION

The samples of membrane were characterized by using three methods which are Fourier Transformed Infrared (FTIR), Differential Scanning Calorimetry (DSC) and scanning electron microscopy (SEM). Next, the membrane undergo FTIR to compare the changes of chemical species in existence of ionic liquid [emim][CF<sub>3</sub>SO<sub>3</sub>]. IR-spectra will give information on chemical compound, chemical bonds and interaction between compounds. DSC has been done to give information on glass transition temperature for each sample. And last but not the least SEM has been done to gain information about the surface and cross section of the membrane

#### 4.1 Morphological Analysis of Developed Membrane

SEM is an important tool for researchers who work in the field of membranes (Mulder, 1996). When the morphology of a membrane has to be studied, SEM is regularly used so that photographs on a micron scale, or even smaller, can be obtained, and the distribution and size of the pores can be observed.

From Figures 4.1 to 4.4, the top Surface Scanning and cross section scanning 1000X Magnification, from top Surface Scanning it can be observed that the membranes are a dense, void free and also homogeneously mixed. Although in some of the top view scanning some small white spots can be seen which might be due to existence of some atmospheric contaminants.

From the cross sectional morphology, it can be observed that from the top layer there are no pores but due to the cutting method that has been used the scan is not really clear.

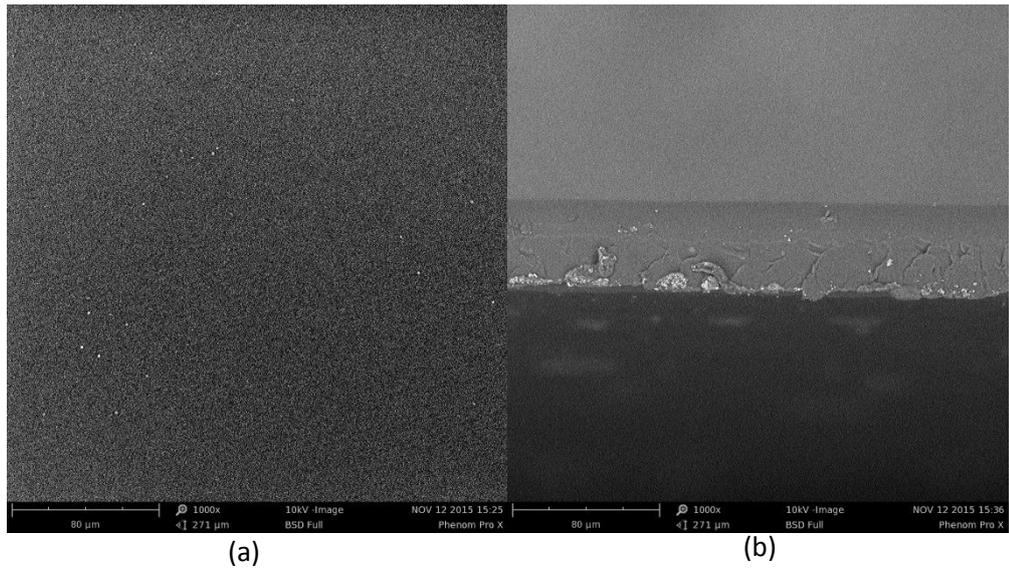


FIGURE 4.1 SEM Image for PSU Membrane (a) Top Surface Scanning and (b) Cross Section Scanning 1000X Magnification.

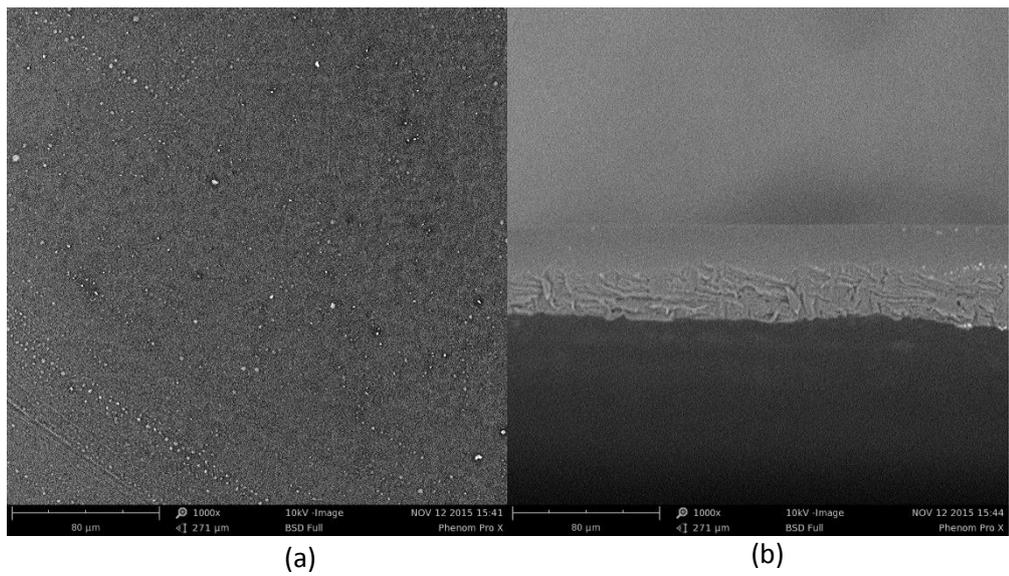


FIGURE 4.2 SEM Image for PSU+10wt% ([emim][CF<sub>3</sub>SO<sub>3</sub>]) (a) Top Surface Scanning and (b) Cross Section Scanning 1000X Magnification.

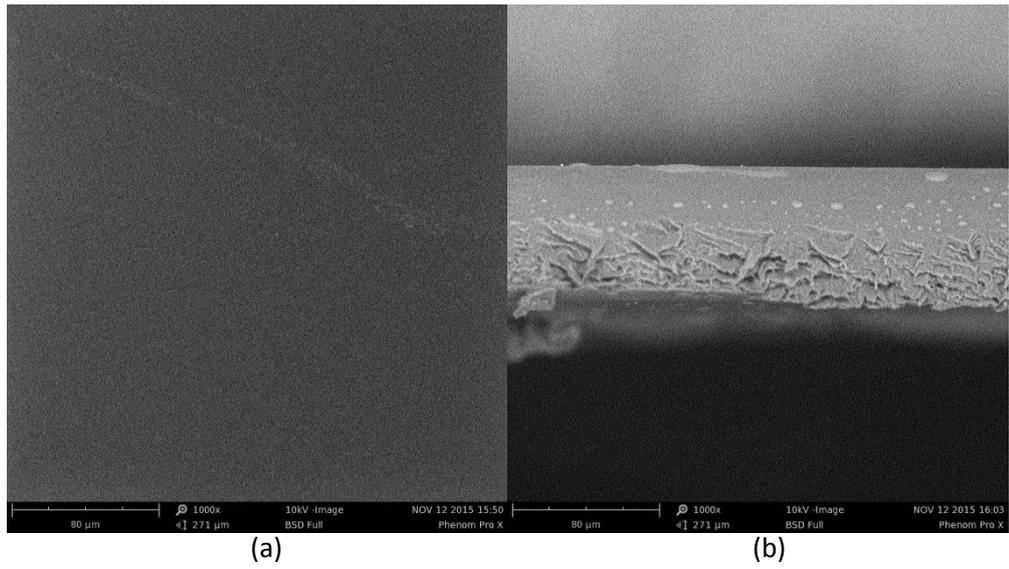


FIGURE 4.3 SEM Image for PSU+15wt% ([emim][CF<sub>3</sub>SO<sub>3</sub>]) (a) Top Surface Scanning and (b) Cross Section Scanning 1000X Magnification

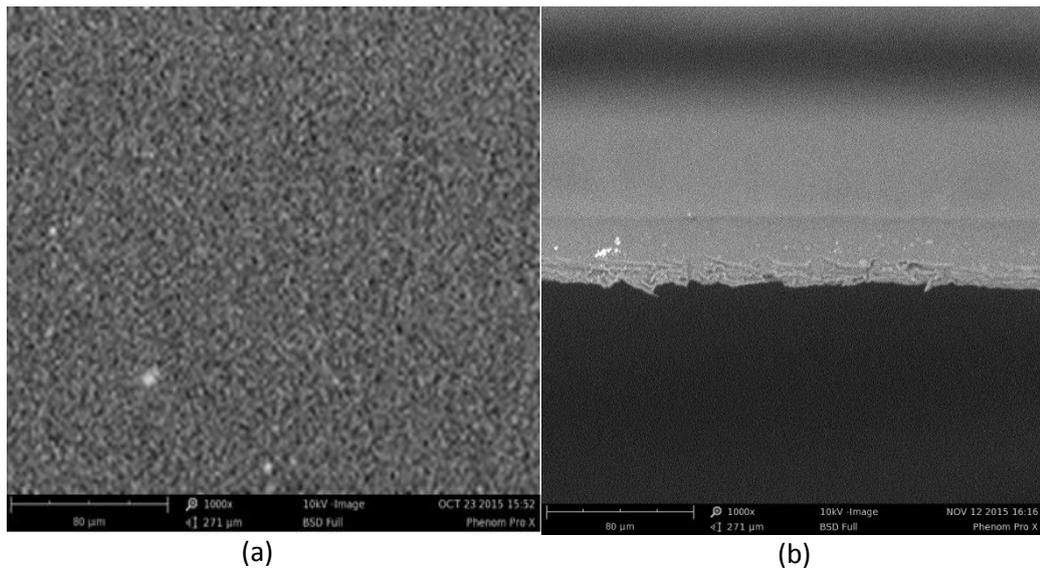


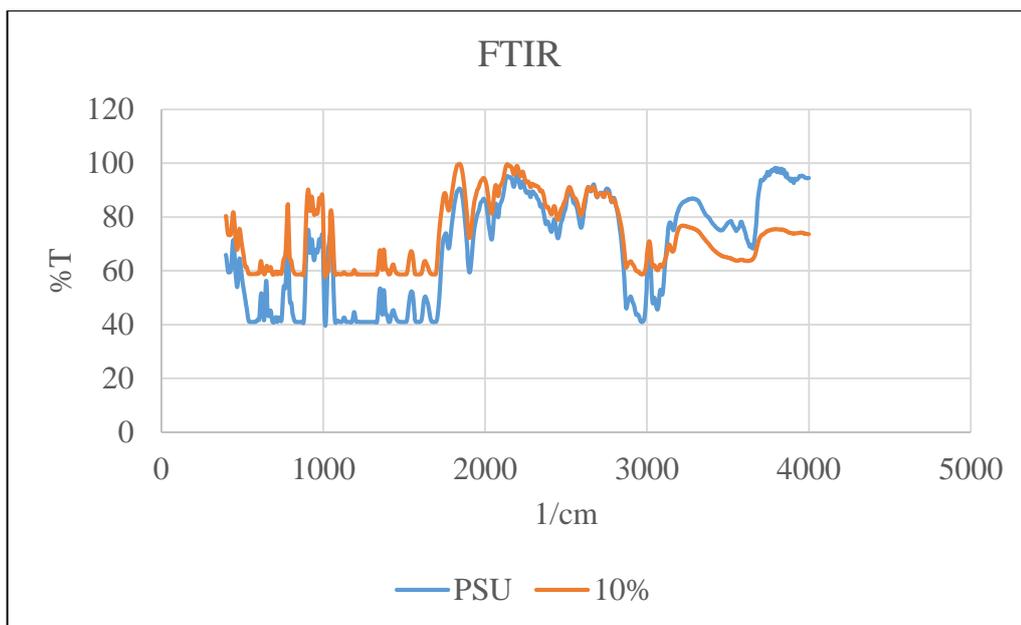
FIGURE 4.4 SEM Image for PSU+20wt% ([emim][CF<sub>3</sub>SO<sub>3</sub>]) (a) Top Surface Scanning and (b) Cross Section Scanning 1000X Magnification.

Base on the previous studies that has been done on PSU, adding PSU to NMP as a solvent can remove macro-void formation during instantaneous mixing. It has been reported that the reduction of the solvent ratio in polymer solutions increases the volatile component concentration and can increase the thickness of the selective skin of the membrane while it decreases the membrane surface porosity(Ahmad Fauzi Ismail & Lai, 2003).

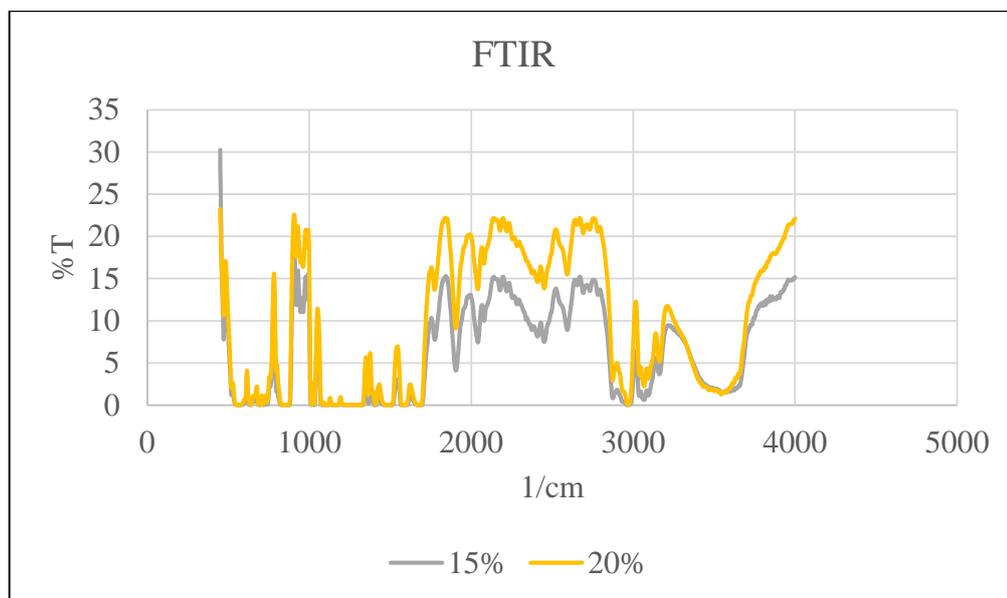
#### **4.2 Characterization using Fourier Transform Infrared Spectroscopy (FTIR)**

FTIR is an important technique in organic chemistry which can shows the presence of certain functional groups.

As it can be seen from Figure 4-5, IR spectra analysis shows that by addition of ionic liquid in PSU membrane there is a significant change in composition of functional group that exists in PSU such as C-H bonds, sulfone and benzene ring. Besides there will be addition of some other functional groups such as amides and C-F bond. However as it can be observed from the graphs by adding different concentration of ionic liquid there is no significant change in composition.



(a)



(b)

FIGURE 4.5 FTIR Analysis for (a) PSU and 10 wt% Ionic Liquid (b) 15 and 20 wt% Ionic Liquid.

The FTIR of polymeric membrane of PSU in NMP. Solvent have the following functional groups. The sulfone group  $S = O$  asymmetric have the wave number  $1150.00\text{cm}^{-1}$ , the peak appears on  $983.63\text{ cm}^{-1}$ . The next functional group is  $CSO_2C$  asymmetric stretch is  $1322.00\text{cm}^{-1}$ , the peak is shifted to  $1290.00\text{ cm}^{-1}$  due to stretching vibration of  $SO_2$  group. The C-O group has wave number  $1244.00\text{ cm}^{-1}$  and that is shifted to  $1162.32\text{ cm}^{-1}$  due to hydrogen shifting bonding. The  $C_6H_6$  ring

stretch has wave number  $1587.00\text{ cm}^{-1}$  which is not shifted due to strong bonding or stable condition.

There has been some investigation also on this matter which shows adding PSU in other solvents such as DMAc has effect on the wavenumber of the functional groups and also addition of some functional groups. It has been found out that the peak for each functional group was shifted(Ahmed, Idris, Noordin, & Rajput, 2011).

### 4.3 Characterization using Differential Scanning Calorimetry (DSC)

Calorimetry is a technique for determining the quantity of heat that is either absorbed or released by a substance undergoing a physical or a chemical change. As it can be seen in the graph in Table 4.1, it shows the effect of temperature on heat flow. It can be seen that by adding 10wt% ionic liquid the glass transition temperature is increasing, although by increasing the concentration to 15wt% the T is decreasing which might be due to displacement of ionic liquid free ions and again it is increasing by adding 20wt% ionic liquid.

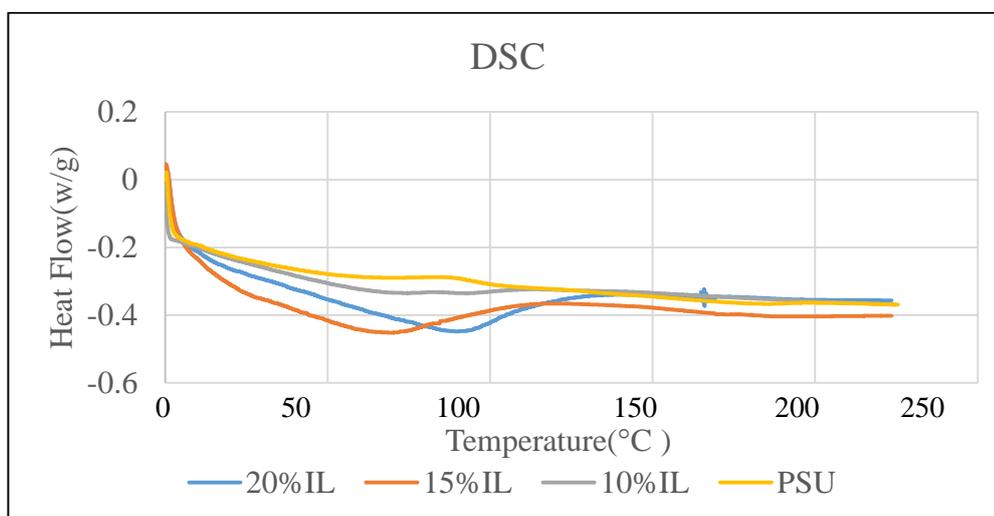


FIGURE 4.6 DSC for PSU, 10, 15 and 20wt% Ionic Liquid.

TABLE 4.1 Glass Transition Temperature

Membrane	T <sub>g</sub> (°C)
PSU	109.58
10wt%	136.39
15wt%	134.96
20wt%	146.51

#### 4.4 Gas Permeability and Selectivity Measurement

Gas Permeation Test has been done in order to measure the permeability of CO<sub>2</sub> and CH<sub>4</sub> across membrane at different pressure. The pressure was increase by two for every consecutive time which are 10, 12 and 14 bar respectively. The results of performance are shown as below:

TABLE 4.2 Permeability of Carbon Dioxide across Different Membrane at Different Pressure.

Permeability of CO <sub>2</sub> at Different Pressure(GPU)				
Pressure(bar)	PSU	10 wt%	15 wt%	20 wt%
10	4.008E-07	5.591E-07	6.175E-07	1.2882E-06
12	3.052E-07	3.306E-07	4.687E-07	7.879E-07
14	1.245E-07	1.658E-07	3.197E-07	5.692E-07

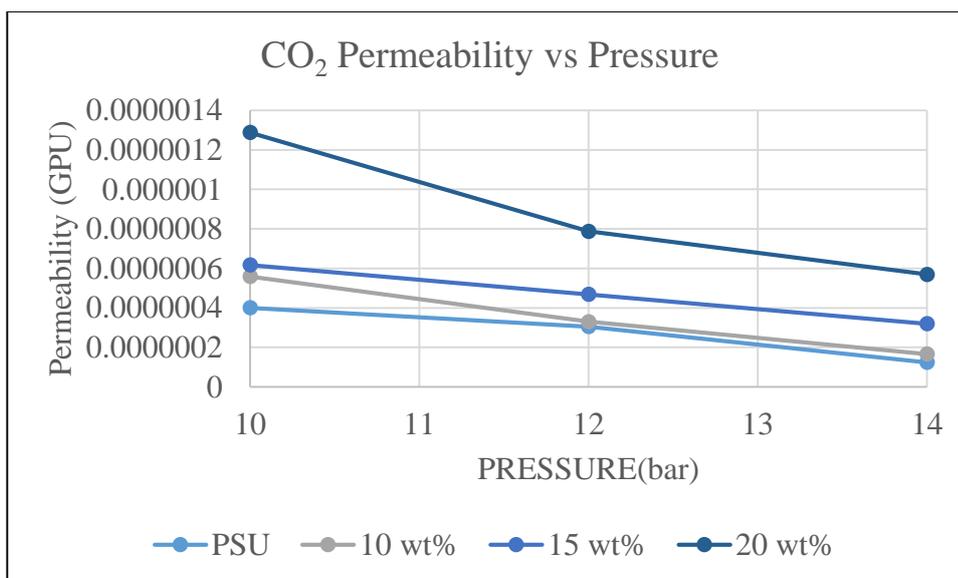


FIGURE 4.7 Graph of Permeability of Carbon Dioxide across Different Membrane at Different Pressure.

Base on some studies that has been done on glassy membrane by increasing pressure, permeability is decreasing. In this study, from Figure 4.7, graph shows that when the pressure increases, the permeability of CO<sub>2</sub> across the membrane decreases. It also can be observed from the figure 4.7, by adding IL from 10 to 20wt% the permeability is increasing. Base on the studies that has been done on blend ionic liquid polymeric membrane, IL improve the capture of more CO<sub>2</sub> due to its properties. This improvement also can be determined from characterization analysis. Although base on figure 4.8, Permeability of CH<sub>4</sub> vs pressure, shows same effect of pressure on permeability. However by adding IL to polymeric membrane it can be observed that by adding IL from 10 to 20wt% the CH<sub>4</sub> permeability is decreasing which according to some researches that prove IL doesn't let CH<sub>4</sub> to pass through.

TABLE 4.3 Permeability of Methane across Different Membrane at Different Pressure.

	Permeability of CH <sub>4</sub> at Different Pressure(GPU)			
Pressure(bar)	PSU	10 wt%	15 wt%	20 wt%
10	3.506E-07	3.287E-07	2.73E-07	1.0168E-07
12	2.795E-07	2.64E-07	2.525E-07	2.143E-07
14	1.201E-07	1.07E-07	8.66E-08	1.95E-08

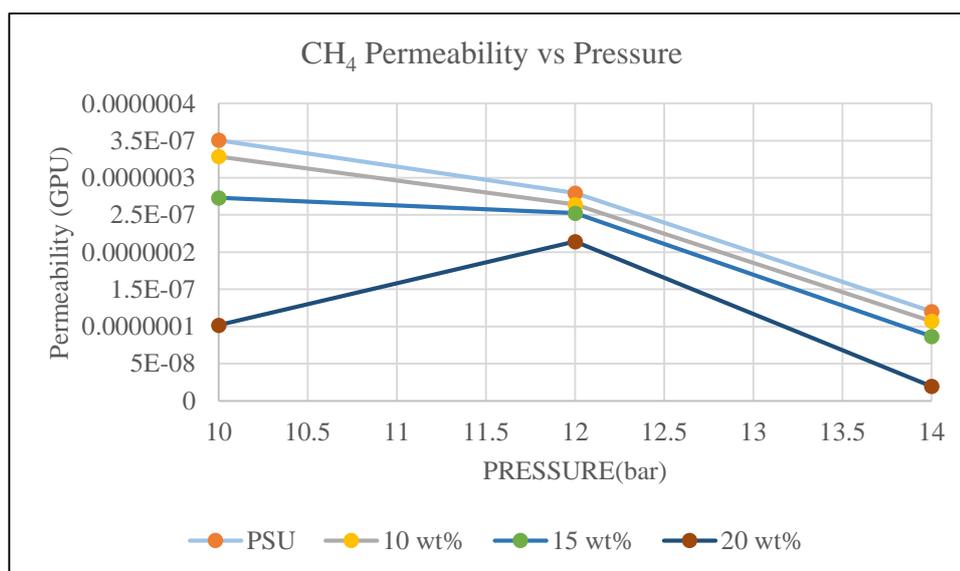


FIGURE4.8 Graph of Permeability of Methane across Different Membrane at Different Pressure.

From figure 4.9, selectivity vs pressure, it can be determined that pressure doesn't affect selectivity. Although from figure 4.10, selectivity vs concentration, it can be observed that by adding IL from 10 to 20wt%, the selectivity is increasing which the studies that has been done before prove this improvement.

TABLE 4.4 Selectivity of CO<sub>2</sub>/CH<sub>4</sub> across Different Membrane at Different Pressure.

Pressure(bar)	SELECTIVITY			
	PSU	10 wt%	15 wt%	20 wt%
10	1.14318311	1.70094311	2.26190476	12.6691581
12	1.09194991	1.25227273	1.85623762	3.67662156
14	1.03663614	1.54953271	3.69168591	29.1897436

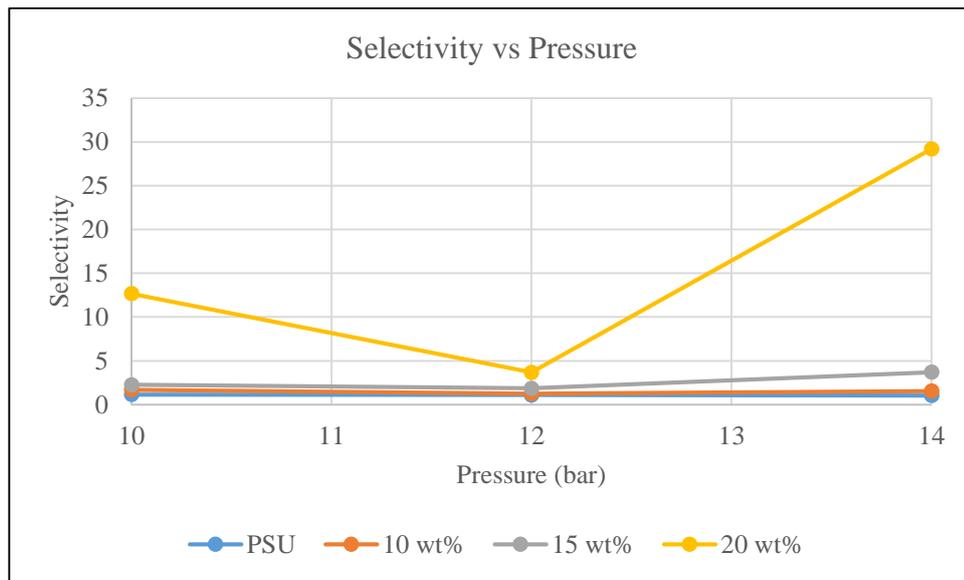


FIGURE4.9 Graph Selectivity of CO<sub>2</sub>/CH<sub>4</sub> across Different Membrane at Different Pressure.

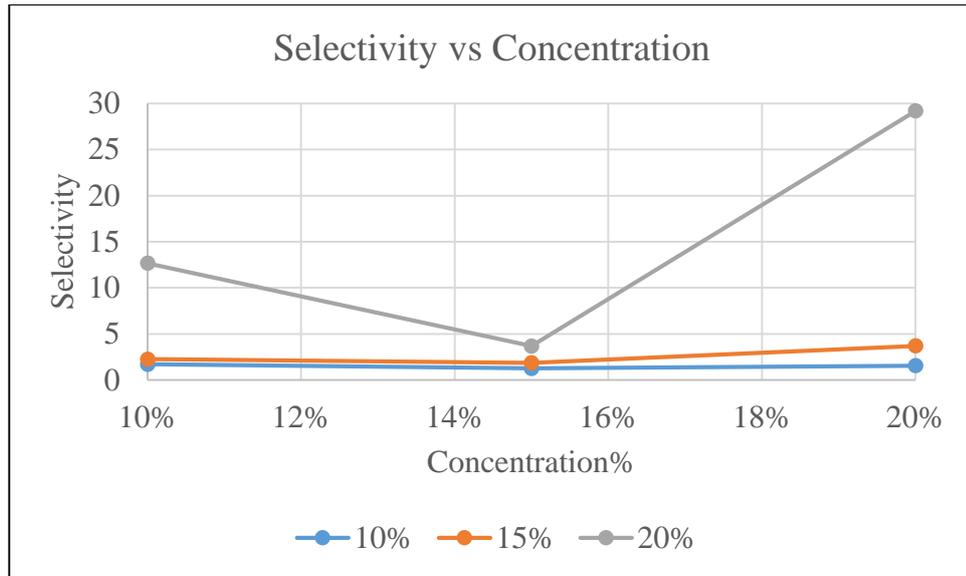


FIGURE 4.10 Selectivity vs Concentration

## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusion

Membrane gas separation has been applied for the treatment of natural gas. It has been shown a great potential for growth for acid gas removal and heavy hydrocarbon recovery. This is because the polymeric membranes applied in these applications have been successfully proven and efficient processes have been implemented. Membrane gas separation will grow in this market as the technology is increasing seen as commercially competitive. The gas fields of the future will be of lower quality with higher CO<sub>2</sub> and H<sub>2</sub>S content which shows the need of using membrane technology for gas sweetening.

In this study the base polymeric membrane and the enhanced membranes were synthesised successfully. In regards to second objective the characterisation of membranes has been done successfully in terms of morphology, composition and glass transition temperature. Based on SEM image results, from top view it can be seen that PSU membrane and enhanced membranes has nonporous and void free structure. According to FTIR analysis by addition of ([emim][CF<sub>3</sub>SO<sub>3</sub>]), there was an addition of some new bonds. Also from DSC analysis can be observed that glass transition has been increased. From gas performance analysis in two terms of permeability and selectivity, it can be observed that the permeability of CO<sub>2</sub> and CH<sub>4</sub> are both decreasing by increasing the pressure. Besides it can be concluded that by adding ([emim][CF<sub>3</sub>SO<sub>3</sub>]) with different concentration, the permeability of CO<sub>2</sub> increasing although the permeability of CH<sub>4</sub> decreasing. It also can be observed based on this study, the selectivity of membrane in 10 bar is increasing from 1.14 to 12.67 by addition of ([emim][CF<sub>3</sub>SO<sub>3</sub>]). The same changes can be observed in different pressure of 12 and 14 bar.

It can be determined that by addition of ionic liquid the two important parameters which are permeability and selectivity of membrane is increasing.

## **5.2 Recommendation**

As a recommendation, in regards to gas performance, it can be experienced in higher pressure. Also, the concentration of ionic liquid can be increased to see its effect of it on gas performance.

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