

Development of Polycarbonate Ionic Liquid Mixed Matrix Membrane

by

Muhammad Shamsul Azwan Bin Hassan

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Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

## **CERTIFICATION OF APPROVAL**

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Chemical Engineering Programme  
Universiti Teknologi PETRONAS  
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BACHELOR OF ENGINEERING (Hons.)  
(CHEMICAL ENGINEERING)

Approved by,

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(AP. DR. HILMI BIN MUKHTAR)

Universiti Teknologi PETRONAS

TRONOH, PERAK

May 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.

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(MUHAMMAD SHAMSUL AZWAN BIN HASSAN)

## ABSTRACT

The monetization of natural gas (NG) having high carbon dioxide (CO<sub>2</sub>) at more than 20% of the content currently facing challenges due to technology gap. The widely used technology, amine absorption can tolerate up to 10% of CO<sub>2</sub> in NG. In idea of filling the gap, blend of polycarbonate (PC)MMMs and EMIMIm were prepared at different loading for CO<sub>2</sub>/CH<sub>4</sub> separation. Each membrane was fabricated and dried under solvent evaporation at room temperature. Poor polymer-filler contact MMMs forming structure was observed using FESEM and improved polymer-filler in ILMMMs contact indicating ionic liquid miscibility and function in the membrane. TGA analysis showed all membrane contains minimal solvent at less than 1% suggesting the drying was efficient. All membranes were tested using single gas CO<sub>2</sub> and CH<sub>4</sub>. Result showed that ILMMMs had 3 times higher selectivity than MMMs at 4 bar and 7 times better reduction of CH<sub>4</sub> permeance. The effect of plasticization was also observed in all membranes while separation index is moderate the permeance is considered low. The preliminary results have shown improved polymer-filler contact using EMIMIm and technically improved the separation performance by restricting permeation of CH<sub>4</sub> through void in the membrane matrix. The potent membrane sample is IL5MM5 which is dense, stable selectivity and permeation at increasing pressure.

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## CHAPTER 1: INTRODUCTION

### 1.0 INTRODUCTION

#### 1.1 Background of Study

Sulphur oxide ( $\text{SO}_x$ ) and carbon dioxide ( $\text{CO}_2$ ) present in natural gas resources reservoir and this can be problematic because both are corrosive to equipment when dissolved in water to produce acid. The acid will slowly or rapidly corrode the pipeline depending on  $\text{CO}_2$  content in the raw gas then will cause leaking and maintenance cost is very high for offshore platform due to transportation issue.

Natural gas in commercial operations includes variable amounts of  $\text{CO}_2$  ranging from  $\text{CO}_2$ -free natural gas in Siberia to as high as 90%  $\text{CO}_2$  content in the Platong and Erawan fields in Thailand (Tan et al., 2011). The Natuna field in the Greater Sarawak Basin in Indonesia is the largest gas field in south Asia, with estimated 46 trillion cubic feet recoverable reserves. Unfortunately, it remains unexplored due to high  $\text{CO}_2$  content of 71% as reported by International Energy agency. In Malaysia,  $\text{CO}_2$  content in natural gas fields varies from 28%–87% and over 13 trillion cubic feet natural gas reserves are undeveloped due to high  $\text{CO}_2$  content (Darman, 2006).

It is required to reduce the composition to a desirable value as requested by the standard of operation which is different at different transport medium. Thus technology for  $\text{CO}_2$  separation is needed where there are several choices such as amine absorption and cryogenic distillation but high content acid gas causes degradation to amine and blockage in piping system in cryogenic which low temperature solidifies  $\text{CO}_2$ .

Gas separation membrane available uses polymeric modules which can't withstand high  $\text{CO}_2$  content due to plasticization effect at high pressure (Rahman, 2006) and unable to withstand extreme pressure and temperature. Individually polymeric membrane has lower selectivity than inorganic membrane but better in strength due to elasticity while inorganic membrane is ductile. By combining polymeric membrane strength and inorganic membrane selective property, mixed matrix membrane is produced.

Mixed Matrix Membrane (MMM) is defined as a membrane consists of combination of two or more chemically different materials with a distinct interface between them (Rahman, 2006). The continuous phase is called the matrix which is the polymer matrix. The other component is filler for reinforcement often inorganic particulates which alter the membrane matrix properties in term of strength and the permeability. Adding CO<sub>2</sub> absorber ionic liquid is expected to further enhance the performance of MMM to separate high CO<sub>2</sub> content in natural gas especially in gas fields around Asia region.

## 1.2 Problem statement

High CO<sub>2</sub> presence (Table 1.2) in natural gas reduces the calorific value of the gas as CO<sub>2</sub> is a product of combustion and generally the maximum allowable CO<sub>2</sub> content in sale gas is 3% mol. However, the problem occurring is the medium and method to remove CO<sub>2</sub> from natural gas is costly and use high energy which is inefficient.

Table 1.2: NG concentration in different NG types (Enbridge, 2014)

Component	Typical NG, % mol	High CO <sub>2</sub> NG, % mol	Sale gas, % mol
CH <sub>4</sub>	70-90	60-80	95
C <sub>2</sub> -C <sub>4</sub>	0-20	0-20	2.7
CO <sub>2</sub>	0-8	> 20	0.7
N <sub>2</sub>	0-5	0-5	1.6
H <sub>2</sub> S	0-5	0-5	trace
Others	trace	trace	trace

Therefore, this project was designed to develop a membrane that can withstand high CO<sub>2</sub> for use at offshore platform with proper membrane separation system which can be built offshore as the system require much smaller space than amine separation system even in performance wise. Thus it will reduce CO<sub>2</sub> transport cost by removal at off-shore platform before being transported to on-shore for further purification.

## 1.3 Objectives

For this final year project, there were several objectives to be achieved through out the period of study. The objectives were listed as the following:

- 1.3.1 To prepare flat sheet polycarbonate (PC) pure membranes, PC mixed matrix membranes (MMM), and PC ionic liquid mixed matrix membranes (ILMMM).

- 1.3.2 To characterize the morphologies of the membranes and determine component presence in the membranes such solvent content and IL presence in the membrane.
- 1.3.3 To characterize the membranes performance produced by permeability test.

#### **1.4 Scope of study**

A few scopes that have been outlined in order to achieve the objectives of this project are as follows:-

- 1.4.1 Preparation and development of flat sheet polycarbonate (PC) pure membranes, PC mixed matrix membranes (MMM), and PC ionic liquid mixed matrix membranes (ILMMM). Pure PC membrane is to be prepared by dissolving 15 weight % PC in 85 weight % dichloromethane (DCM), casted using casting machine and dried in closed area at room temperature. MMMs will be added with same proportion of pure membrane, plus 5 and 10 weight % of carbon molecular sieve (CMS) base on PC's weight respectively. Using MMMs composition, EMIMIm will be added 5 and 10 weight % base on PC's weight respectively. Thus 7 samples are going to be fabricated.
- 1.4.2 Morphological studies on flat sheet membrane prepared using FESEM is to study the surface and cross-section of the membrane. Voids can be seen clearly using this characterization method which determines membrane porosity as porous membrane often lead to low selectivity membrane due to both CO<sub>2</sub> and CH<sub>4</sub> passes through the membrane unhindered.
- 1.4.3 Studying the functional group using Fourier Transform Infrared Spectrometer (FTIR) to determine component presence and functional group change probable due to reaction. FTIR result will form a graph

where the functional group can be determined at different wavelength shown in the graph.

1.4.5 Thermogravimetric Analysis (TGA) will be used to component presence by weight % in the membrane through weight loss at boiling point for volatile and decomposition temperature of non-volatile component. Due to large boiling temperature difference of DCM (39.6°C), PC (784.3°C) and EMIMIm (190.5°C) the result will DCM loss from the membrane but expected to be minimal and detectable presence of EMIMIm.

1.4.2 Permeability tests will be done on the prepared membranes using bench scale permeation test unit at 4-8 bar pressure by increment of 2 bar for each reading taken where 10 minutes stabilization time given for every change of pressure and samples. The tests will provide the best pressure parameter to be used with the membrane and the effect of pressure change on membrane permeability.

## **1.5 The relevancy of the project**

Global gas demand was estimated at 3427 billion cubic metres (bcm) in 2012, up 2% from 2011 levels as International Energy Agency reported. Gas demand has increased by around 800 bcm over the last decade, or 2.8% per year. Gas has a 21% share in the global primary energy mix; behind oil and coal. Membrane technology can also minimize the size of an amine system. Polymeric membrane has been used commercially in CO<sub>2</sub>/CH<sub>4</sub> separation applications. Therefore, it is relevant to study mixed matrix membrane for CO<sub>2</sub> separation which can be applied in natural gas purification for performance enhancement. With more basic understanding on the material composition, fabrication parameters and further enhancement to MMM by addition of ionic liquid, the commercialization of MMM for gas separation might be technically and economically feasible.

## **1.6 Feasibility of the project**

Project research can be done within time frame but it should not be done carelessly just to be in line with the planned duration. Research project require quite a lot of time as even the work is organize, studying and observing the results may require more time than expected. Therefore, the project shall be completed within the time line; 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 needed are available in the department and the characterization equipment present at the university.

## CHAPTER 2: LITERATURE REVIEW

### 2.0 LITERATURE REVIEW

#### 2.1 Membrane Separation

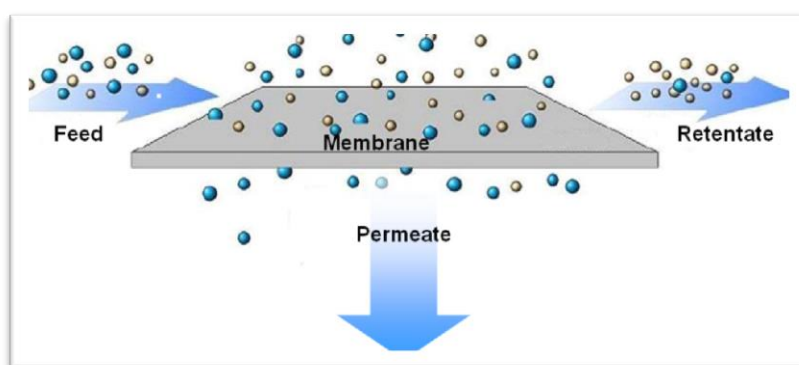


Figure 2.1.1: Basic concept of membrane separation process

Membrane separation involved partial separation of a feed comprising of mixture of two or more components through a membrane which acts as semipermeable barrier which allows one component of a mixture to pass through the membrane freely while hindering the other components permeation. In practical, the separation of  $\text{CO}_2$  from  $\text{CO}_2/\text{CH}_4$  gas stream using polymeric membrane always come at a cost with hydrocarbon loss depending on membrane selectivity. There are different gas separation mechanisms associated with different type of membrane materials and type of membrane such as dissolution-diffusion and size-selective exclusion and structure-selective exclusion.

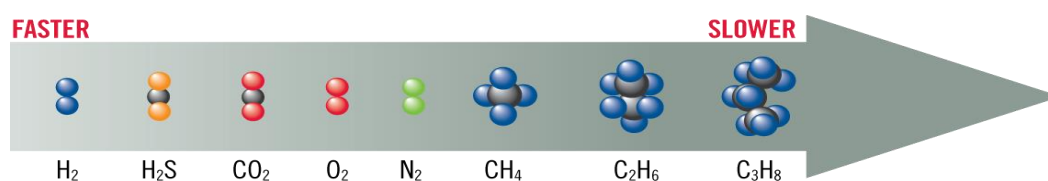


Figure 2.1.2: Relative transport rates of gases through membranes

Membrane separation has been developed through the last 40 years and had been used since then to separate different type of gasses pair. Different type of polymer such as rubbery type cellulose acetate and glassy type polyimide and different form of membrane were used to achieve the separation goal including spiral wound membrane and hollow fibers membrane.

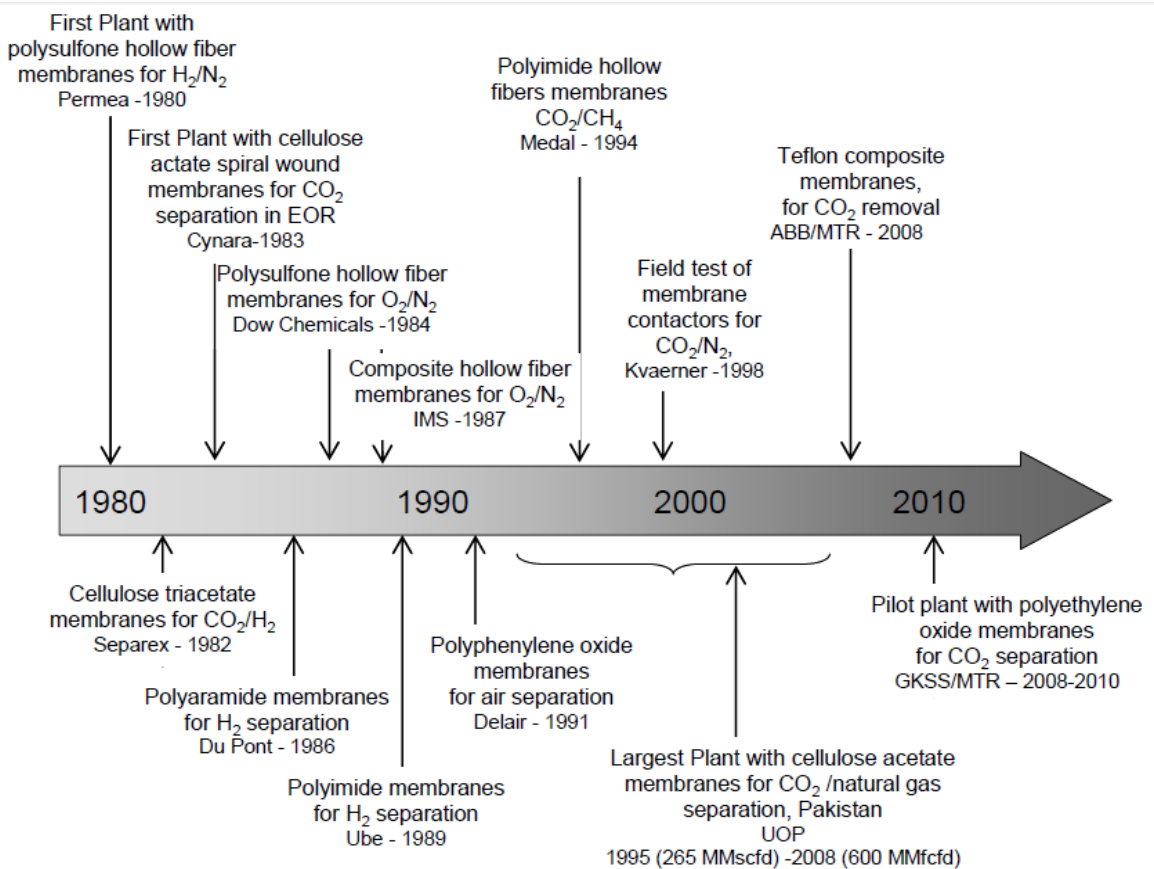


Figure 2.1.3: Membrane system timeline

## 2.2 Polymeric Membrane

Polymeric membranes of dense type or asymmetric membranes could be further categorized based on rubbery or glassy polymers. Rubbery polymer is soft and elastic due to the flexibility of the polymer backbone segments that can rotate freely around their axis. Glassy polymer is a rigid and tough polymer resulted from the steric hindrance along the polymer backbone that prohibits the rotations of polymer



segments (Ismail, Goh, et al. 2009). The disadvantage of this type of membrane instead having good mechanical strength and acceptable combination of gas permeability and selectivity is the polymer deteriorates when used in harsh environment and high temperature due to its thermal limitation. Plasticization which is due to high solubility gases such as CO<sub>2</sub> and H<sub>2</sub>S are seriously affecting the surface of polymeric membrane (Rahman, 2006).

Even though it is said to have acceptable combination of gas permeability and selectivity, the trade-off between the two properties had been identified by Robeson meaning that one of the two properties will decrease if the other is high. Commercially available polymeric membrane (blue dots) lies below Robeson upper bound curve below.

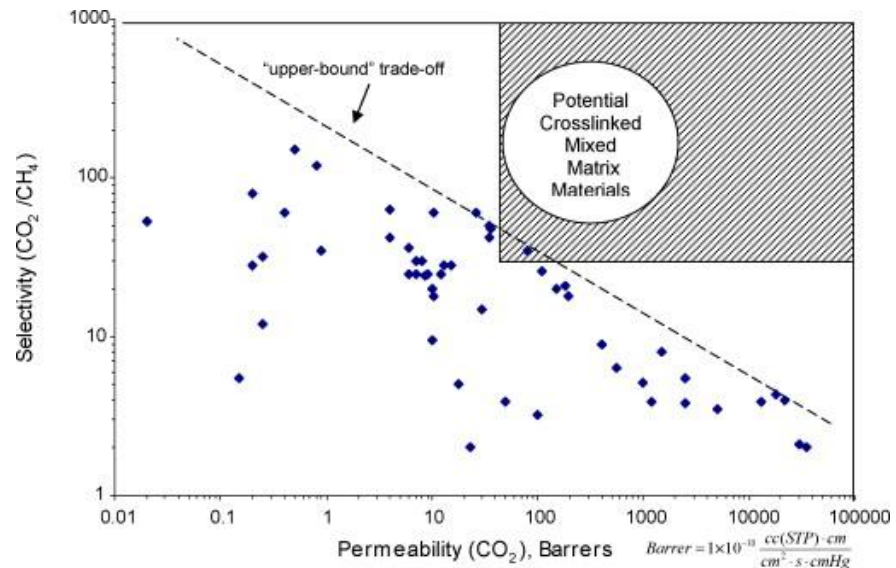


Figure 2.2: Robeson “upper bound” curve for CO<sub>2</sub>/CH<sub>4</sub> separation

### 2.3 Inorganic Membrane

Inorganic membrane was studied and manufactured in order to overcome the limitation of polymeric membrane. Research is undergone for this alternative membrane which made from metals, ceramics or pyrolysis (heating at very high temperature under inert environment) carbon or polymer. According to Li, Zhou et al. (2007), inorganic membrane has attractive features such as high solvent-resistivity

which prevents deterioration of membrane from solvent vapour diffusion, high thermal and pore structure stability. Moreover, these inorganic membranes are found to lie well above the upper bound polymeric trade-off curve and in or near the commercial attraction region (Zimmerman et al. 1997).

However, these types of membranes are far from perfection where handling issues such as brittleness has greatly bounds their cost-effective use as continuous membranes in module form. It was also found that these materials are difficult to process and expensive to fabricate (Vu, Koros and Miller, 2003). The expensive fabrication has to deal with the heating when processing, thus modifications must be done to the fabrication system to get acceptable processing condition suggested and defect-free membrane.

#### 2.4 Mixed Matrix Membrane (MMM)

Hindered by the upper bound trade-off of polymeric membrane , high production cost and handling issue (e.g. inherent brittleness) in manufacturing continuous and defect-free ceramic membranes, (Chung et al. 2007). MMM has been proposed by taking the advantages of both polymeric and ceramic membrane for gas separation.

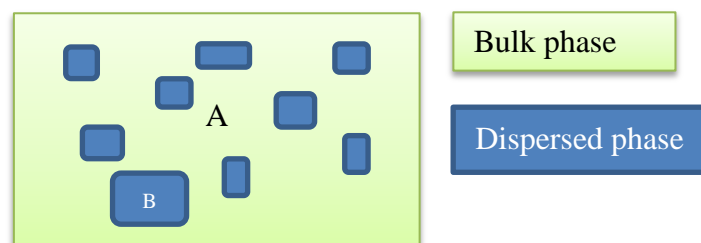


Figure 2.4.1: Schematic diagram of a mixed matrix membrane (MMM).

The bulk phase (phase A) is typically a polymer; the dispersed phase (phase B) represents the inorganic particles, which may be zeolite, carbon molecular sieves, or nano-size particles. MMMs have the potential to achieve higher selectivity, permeability, or both relative to the existing polymeric membranes, resulting from the addition of the inorganic particles with their inherent superior separation

characteristics. At the same time, the fragility inherent in the inorganic membranes may be avoided by using a flexible polymer as the continuous matrix (Chung et al. 2007).

Table 2.4.2: Example of MMM composition, additives, gas pair and performance (Goh et al. 2011)

MMM Composition		Details		
Polymer	Filler	Coupling agent/additives	Gas pair	Selectivity
Polyethersulfone (PES)	SAPO-34	HMA	H <sub>2</sub> /CO <sub>2</sub>	4.64
Polysulfone (PSU)	Zeolite 3A	APTMS	H <sub>2</sub> /CO <sub>2</sub>	41.9
Polycarbonate (PC)	Zeolite 4A	p-NA	CO <sub>2</sub> /CH <sub>4</sub>	51.8
PEEK	Zeolite NaA	DEA	O <sub>2</sub> /N <sub>2</sub>	4.2

## 2.5 Ionic Liquid Mixed Matrix Membrane (ILMMM)

Room temperature ionic liquids (RTILs) are organic salts that are liquid at or below 298 K and has been determined to have negligible vapour pressure leading to highly stable structure since IL is non-volatile (Noble & Gin, 2010). Due to the non-volatile properties and attention for CO<sub>2</sub> capture because they can be designed to possess high CO<sub>2</sub> affinity (Hao et al. 2012) IL suits in many application of membrane system such as in membrane contactor, supported liquid membrane and mixed matrix membrane (MMM). For producing ILMMM the method can be by impregnating IL in MMM through miscible mixing, polymerization of IL by coating on MMM surface. There are a lot of researches currently done to obtain reliable ILMMM where the membrane will probably possess high separation and permeability properties.

Table 2.5: Permeability and selectivity values in IL components(Scovazzo,2009)

Type of Ionic Liquid	[EMIM]TfO	[EMIM]Tf <sub>2</sub> N	[EMIM]dca
Gas type	Permeability(Barrer)		
CO <sub>2</sub>	1171	1702	1237
CH <sub>4</sub>	63	139	53.8
Selectivity	18.5	12.2	23

## 2.6 Membrane Technology for Gas Separation

Gas separation membranes were first commercialized in 1977 when Monsanto released their hydrogen recovery system (Bos et al. 1998). The success of this and the other gas membrane system by Cynara, Separex and Generon (Bos et al. 1998) lead to substantial innovation during the 1980s and 1990s into membrane material. Acid gas removal from natural gas was one of the areas of interest. Commercial acid gas separation from natural gas using membrane was first introduced by Monsanto Prism System (Permea) in early 1980s. The development of membrane for CO<sub>2</sub>/CH<sub>4</sub> has grown rapidly since then which led to introduction to asymmetric membrane, composite membrane and aromatic membrane commercialization by certain company which developed the respective membrane.

Most of the membranes used in gas applications today are still in polymeric solution diffusion materials and among these, the glassy materials separating according to diffusion mechanism are dominating the market. The selection of membrane material and module design will be governed by the gas mixture and the process conditions such as volumes, pressures, temperature, and product purity intended. The industry membrane application is mostly focusing on getting high purity nitrogen, recovery of hydrogen from gas streams and removal of carbon dioxide. The table in the next page provides an overview of commercial-scale membrane suppliers and products of separation from membrane technology.

Table 2.6: Commercial-scale membrane supplier for gas separation (Hägg, 2009)

<b>Company</b>	<b>CO<sub>2</sub></b>	<b>H<sub>2</sub></b>	<b>O<sub>2</sub></b>	<b>N<sub>2</sub></b>	<b>Other*</b>
<b>A/G Technology (AVIR)</b>	x		x	x	
<b>AGA (Linde)</b>			x	x	
<b>Aquilo (Whatman)</b>				x	
<b>Asahi Glass (HSEP)</b>			x	x	
<b>Borsig</b>					x
<b>Cynara (Dow)</b>	x				x
<b>Generon (Dow)</b>			x	x	x
<b>Grace MS (Aker-Kvaerner)</b>	x	x			x
<b>Medal (Du Pont/ Air Liquide)</b>	x	x		x	
<b>Membrane Techn. And Research</b>				x	x
<b>Nitto Denko</b>	x				x
<b>Osaka Gas</b>			x		x
<b>Permea (Air Products)</b>	x	x	x	x	x
<b>Praxair</b>			x	x	
<b>Toyobo</b>			x		x
<b>Ube Industries</b>	x	x	x	x	x
<b>Union Carbide (Dow)</b>	x	x	x		
<b>UOP (Separex)</b>	x	x			x

\*solvent recovery, dehumidification, pervaporation, and helium recovery membranes

Many researches have been done in the last 40 years since the first commercial membrane introduced to improve membrane performance including finding new membrane materials and new method to produce membrane, but only recently, enhancement of selectivity beyond intrinsic selectivity of the polymer membrane have become the main factors of the study (Sunarty, 2004). The real challenge for industrial application was to fabricate membrane with both higher selectivity and permeability while having high durability to withstand harsh environment such as high pressure and high temperature of gas stream from these polymers. Henceforth, vast studies and experiments were centred on developing high performance membrane for gas separation such as MMM and ILMMM.

## CHAPTER 3: METHODOLOGY

### 3.0 METHODOLOGY

#### 3.1 Material Selection and Dope Preparation

Material or chemicals for preparing the membranes were CALIBRE™ polycarbonate (PC) pellets from Merck, solvent dichloromethane (DCM), ionic liquid EMIMIm and carbon molecular sieve (CMS), bought from Sigma-Aldrich. Polycarbonate is known for its excellent physical properties for a glassy polymer such as high boiling point at 784.3°C, melting point of 225°C, excellent toughness and more importantly being selective. PC also tolerant to mild acids and base in which carbonic acid formed in the natural gas is tolerable. Dichloromethane was chosen as the solvent to apply dry method to get non-porous membrane because DCM easily evaporated in room temperature thus solvent removal can be maximized but control needed to prevent solvent loss during mixing. CMS is widely used in adsorption of CO<sub>2</sub> and was used as the filler in MMM and ILMMM. CMS porous nature will enhance the permeation rate but still being selective due to the pore size exclusion and the superior adsorption capability. To further enhance the membrane performance, IL was blended into the membrane sol as IL chosen was superb CO<sub>2</sub> absorber. EMIMIm was reported to increase about 150% CO<sub>2</sub> permeance by Dzeti, Hilmi and Zakaria, (2013) in comparison with pure polyethersulfone (PES) polymeric membrane and EMIMIm blended with PES polymeric membrane. The ILMMM samples were expected to give better performance with higher selectivity and permeance compared to pure PC membrane and MMM.

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

Table 3.1: Pure PC, MMM and ILMMM compositions and name code.

Sample Code	Weight of PC, g	Weight of DCM, g	EMIMIm,( weight % of PC)	Weight of CMS, g (weight % of PC)
PM (Pure)	4.50	25.5	-	-
MM5	4.50	25.5	-	5
MM10	4.50	25.5	-	10
IL5MM5	4.50	25.5	5	5
IL10MM5	4.50	25.5	10	5
IL5MM10	4.50	25.5	5	10
IL10MM10	4.50	25.5	10	10

The procedure for ionic liquid MMM polycarbonate dissolved in DCM, incorporated with CMS and EMIMIm are as following:

- I. Polycarbonate pellets and ground CMS were dried in the drying oven for 24 hours.
- II. DCM was weighed into 50ml Schott Duran containing magnetic bar and added with weighed EMIMIm (for IL coded samples). The mixture was stirred for 30 minutes at stirring speed number 2.
- III. CMS was weighed and added into the bottle while stirring at speed number 1.
- IV. The bottle neck was covered with covering film to reduce solvent loss.
- V. The mixture was put into sonication for 5 minutes at room temperature.
- VI. The bottle was dried using tissue.
- VII. 0.45 g or 10% total of PC was added into the mixture and stirred for 30 minutes for surface priming process.
- VIII. The remaining polycarbonate was added 1 g every 15 minutes while stirring until fully dissolves. The dope was left for 5 hours stirring.
- IX. The magnetic bar was removed and the dopes were degassed for 1 hour before casting to remove bubbles and to prevent phase separation.

### **3.2 Surface Priming**

To help promote the polymer/particle interface adhesion, a surface priming protocol (as is at Step VI) was suggested by Mahajan (2000) in which the particles were coated with an ultrathin layer of the matrix polymer. This method can reduce stress at the polymer-particle interface. In the priming technique, the particles are mixed in a suitable solvent and a small percentage of the total polymer used to form a membrane polymer solution (typically 5-10 wt. %), is added to a suspension of CMS particles prior to the addition of bulk polycarbonate.

### **3.3 Casting and Drying of Membrane**

Casting is the process of forming flat-sheet membrane from polymer dope using flat sheet membrane casting unit in the laboratory. The half of 30 g polymer dope was poured on a dry flat glass and the casting knife (thickness/gap to glass plate at 150 $\mu$ m) was then moved using automated motor at projected speed. The membrane film was moved into a closed area at room temperature immediately. Drying process was done for 24 hours to allow evaporation of DCM. The parameters controlled were the speed of glass plate passing through casting knife (casting speed), the thickness (gap between glass plate and casting knife) and closed area to prevent crack formation due to rapid solvent evaporation forced by moving air. Membrane was cut and dried for another 24 hours before permeation test was done.

### **3.4 Morphological Characteristic Studies**

The other characterization of the polymer membrane done was morphological studies using Field Emission Scanning Electron Microscope (FESEM) to observe the surface and cross-section of the membrane, the thickness of the membrane, void existence, impurities existence, filler size, and defect on surfaces. With limited usage



time and sophistication of the machine, only 2 samples can be analysed using FESEM.

The sample was cut in dimension of 0.5-1cm width and 5-8cm length. Then the sample was cut in two pieces with a  $\frac{3}{4}$  and  $\frac{1}{4}$  lengths. The longer piece was used for cross-section morphology and the other was for surface morphology. To study the cross-section morphology, the flat sheet membrane with longer dimension was soaked into an alcohol solution before liquid nitrogen immersion to prevent membrane structure deformation during sample preparation. After soaking for a while in the alcohol, the membrane was bent, the end of bent part was immersed into the liquefied gas liquid and using forceps the membrane was cut rapidly to get the cross-section of the membrane for scanning.

The membrane cross-section was attached on the side of the sample holder using double-sided tape and labelled accordingly as both 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.

### **3.5 Fourier Transform Infrared Spectrometer (FTIR)**

FTIR test was required to determine the functional groups that presents in the membrane. The method used was KBr pellet method by preparing 13 mm-diameter pellets. Approximately 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 pronounce the related main functional group in PC, DCM (if there is trapped solvent), CMS and EMIMIm. For PC, carbonyl group (C=O) was expected to give characteristic absorption of  $1670-1820\text{ cm}^{-1}$  with strong intensity while for DCM were C-H and C-Cl stretches. S=O characteristic absorption characteristic was expected from EMIMIm.

### 3.6 Thermogravimetric Analysis (TGA)

TGA is a technique that measures the change in weight of a sample when it is heated, cooled or held at constant temperature. 4 samples were tested and the amount of membrane samples needed were about 10-20 mg each which 5-20% weight loss was expected from each samples. The heating temperature range was 20°C to 800°C with 10°C/minute and nitrogen gas purge due to DCM room temperature evaporation and boiling point of 40°C for lower limit. For upper limit was based on PC boiling point of 784.3°C. The gradual weight loss based on the temperature will determine the component.

### 3.7 CO<sub>2</sub>/CH<sub>4</sub> Single Gas Permeation Test

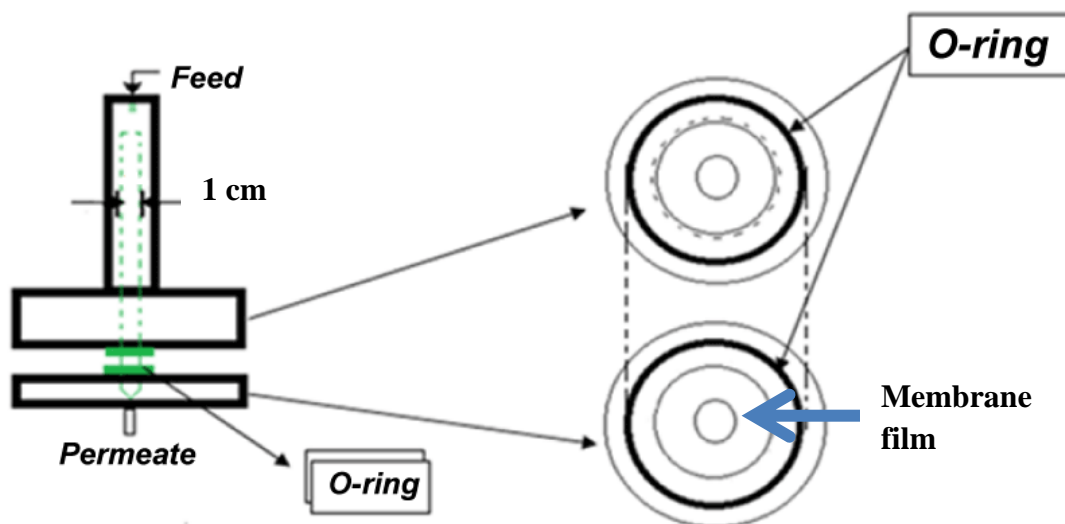


Figure 3.4: Schematic permeation test unit cell (omicsonline.org)

The membrane was cut into round shapes, placed at the casing (shown by blue arrow) beneath the O-ring and tested for permeation study, the testing equipment was represented by the schematic diagram where the mechanism was passing the feed gas from top (red arrows) or to the surface of the membrane and the O-ring used for leak prevention at constant feed gas pressure. In this project, the 5 flat sheet membranes were fed with CH<sub>4</sub> and CO<sub>2</sub> each at 4 to 8 bar pressure with 2 bar increment for each reading. CH<sub>4</sub> was used first as CO<sub>2</sub> may cause plasticization and defect the membrane structure. For each type of gas, pressure and sample used, the permeation was left for 10 minutes for conditioning the flow. Using bubble flow meter, permeate volumetric

flow rate was measured for 3 times each. Using Fick's Law permeation rate and selectivity were calculated in Excel spread sheet.

### 3.8 Project Key Milestones and Gantt chart

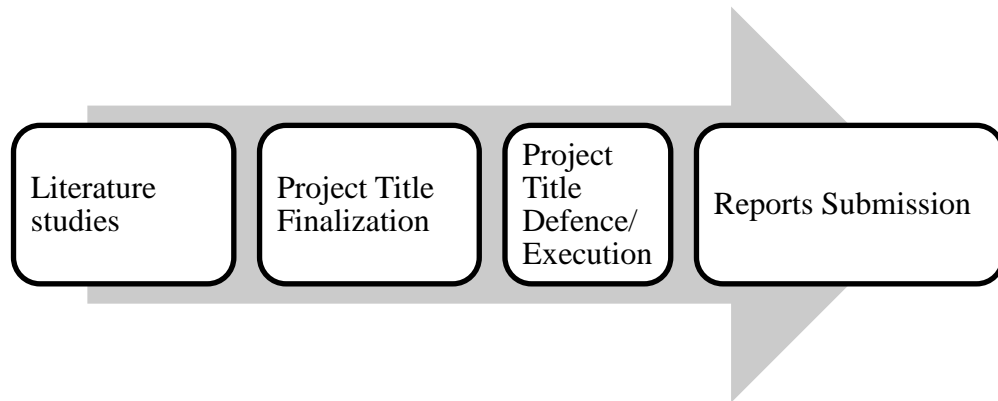


Figure 3.8.1: Key milestones

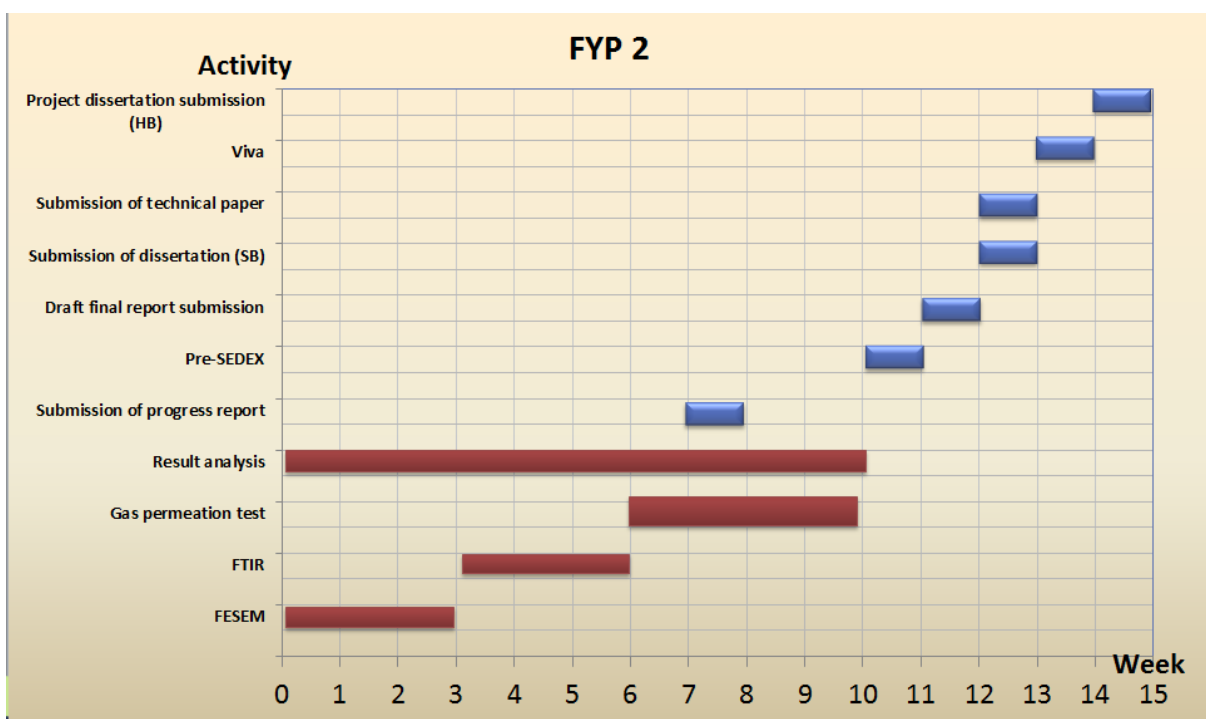
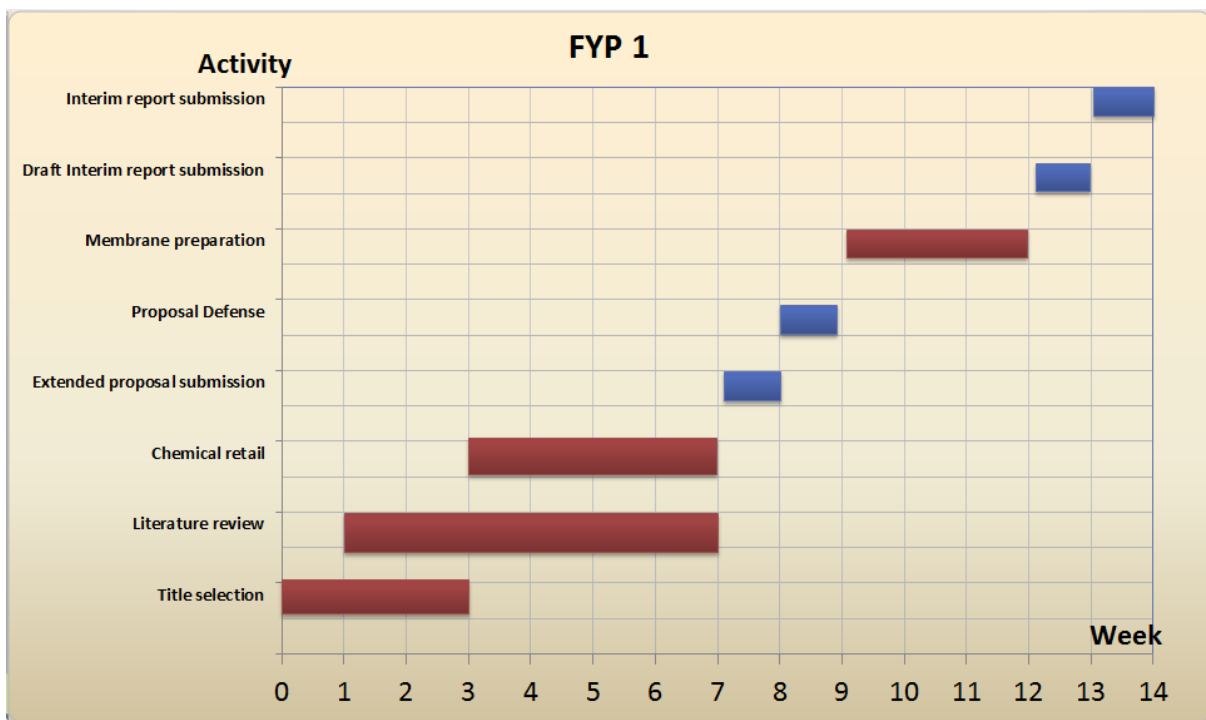


Figure 3.8.2: Gantt Charts

## CHAPTER 4: RESULT AND DISCUSSION

### 4.0 RESULT AND DISCUSSION

#### 4.1 Physical observation of casted membrane



Figure 4.1a: Pure PC membrane

Figure 4.1a shows the membrane formed bends. This problem might be caused by imbalance membrane thickness and the rate of solvent evaporation on top and bottom of the membrane was not the same as the bottom membrane layer wasn't exposed to air. This problem was countered by covering the membrane on the edges and surface with light load after the membrane was dry and at the same time reducing the membrane surface contact with air to stabilize solvent evaporation.

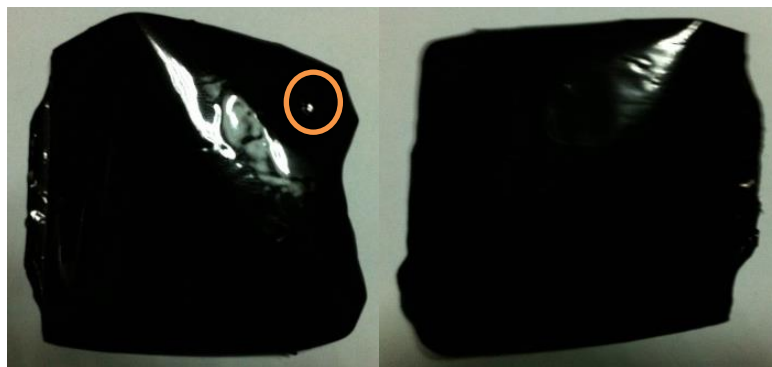


Figure 4.1b: Mixed matrix membranes (left MM5, right MM10)

Figure 4.1b shows both membranes had the same bending issue as pure PC but poor pouring procedure when casting lead to major defect where a large void formed (in

circle). From the white part from lighting effect it was observed that MM5 bends more than MM10 suggesting 10 weight % CMS content lead to a stronger membrane.



Figure 4.1c: 5 weight % EMIMIm added MMMs ( Left IL5MM5, right IL5MM10)

Figure 4.1c shows MMMs containing 5 weight % EMIMIm formed good membranes where IL5MM5 contains 5 weight % CMS while the other was 10 weight % based on PC weight. IL5MM10 surface was uneven at the end of the membrane (circled and are not void or holes) probably due to rapid solvent loss during the front part being casted by the casting blade. The minor solidified area was pushed behind by the casting blade and dried normally with the remaining surface area. The wrinkled part was formed at the side of glass plate and can be neglected.



Figure 4.1d: 10 weight % EMIMIm added MMMs ( Left IL10MM5, right IL10MM10)

Figure 4.1d shows membrane containing 10 weight % EMIMIm but 5% and 10% CMS composition respectively. IL10MM5 formed smooth surface with cracks compared to IL10MM10 which is coarse and shattered even when the procedure was repeated. EMIMIm was observed to fastened the peel-off time between glass plate and membrane.

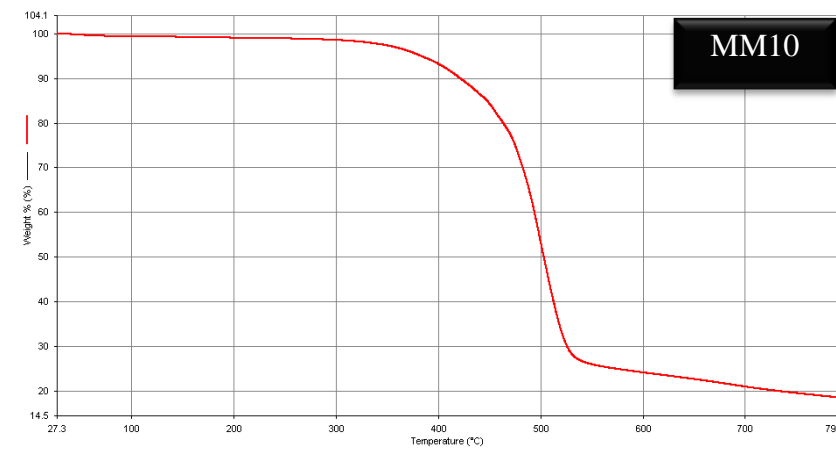
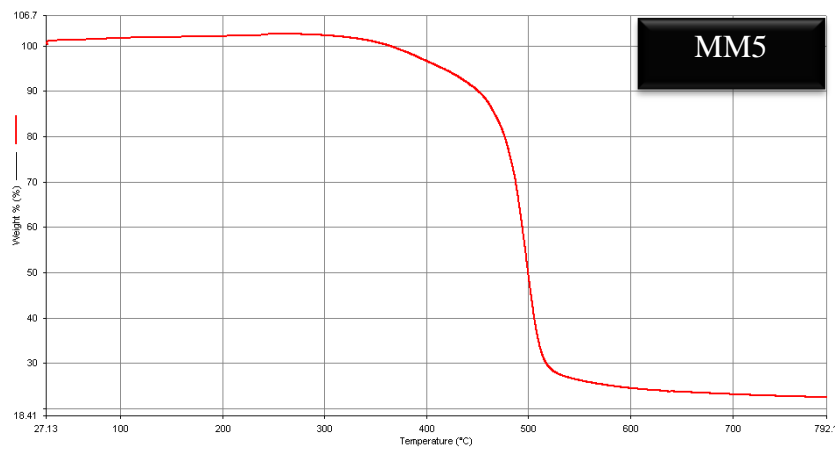
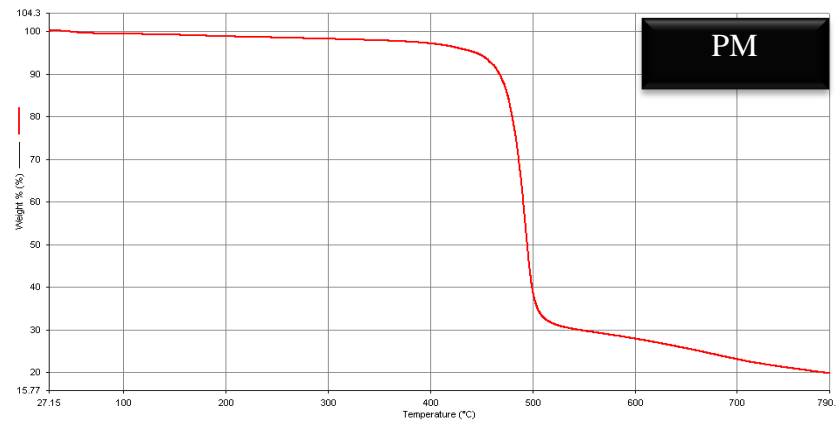
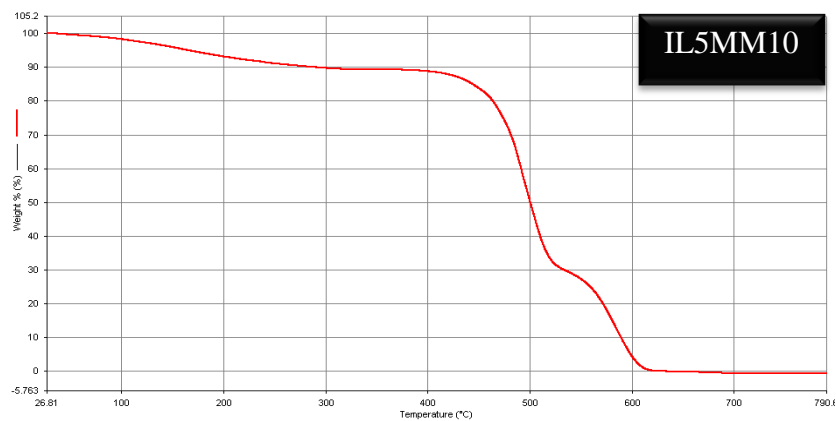


Figure 4.2: Thermo Gravimetry Analysis Results

## 4.2 Thermogravimetry Analysis Results

Figure 4.2 in appendices shows Thermogravimetric analysis (TGA) for fabricated polymeric membrane PM; MMMs MM5 and MM10; and ILMMM, IL5MM10. TGA provides measurement of mass change in materials that are associated with transition and degradation due to change in temperature or thermal change. Except IL5MM10, all other samples PM, MM5 and MM10 start to have weight reduction as soon as heating introduced due to low solvent boiling point and the weight percent loss after 45°C was not exceeding 1% suggesting DCM presence in membrane was minimum.

The component loss started above 300°C where PC flash ignition point range from 375-467°C for all membrane without ionic liquid EMIMIm. IL5MM10 analysis shows the weight loss happens earlier due to ionic liquid loss above 200°C thus PC loss from IL5MM10 occurs at lower weight percentage than other samples tested. Sharp slope at above 400°C occurs to all samples where PC loss is highest between its degradation points 420°C-620°C.

## 4.3 FTIR Analysis Results

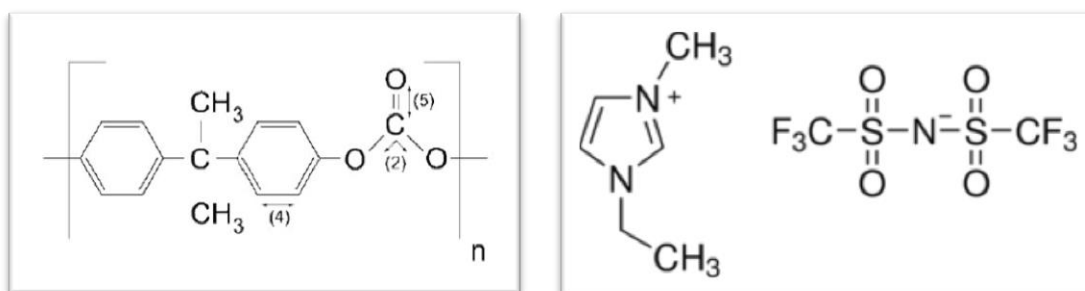


Figure 4.3: Chemical Structure of PC (left) and EMIMIm (right)



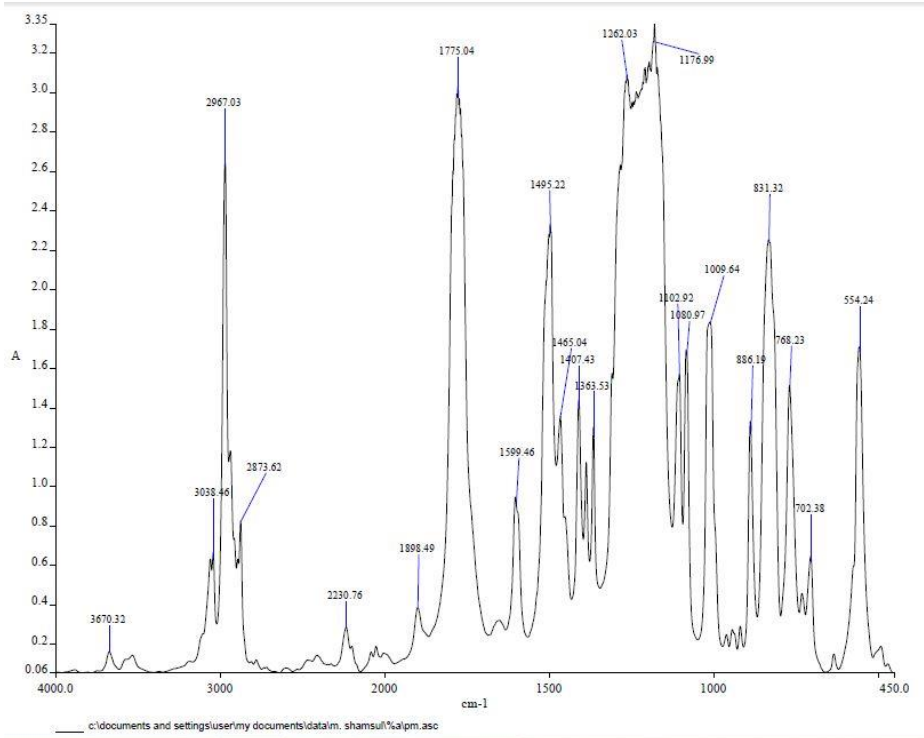


Figure 4.3.1: PM FTIR Graph of Absorption

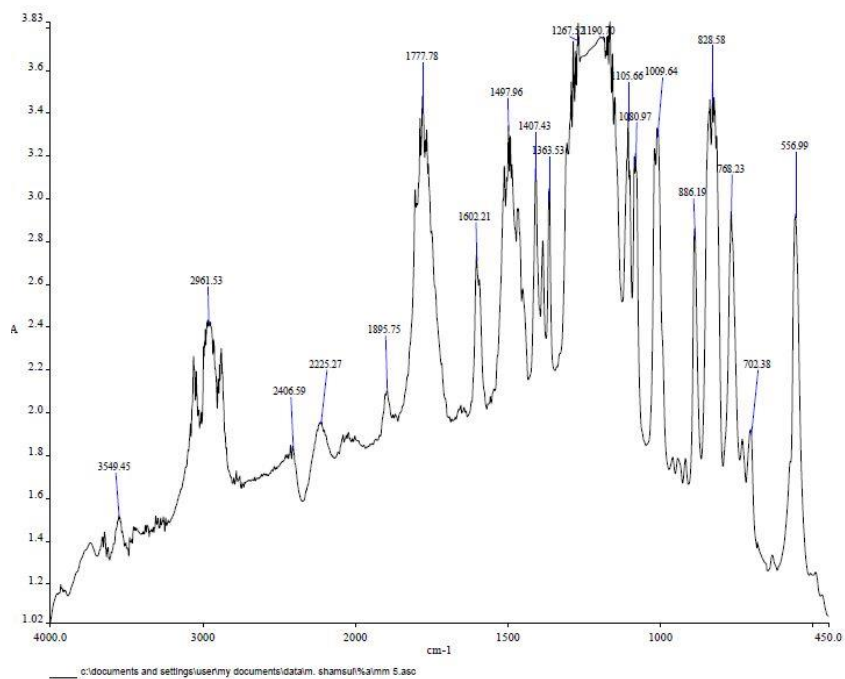


Figure 4.3.2: MM5 FTIR Graph of Absorption

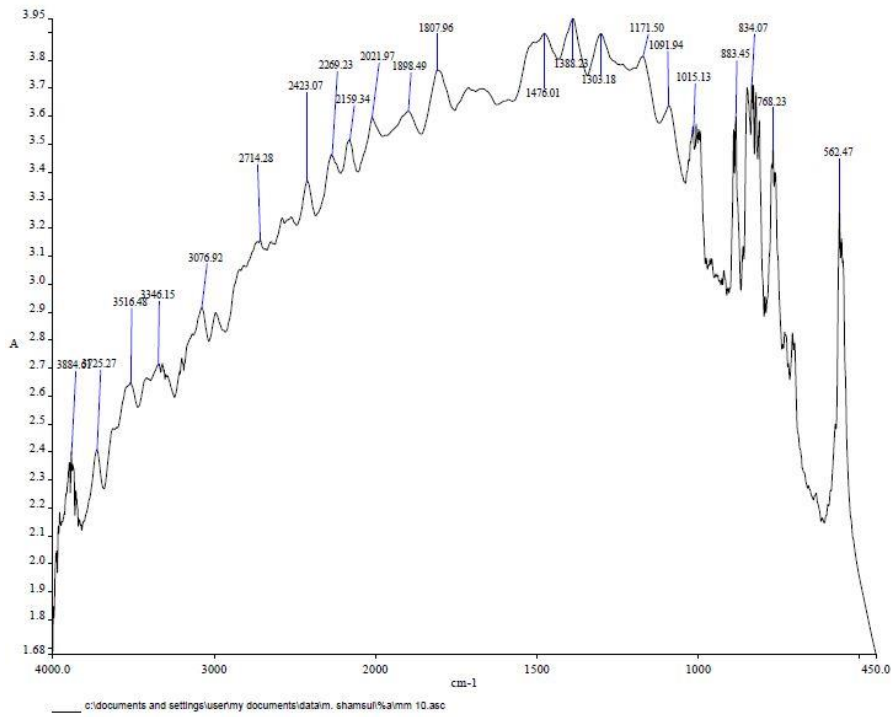


Figure 4.3.3: MM10 FTIR Graph of Absorption

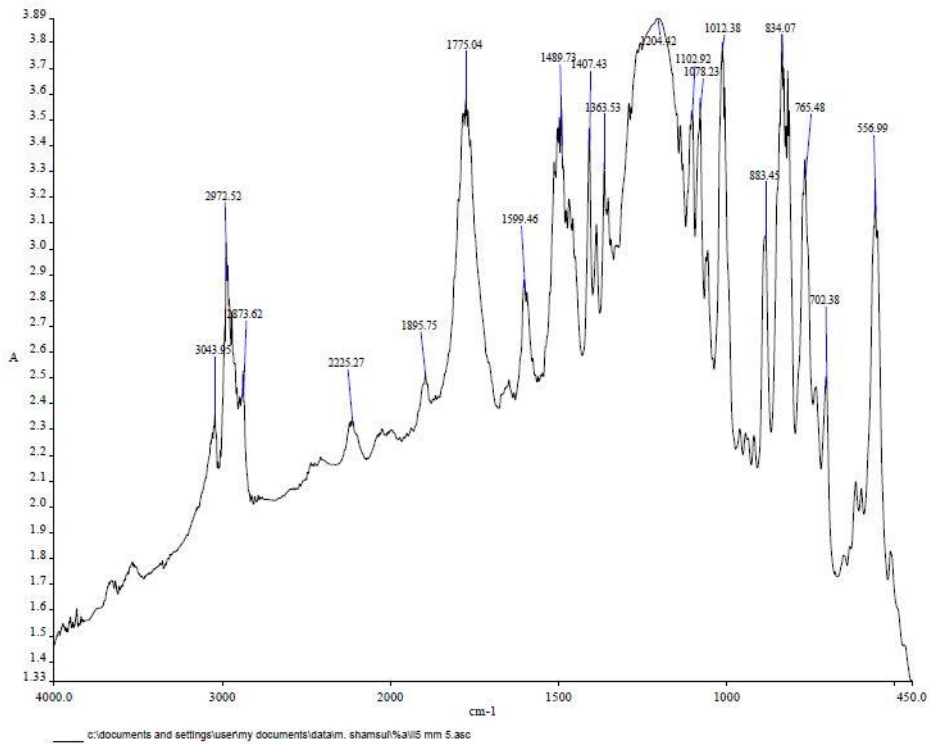


Figure 4.3.4: IL5MM5 FTIR Graph of Absorption

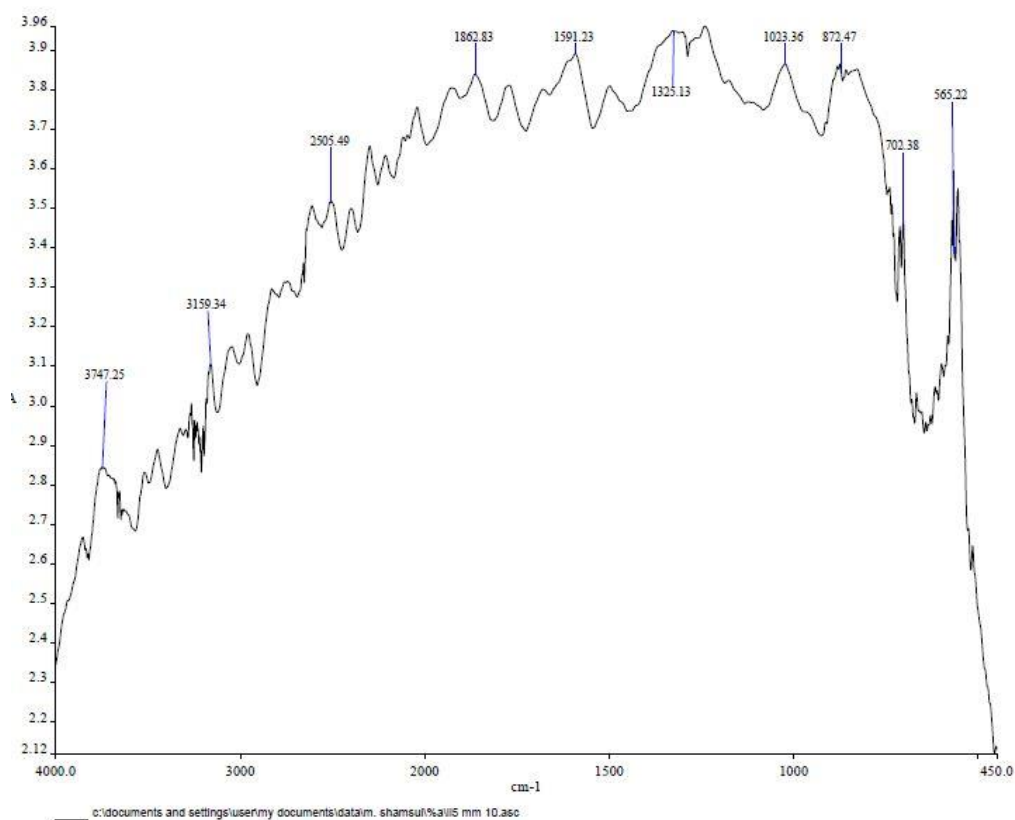


Figure 4.3.5: IL5MM10 FTIR Graph of Absorption

The chemical structure of repeating PC monomer was illustrated in Figure 4.3 and FTIR test is required to determine the functional groups that present in the membrane. For the fabricated membranes, FTIR spectra was focused on some pronounced peaks of the main functional groups in PC ( $3670\text{ cm}^{-1}$  for H bonded with OH,  $1775\text{ cm}^{-1}$  for C=O,  $1505$  for ring of C-C),  $850\text{-}550\text{ cm}^{-1}$  shows C-Cl bands which means for all samples there was DCM trapped in the membrane matrix and ionic liquid at about  $1325\pm 25$  shows S=O which only detected in IL5MM10 but not in PM, MM5 and MM10. The spectra for each membrane is in the appendices.

## 4.4 Morphological Characterization of Membranes

### 4.4.1 Cross-sectional Morphology

The FESEM images of the cross-sections of MMMs with 5 wt.% and 10 wt.% of CMS in PC matrix and ILMMMs with 5 wt.% EMIMIm and 5 wt.% and 10 wt.% of CMS respectively are shown in Figure 4.4.1a. The

membranes have voids formed porous structures with addition of CMS in MMMs due to poor polymer-filler contact but dense in ILMMMs due to increased polymer-filler contact with addition of EMIMIm. Membrane thickness range from 63.10  $\mu\text{m}$  to 95.0  $\mu\text{m}$  where it was observed that increasing CMS loading increases the thickness by  $\pm 10 \mu\text{m}$ .

In contrast to MMMs, ILMMMs forms more homogeneous membrane where the structures are less porous probably due to IL effect on polymer-filler surface contact. CMS distributions seems good but agglomerations were seen in all membranes which were probably contributed by poor grinding of CMS or CMS and particles affinity to agglomerates when the size was smaller than its regular size.

IL presence in ILMMMs can be hardly determined but fiber-like wavy patterns were observed in both ILMMs suggesting the presence of IL which were not seen in MMMs. The two layered color formed in the image of IL5MM5 was observed and deduced that the cross-section was unintentionally exposed to nitrogen liquid when cutting giving a sharp white layer.

The cross-sectional FESEM images of MMMs and ILMMMs were illustrated in Figure 4.4.1b at higher magnification (x3000) compared to Figure 4.4.1a were only at x1000 magnification. As can be seen from the figures yellow boxes, dark area between the CMS particles and PC matrix revealed empty space existence which is called interfacial void.

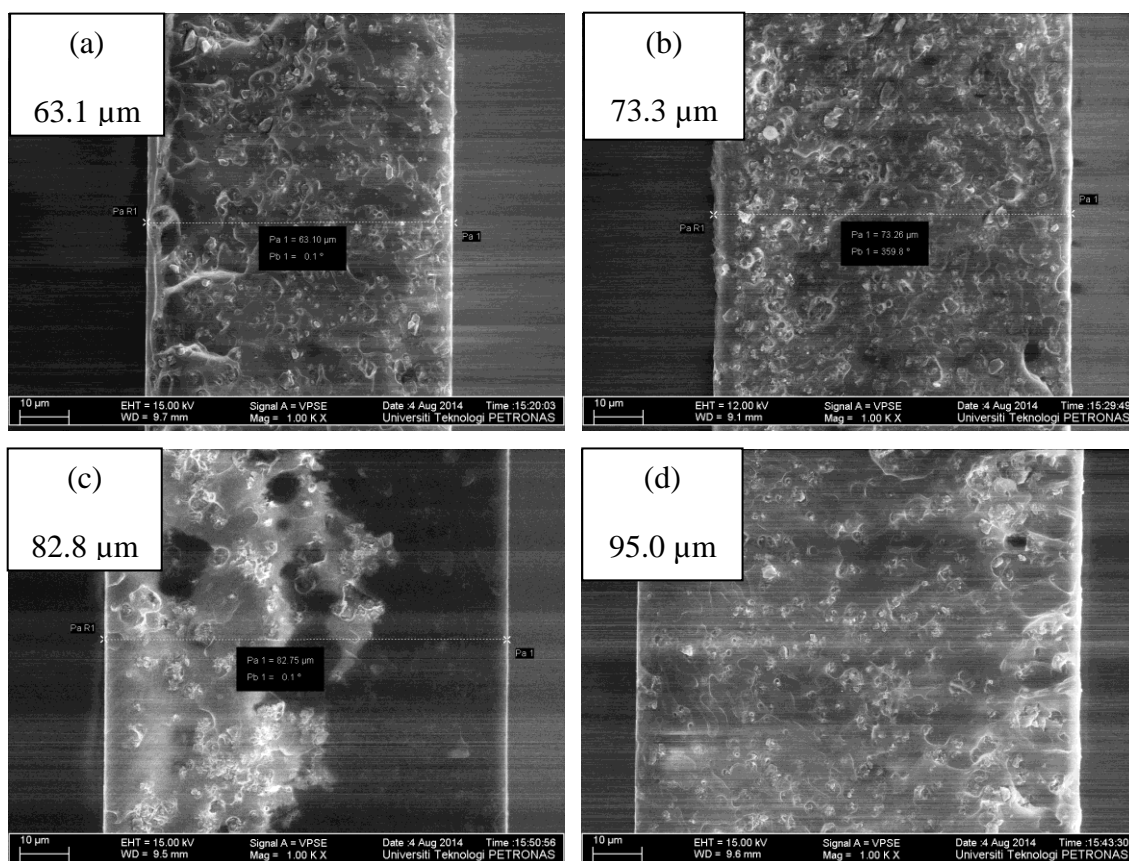


Figure 4.4.1a: Cross-sectional FESEM images of (a) PC/CMS (5%), (b) PC/CMS (10%), (c) PC/CMS/IL (5%) (5%), and (d) PC/CMS/IL (10%) (5%). (PC/DCM=15% w/w)

The voids formed around the filler probably due to low adhesion between the glassy polymer matrix and CMS particles (Mahajan, 2002). It is undesirable since such structure may cause lower selectivity relative to pure polymeric membrane (Mahajan, 2002). However, MMMs seems formed more frequent voids than ILMMMs (refer Figure 4.4.1b) further suggesting that IL increased interfacial contact between CMS and PC matrix.

Addition of 5 wt.% IL may intensify PC/CMS structure but at higher loading such as 10 wt. % of EMIMIm the membrane can't be formed due to lack of mechanical stability of the membrane causing it to fracture and broke to pieces. Further studies can be widen to determine the upper limit of EMIMIm loading in PC and CMS MMMs by studying the loading at smaller range of loading increment.

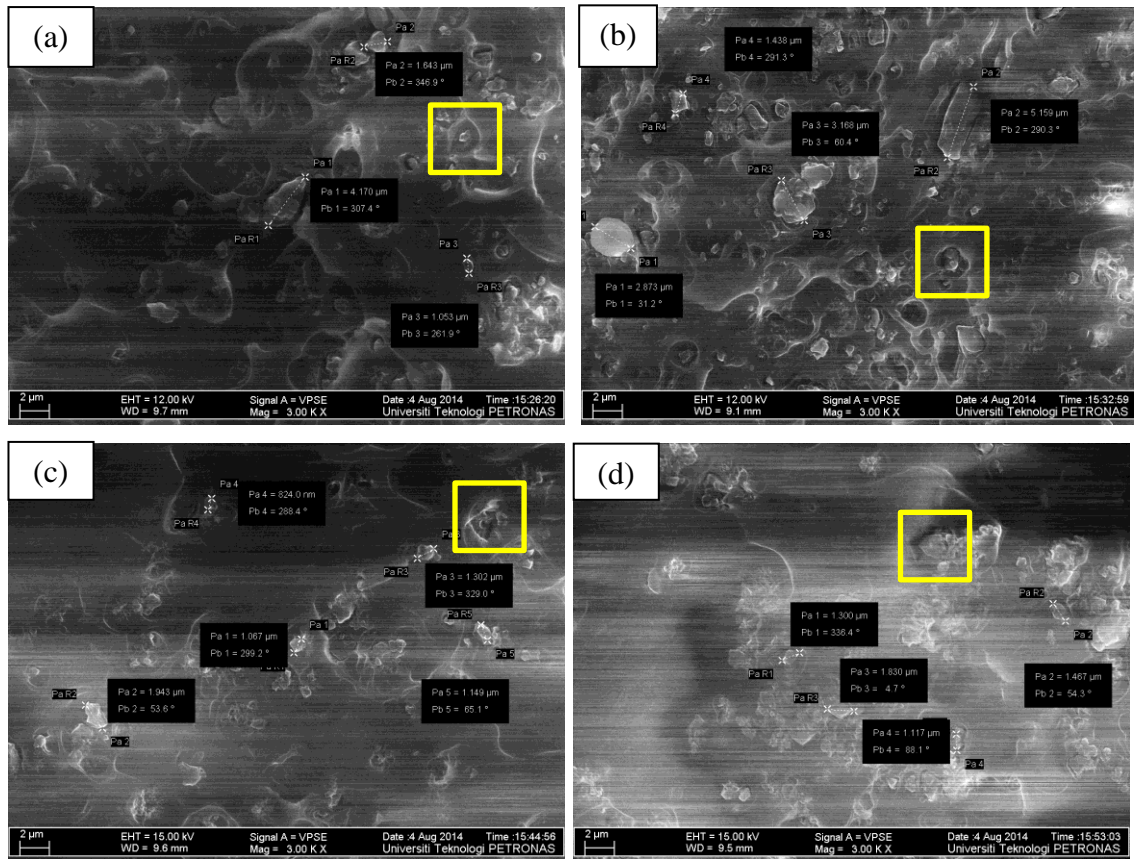


Figure 4.4.1b: Zoomed cross-sectional FESEM images of (a) PC/CMS (5%), (b) PC/CMS (10%), (c) PC/CMS/IL (5%) (5%), and (d) PC/CMS/IL (10%) (5%). (PC/DCM=15% w/w)

#### 4.4.2 Top and Bottom Morphology

The images of top and bottom surface of membranes show all membrane is well-fabricated without visible pin-holes in the scanned area. However there is difference between MMMs and ILMMMs top surface. Top surface of ILMMMs is bright with puddle patterns suggesting ionic liquid distribution on the surface of the membrane. Impurities were also visible such as dust and agglomerations. The images are as following:

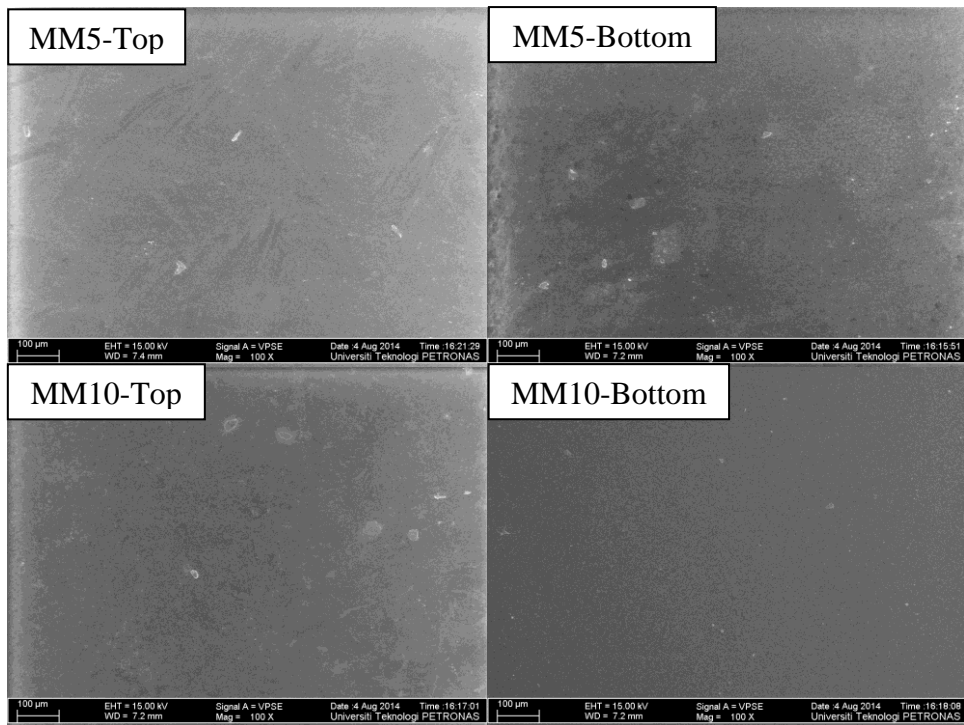


Figure 4.4.2a: Top and bottom morphology of MMMs

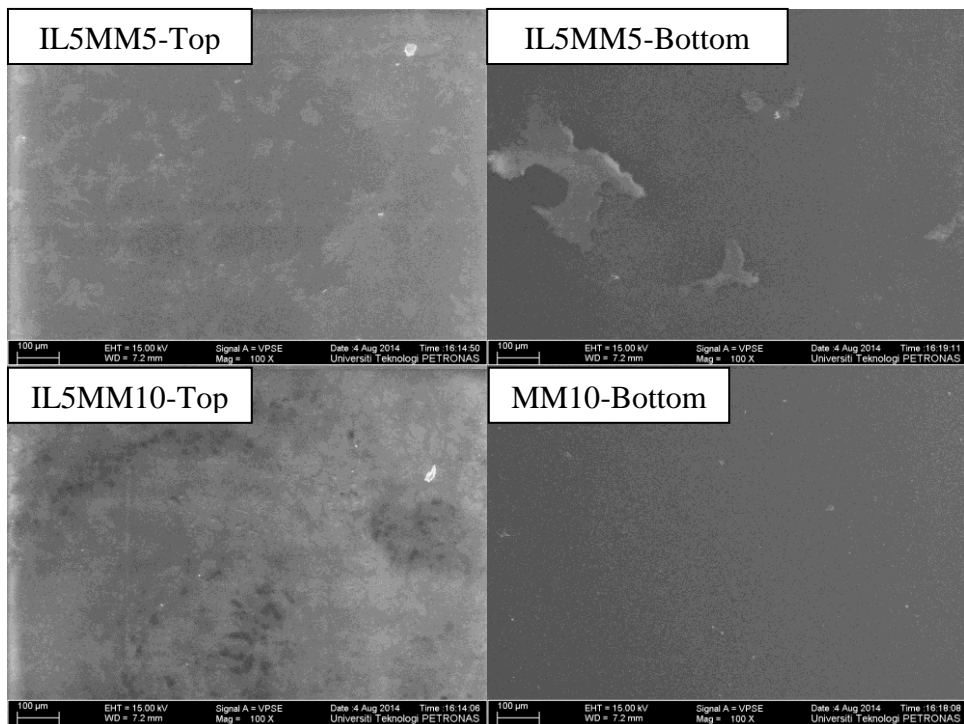


Figure 4.4.2b: Top and bottom morphology of ILMs

#### 4.5 Permeability Test Result

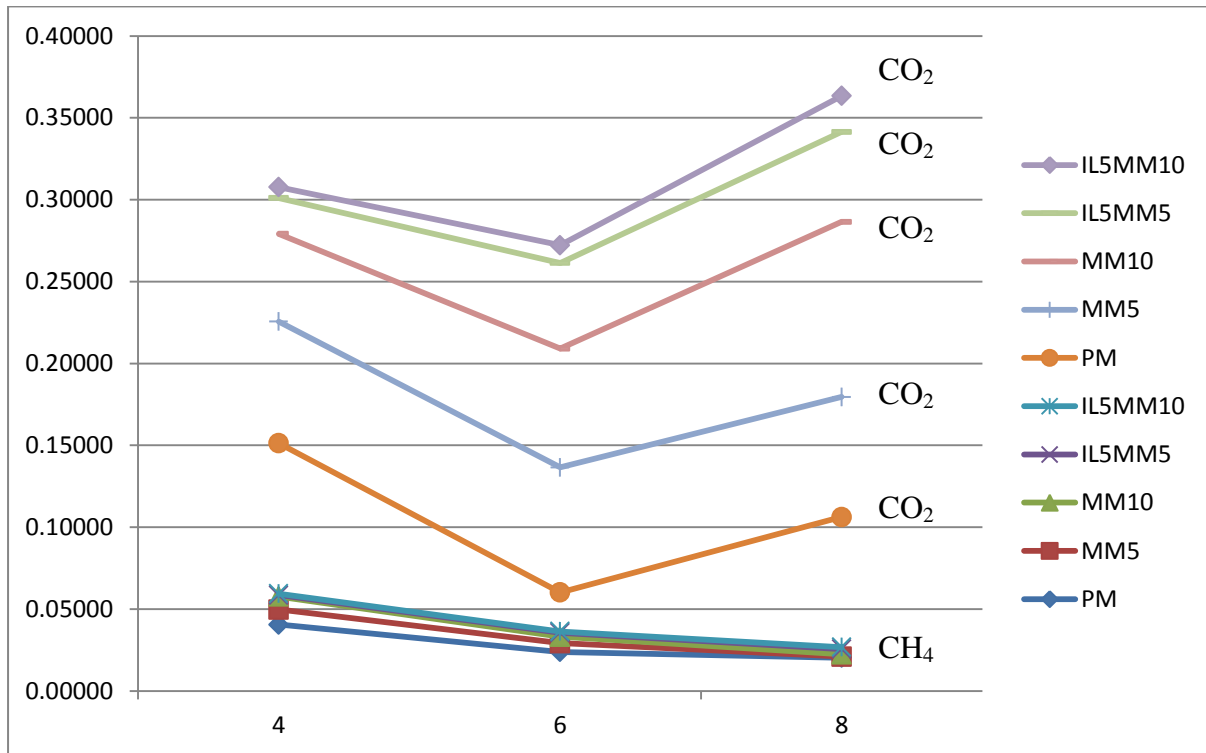


Figure 4.5: Graph of permeability for both CH<sub>4</sub> and CO<sub>2</sub>

Table 4.5: Permeability and selectivity of membranes at increasing pressure and at room temperature using CH<sub>4</sub> followed by CO<sub>2</sub>

Membrane	Pressure						Thickness, $\mu\text{m}$
	4 bar		6 bar		8 bar		
	GPU (CO <sub>2</sub> /CH <sub>4</sub> )	$\alpha$	GPU (CO <sub>2</sub> /CH <sub>4</sub> )	$\alpha$	GPU (CO <sub>2</sub> /CH <sub>4</sub> )	$\alpha$	
<b>PM</b>	0.09/0.04	2.26	0.08/0.02	3.34	0.18/0.02	8.82	61.59
<b>MM5</b>	0.07/0.009	8.21	0.07/0.005	15.28	0.073/0.001	107.33	63.10
<b>MM10</b>	0.05/0.008	6.80	0.07/0.004	18.69	0.11/0.001	76.88	73.26
<b>IL5MM5</b>	0.02/0.0009	23.87	0.05/0.002	21.58	0.06/0.003	16.97	82.75
<b>IL5MM10</b>	0.01/0.0009	7.26	0.01/0.0007	16.94	0.02/0.001	18.40	95.50

Legends:

- I. Permeability in GPU= Gas Permeation Unit(rounded off to 2 decimal places thus selectivity can't be calculated using this data) (average value)



II.  $\alpha$  = Selectivity (rounded off to 2 decimal places) (average value)

#### 4.5.1 PC Polymeric Membrane and PC/CMS Mixed Matrix Membrane

Effect of CMS loading on performance of PC/CMS membranes MM5 and MM10 were investigated at 5 wt% and 10wt% loading compared to pure membrane PM. The single gas permeabilities and ideal selectivities of PC/CMS MMMs were presented in Table 4.5. The highest loading was 10 wt% CMS based on PC weight.

The permeabilities of carbon dioxide through PC/CMS MMMs were lower than through pure PC membrane but CMS significantly decreased  $\text{CH}_4$  permeation when added into MMMs. MM10 showed close permeability of  $\text{CO}_2$  against pure membrane at 8 bar, MM5 showed lowest  $\text{CO}_2$  permeability at 8 and opposingly MM10 had lowest  $\text{CO}_2$  permeation at 4 bar. Due to only two loading range were investigated no data trend can be concluded.

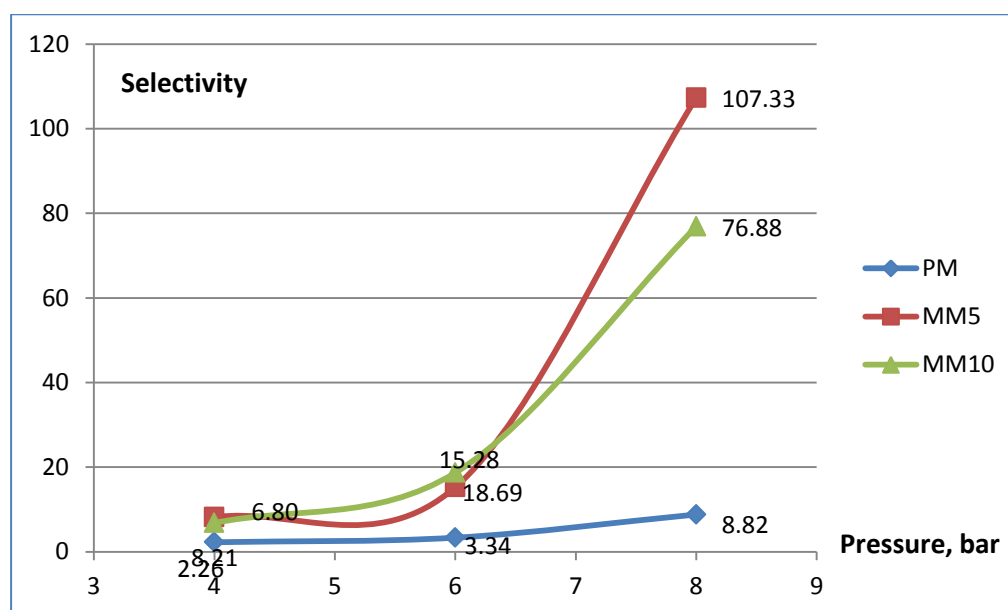


Figure 4.5.1: Permeation performance of polymeric membrane versus MMMs

In term of selectivity, pure PC membrane and both MMMs presented increasing trend of selectivity with the increment of pressure from 4 bar, 6 bar to 8 bar. Visually the data was presented in the figure above.

The decreasing behaviour of permeability and opposite performance of selectivity of PC membranes with addition of CMS can be explained by mechanistic speculations as reported in various papers of membrane science; the CMS acts as molecular sieves while altering the trade-off between selectivity and permeability in relation with molecular size of the penetrants.

Filler particles can disrupt polymer matrix resulting in micro-cavities or hence change the permeability and selectivity they can extend the diffusion pathways of the penetrants through the membrane and reduce permeability (Şen, 2008). Thus it was concluded that CMS is a molecular sieve having intrinsic properties that reduces CH<sub>4</sub> permeability even though at the same time decrease CO<sub>2</sub> permeability, the value was not as significant as CH<sub>4</sub> 77.5% decrement in the MM5 compared to pure PC membrane, PM at 4 bar while CO<sub>2</sub> decrement was only 17.7%.

#### 4.5.2 PC and PC/CMS/EMIMIm Ionic Liquid MMMs

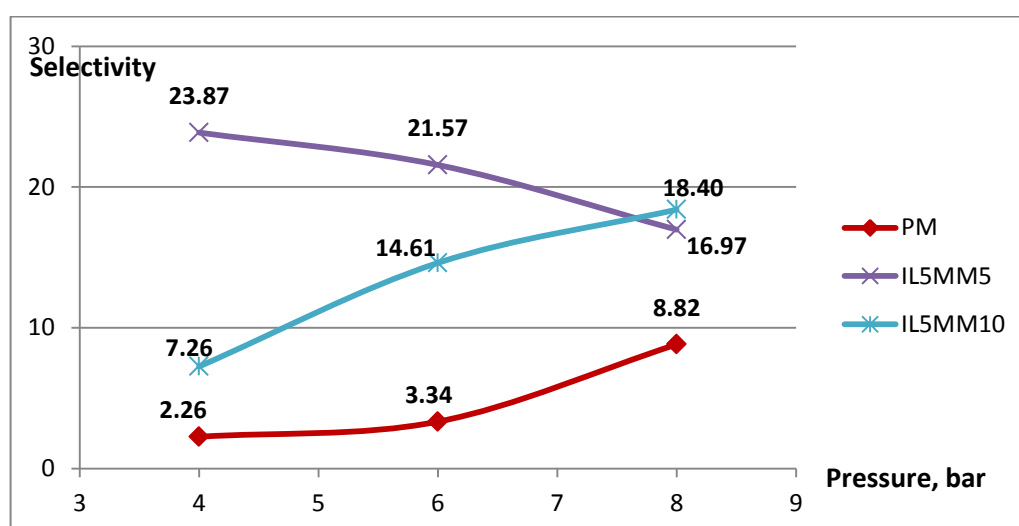


Figure 4.5.2: Permeation performance of polymeric membrane versus ionic liquid MMMs

The effect of ionic liquid addition was studied using the permeance data against all samples. IL5MM5 permeance data in Gas Permeation Unit (GPU), showed that the permeance for CH<sub>4</sub> decreased for the membranes

added with ionic liquid in up to 4444.44% reduction (at 4 bar pressure) compared to polymeric membrane and up to 1022.22% reduction compared to MM5. IL5MM10 shows the same reduction of CH<sub>4</sub> permeability as IL5MM5 as to PM performance while 777.78% reduction when compared with MM10. The permeation data suggest that addition of ionic liquid further decrease CH<sub>4</sub> permeance drastically but at the same time reduce CO<sub>2</sub> permeance resulting in lower selectivity compared to MMMs.

Evidences of membrane plasticization are the increase of gas permeability with feed pressure, the reduction of permselectivity coefficients, and the suppression of glass transition temperature, (Koops, 2003). Glassy polymer was known to be affected by highly sorbing gas such as CO<sub>2</sub> as reported in several reports and PC is a glassy polymer which has the potential to plasticize, thus observation was done on the data showing that IL5MM5 was plasticized having the first two evidences, increasing both CO<sub>2</sub> and CH<sub>4</sub> permeability from 4 bar till 8 bar even though only CO<sub>2</sub> was reported to plasticize at higher pressure, this phenomenon was also observed in all CO<sub>2</sub> permeance for all membranes. Then, Figure 4.5.2 shows plotted selectivity of the membranes showing that IL5MM5 selectivity reduction over time (by increase of pressure increase exposure time to CO<sub>2</sub> supporting the second evidence).

Compared to MMMs selectivity, ILMMMs selectivity was poor at 8 bar but on-par and better at 4 bar to other membrane and superior in term of CH<sub>4</sub> permeability reduction factor. At 4 bar, IL5MM5 has the highest selectivity almost 10 times better than PM and almost 3 times better than MM5. Even at 6 bar IL5MM5 outclassed all other membrane selectivity but plasticization effect caused IL5MM5 selectivity to drop as mentioned before. Thus, addition of additives or blending with polymer harder to plasticize was suggested.

## CHAPTER 5: CONCLUSION

### 5.0 CONCLUSION

This project has successfully developed mixed matrix membrane (MMM) and ionic-liquid-enhance mixed matrix membrane (ILMMM) from polycarbonate and CMS base. The developed MMMs has analysed FESEM images showed that IL addition improves interfacial contact between CMS and polymer matrix Permeation test showed ILMMMs performance was low at higher pressure probably due to plasticization effect that was observed. To conclude, MMMs are better in term of selectivity at higher pressure probably due to poor polymer-filler contact causing the pore to expand at higher pressure but ILMMMs are superior in prevention of CH<sub>4</sub> permeation at more than 700% for IL5MM5 as the effect of good contact of polymer and filler reducing voids for CH<sub>4</sub> permeation prevention when added with EMIMIm. The preliminary data has shown EMIMIm blend mixed matrix membranes are showing promising result and can be explored further to achieve promising membrane for high CO<sub>2</sub> separation where the best membrane is IL5MM5, shows promising result of 23.87, 21.58 and 16.97 selectivity at 4, 6, and 8 bar respectively towards CO<sub>2</sub> and CH<sub>4</sub> permeation.

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