Development of Polyetherimide (PEI) - Polyvinyl acetate (PVAc), Glassy-rubbery Polymeric Blend Membrane for CO_2/CH_4 Separation

by

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14980

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

JANUARY 2015

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CERTIFICATION OF APPROVAL

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Approved by,

(Associate Professor Dr. Hilmi Bin Mukhtar)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
JANUARY 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.

TAN MING YIH

ABSTRACT

In membrane technology, polymeric membrane has been widely used for natural gas purification but the tradeoff limitation between permeability and selectivity has restricted the overall gas separation performances. This project aimed to develop and synthesis a novel glassy-rubbery polymeric blend polymeric membrane which composed of polyetherimide (PEI) and polyvinyl acetate (PVAc) polymers in N-Methyl-2-pyrrolidone (NMP) solvent. Solution casting and evaporation technique was selected in synthesizing the proposed blend polymeric membranes. In addition, morphology, interaction of chemicals, thermal stability as well as the miscibility of polymer blending were characterized by FESEM, FTIR, TGA and DSC respectively. The overall gas separation performances of the membrane were evaluated in terms of permeability and selectivity.

In this study, all membranes were casted successfully. FESEM results showed that all pure and blend membranes were homogeneous in structure and no void were observed at molecular level. This observation has confirmed the miscibility of polymers blending. Moreover, FTIR analysis was conducted and it reviewed that the functional groups of individual polymers such as aldehyde, ketone and ether were remained in the structure of blend membranes which indicated no alternation and changes of chemical structure in blend membranes. On top of that, TGA result presented that a slightly lower degradation temperature in blend membranes. This reflected that thermal stability of blend membrane has been reduced compared to pure PEI membrane. Furthermore, a single and lower glass transition temperature were found in DSC analysis which confirmed the compatibility and good interaction between PEI and PVAc. However, the present of PVAc in PEI polymer has reduced the glass transition temperature of pure PEI membrane.

Last but not least, gas separation test was conducted and the outcomes showed a decreasing trend in CO_2 permeability with respect to feed pressure for pure PEI membranes. For pure PVAc and blend membranes, permeability of CO_2 increases as the feed pressure increases. In overall, an impressive result with up to 95% improvement in CO_2 permeability was achieved in polymeric blend membranes. In term of ideal selectivity, the trend was increasing for pure PEI membranes but decreasing for both pure PVAc and blend membranes with respect to feed pressure. Most importantly, ideal selectivity of blend membranes were found to be 40% higher compared to pure PEI membranes.

In short, this present study showed that casted polymeric blend membranes have improved the overall performances of polymeric membrane and it has a great potential to be used for natural gas purification application.

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CHAPTER 1

INTRODUCTION

This chapter discusses about the background of study for the final year project. Besides that, this chapter also defines the problem statement, the objective and the scope of the research work.

1.1 Background

1.1.1 Natural Gas

Natural gas has been reported as the fastest growing energy source in the world as it is considered as the largest fuel source needed after coal and oil. Generally, it is fossil fuel which formed from the animals and plants remain millions years ago. The consumption of natural gas is not only limited to the industry, at the same time it is also consumed in various sectors such as transportation, agricultural, raw materials for petrochemicals well as power generation (Lundvall, 2010). On top of that, it supports the idea of going toward sustainability and green technology as the natural gas is found to be generate less-toxic gases and effective source of energy.

Natural gas is a mixture hydrocarbon gases such as methane, ethane, propane, and butane. Commonly, methane comprises around 70% of the gas. Besides, there are other components such as carbon dioxide, hydrogen sulfide, and water as outlined in Table 1.1.

Table 1.1: Typical feed composition of natural gas well and sale specification (Asim Mushtaq, 2013; Shimekit & Mukhtar, 2012)

Components	Formula	Typical Feed Composition	Market Sales Specifications
Methane	CH_4	70-80%	90%
Carbon dioxide	CO_2	5-45%	$< 2\%$
Ethane	C_2H_6	3-4%	3-4%
Propane and butane	C_3H_8, C_4H_{10}	$\sim 3\%$	$\sim 3\%$
Nitrogen	N_2	$\sim 1-4\%$	$< 4\%$
Hydrogen sulphide	H_2S	< 100ppm	< 4ppm
Water	H_2O	saturated	< 100 ppm

1.1.2 Carbon Dioxide Content of Various Natural Gas Reserves in Malaysia

In Malaysia, there are a total of 379 fields have been discovered, in which 163 are oil fields whereas 216 are gas fields (Rahim, 2008). Basically, its composition can be varied from one well to another due to its geographical condition. Table 1.2 shows the summary of high carbon dioxide percentage of natural gas fields in Malaysia.

Table 1.2: High carbon dioxide content natural gas fields in Malaysia (Nasir Haji Darman, 2006)

Peninsular Malaysia					
Holder	**Field**	**Total EUR(TSCF)**	**EUR Net of CO_2 TSCF**	**CO_2 content**	**CO_2 Volume TSCF**
PETRONAS	Bujang	1.47	0.5	66%	0.97
PETRONAS	Sepat	1.2	0.48	60%	0.72
PETRONAS	Noring	0.58	0.23	60%	0.35
PETRONAS	Inas	1.04	0.42	60%	0.62
PETRONAS	Tangga Barat	0.33	0.22	32%	0.11
PCSB	Ular	0.14	0.07	50%	0.07
PCSB	Gajah	0.12	0.06	50%	0.06
PCSB	Bergading	1.36	0.82	40%	0.54
PCSB	Beranang	0.08	0.06	28%	0.02
EMEPMI	Palas NAG	0.38	0.2	46%	0.18
TOTAL		6.70	3.06		3.64

Sarawak					
Holder	**Field**	**Total EUR(TSCF)**	**EUR Net of CO_2 TSCF**	**CO_2 content**	**CO_2 Volume TSCF**
PETRONAS	K5	25.70	7.70	70%	17.95
PETRONAS	J5	5.37	0.70	87%	4.67
PETRONAS	J1	1.43	0.59	59%	0.84
PETRONAS	T3	1.04	0.39	62%	0.65
PETRONAS	Tenggiri Mrn.	0.33	0.18	47%	0.15
TOTAL		33.82	9.56		24.26

Table 1.2 demonstrates that majority of natural gas fields in Malaysia that are having the carbon dioxide range from 28% up to 85%. In addition, it is also noticed that K5 and J5 fields located in Sarawak having more than 70% of carbon dioxide (Nasir Haji Darman, 2006).

A significant and high concentration of carbon dioxide in natural has become the main problem as the conventional separation methods available is only capable to treat the natural gas with the maximum of carbon dioxide content from 30 to 40% (Ahmed & Ahmada, 2011). Thereby, modification or new technology should be developed so that the removal of carbon dioxide content is higher than 40% or even more.

1.1.3 Problems and Issues of Carbon Dioxide

The presence of carbon dioxide in natural gas will lead to the drop in calorific value. Consequently, the selling price of natural gas will be reduced. Furthermore, carbon dioxide will corrode the pipeline or equipment because carbon dioxide will dissolve in water to form carbonic acid. Normally, pipeline requirements and specifications for natural gas demand the concentration of carbon dioxide to be lower than 2% (Baker & Lokhandwala, 2008). In addition, it will lower down the heating value of natural gas and imposes unnecessary transportation cost. Therefore, natural gas must be undergoes particular treatment to remove carbon dioxide so that the quality of the product can be improved (Aspelund & Jordal, 2007).

1.1.4 Current technology for carbon dioxide removal

The process of removing carbon dioxide from natural gas is known as gas sweetening process. Generally, there are several technologies that have been widely used in industry such as absorption, adsorption, cryogenic distillation and membrane. These technologies have been developed over years with an ultimate goals of optimizing cost and meeting gas specifications (Ebenezer & Gudmundsson, 2006). In the following section, each technology is briefly described.

1.1.4.1 Absorption Process

Absorption processes are the most widely technology for natural gas purification which involving the uses of amine solvents (W. N. W. S. a. A. F. Ismail, 2011). Generally, this technology is achieving by counter current the natural gas with the solvent in a column or plate. The impurities such as carbon dioxide will be then dissolved and absorbed by the solvent (Hillock, 2005). Amine absorption can be classified into physical absorption and chemical absorption. Specifically, physical absorption will absorb the impurities based on the solubility while chemical absorption will absorb impurities based on the chemical reaction between the gas components and solvent. The most common solvents used in industry are Monoethanolamine (MEA) and Diethanolamine (DEA) (Amelia Suyono Wiryoatmojo, 2010).

However, this technology has its challenges and drawback. Besides, in a single process of amine absorption, it has limited capability which can only purify the natural gas carbon dioxide from 5-15% down to quality of pipeline (Amelia Suyono Wiryoatmojo, 2010). At the same time, conventional amine absorption towers are required to big scale to operate. This will be very inconvenience to be installed at offshore application. In addition, higher operation cost is needed in absorption process due to longer operational time is required for absorption process. Lastly, the solvents used in this technology basically cannot be recycle and solvent disposal will lead to the environmental issues due to hazardous of chemical solvents (Ebenezer & Gudmundsson, 2006).

1.1.4.2 Adsorption Process

In this technology, a solid surface called adsorbent is used to remove particular component from feed gas stream. Basically, this particular component will adhere to the surface of adsorbent which characterized according to its microporous structure. The most common adsorbents used in industry are carbon, zeolite, silica gel and molecular sieves (Amelia Suyono Wiryoatmojo, 2010).

This technology is not appropriate for continuous process due to the risk of attrition and mechanical issues. Adsorption process is usually used in fixed beds. For the simple adsorption process, there are two beds involved. One will be operate in adsorption and the other one is operating in desorption. Both processes basically will be switched periodically (Langmuir, 1918).

However, adsorption process is only suitable for low carbon dioxide content feed gas at moderate operating pressure. Furthermore, it has a very complicated design and also not appropriate for continuous process (Ebenezer & Gudmunsson, 2005). On top of that, limited life time of adsorption column due to degradation through oxidation and corrosion problems were observed in aqueous amine processes (Goff & Rochelle, 2004).

1.1.4.3 Cryogenic Process

Cryogenics process requires a very low temperature (less than -150℃) to operate. According to literature, there are a few methods for the system to be performed at such a low temperature and it was found that the most effective method is by using turbo expander process where it uses refrigerants to chill the feed gas stream (Tobin J., Shambaugh P. et al., 2006). This technology is widely used to separate hydrogen from feed gas containing impure hydrogen (Meyers, 2001).

However, this method is not suggested as the operation requires high consumption of energy and might reduce the overall efficiency of the plant. On top of it, huge area is necessary for this technology to operate. Lastly, there are some cryogenic fluids such as ethane and acetylene are flammable and toxic (Ebenezer & Gudmundsson, 2006).

1.1.4.4 Membrane

Due to the problems and limitations mentioned above, membrane technology was developed. Membrane technology has received significant attention especially gas separation technology on natural gas sweeting since the last few decades. Specifically, membrane is defined as a thin semipermeable active or passive barrier and under certain driving force, which will separate two phases and permits preferential passage of one or more selected species or components (molecules, particles or polymers) in gaseous and/or liquid mixture solution in selective manner (J.-H. Kim & Lee, 1998).

Based on literature, there are many advantages found in membrane technology. Firstly, it has a simple design and this a lower cost is needed to operate. On top of it, it is very stable even at very high pressure. Besides, it does not require a large area for the system and thus it can be installed and operated easily at offshores. In addition, it has no environmental issue as the solvents used is not hazardous (Amo, Baker, & Lokhandwala, 1995).

In industrial applications, permeability and selectivity are the two parameters used in determining the gas separation performance of a membrane. A significant permeate flux is indicated by the scale of permeability whereas selectivity determines the separation performance. However, up to now, selection of suitable materials for membrane fabrication that satisfy both behaviors mentioned is still a challenge (Lokhandwala, Jariwala, & Malsam, 2007).

In this technology, it can be divided into polymeric and inorganic membranes. In polymeric membranes, polymers such as glassy or rubbery polymers are used to manufacture the membrane whereas materials such as metals or ceramics area are used in inorganic membranes. According to the literature, polymeric membranes are normally used for natural gas purification due to high selectivity of polymeric membranes (Baker & Lokhandwala, 2008).

However, there are drawbacks reported for both polymeric and inorganic membranes. Trade-off limitation between permeability and selectivity is observed in polymeric membrane. Glassy polymers generate a high selectivity but low permeability and vice versa in rubbery polymers. For inorganic membranes, they are very sensitive to temperature gradient which will cause the membrane to crack easily due to the brittleness affected by high temperature (Mannan et al., 2013). Therefore, novel approach by blending glassy and rubbery was developed so that the beneficial properties of individual polymers can be incorporated in to a single blend membrane.

1.2 Problem Statement

Monetization of sour natural gas containing up to 85 mole % of carbon dioxide is very challenging in term of technology. The performance of current technologies such as absorption, adsorption and cryogenic distillation to remove carbon dioxide from sour natural gas are still far away from the desired result. In addition, those existing technologies have their own limitations. For example, the conventional separation method using amine absorption has some technology gaps such as large area needed and high operation cost. Besides, this method is only applicable with the natural gas containing carbon dioxide up to 15 mole %. Therefore, a new technology should be developed in order to solve the problem mentioned.

It is also suggested that the separation technology should be installed at offshore so that carbon dioxide can be removed first before transporting to onshore. This definitely will reduce the transportation cost. It has been found that membrane technology is the most suitable technology for carbon dioxide removal which can be easily installed at offshore due to its simplicity, lower capital cost as well as environmental friendly. However, the selection of materials for synthesizing membrane is still a big issue in industry. At the same time, challenge such as tradeoff limitation between permeability and selectivity is observed in polymeric membrane.

This has led to the initiative of this research project with the idea to develop membrane technology which can be installed at offshore and remote areas application for natural gas containing high CO_2. In this project, novel approach by blending glassy and rubbery was developed so that the beneficial properties of individual polymers can be incorporated in to a single blend membrane. It is important to note that PEI/PVAc polymeric blend membrane in this study has not been reported in past studies, and hence the casting solution formulation has to be investigated in order to determine the most suitable solvents to be used as well as the composition of polymers and solvent in synthesis of polymeric blend membrane. Lastly, the proposed membrane will be evaluated for the separation of carbon dioxide from natural gas in terms of selectivity and permeability.

1.3 Objectives

The main objectives of this study are as follows:

1. To investigate the compatibility between polyetherimide (PEI) and polyvinyl acetate (PVAc) as well as to determine the maximum composition of PVAc that is best suitable for the project.
2. To synthesis a novel glassy-rubbery polymeric blend membrane by using polyetherimide (PEI) and polyvinyl acetate (PVAc) with N-Methyl-2-pyrrolidone (NMP) as solvent.
3. To characterize the physical, chemical and thermal properties of the developed polymeric blend membranes using FESEM, FTIR, TGA and DSC.
4. To evaluate the performance of polymeric blend membrane in terms of permeability and selectivity through gas permeation test unit at variable feed pressure.

1.4 Scope of Study

Basically, this project involves experimental works. It will be focusing on the initial miscibility study, membrane synthesis, characterization as well as the evaluation of polymeric blend membrane composed of PEI and PVAc. The scopes of study are described in the following sections.

1.4.1 Initial Miscibility Study of Polymeric Blend Membrane

Before synthesizing polymeric blend membranes, it is important to determine the maximum composition of PVAc rubbery polymer in PEI glassy polymer. In this part of project, the ratio of polymers will be varied to determine the compatibility and miscibility of the membranes. Table 1.3 lists the composition of PEI and PVAc in initial miscibility study.

Table 1.3: Composition of PEI and PVAc for initial miscibility study

Sample test	Ratio of PEI : PVAc		Weight percent of solution (wt %)	
	PEI (wt) %	PVAc (wt) %	Polymers (PEI+PVAc)	Solvent (NMP)
1	99	1	20	80
2	98	2		
3	97	3		
4	95	5		
5	90	10		
6	85	15		

1.4.2 Synthesis of Polymeric Blend Membrane

Five membranes with different composition of polymers will be synthesized with the solvent. The novel polymeric blend membrane is composed of PEI and PVAc polymers in NMP as solvent. The composition of PEI and PVAc used for synthesis of polymeric blend membrane will be based on the stability of membranes in initial miscibility study. All membranes in this project will be casted by using solution casting and evaporation technique.

1.4.3 Characterization of Polymeric Blend Membrane

In this part, physicochemical and thermal properties of the synthesized membrane will be investigated and characterized by using specific equipment that are available in UTP laboratory as shown below:

- ✓ Field Emission Scanning Electron Microscope (FESEM)
  - To study the morphology of blend membranes
- ✓ Fourier Transform Infrared Spectroscopy (FTIR)
  - To investigate the interaction of chemical structure in blend membranes

- ✓ Thermogravimetric analyses (TGA)
  - To determine the thermal stability of blend membranes
- ✓ Differential Scanning Calorimeter (DSC)
  - To study the effect of polymers blending on miscibility and glass transition temperature of blend membranes

The details of FESEM, FTIR, TGA and DSC will be further described in chapter 3 and 4.

1.4.4 Evaluation on the Performance of Polymeric Blend Membrane

The developed membrane will be evaluated on its performance through pure CO_2 and CH_4 permeability and selectivity by using gas permeation test. Generally, the developed membrane will be evaluated on CO_2 and CH_4 permeability at ambient temperature with variable pressure of 2, 4, 6 and 8 bars. Lastly, the ideal selectivity will be calculated as explained in chapter 4.

1.5 Relevancy and Feasibility of the Project

Final year project basically is divided into two parts which are FYP 1 in the first semester and FYP 2 in the second semester. Referring to the scope of study highlighted, it is clear that every single activities involved in the project need to be studied and carried out precisely in order to achieve the objectives of the project.

This experimental based project is expected to be completed within 7 months in duration. A feasible and details plan with specific time allocated for each part of the project are measured. Discussion on the research project must be constantly conducted for the development of project. In addition, all chemicals, glassware and equipment required are available in the department. Therefore, within these 7 months of proper planning with relevance to the research project, the author can manage his time properly into reaching the objectives set out by the project. In doing so, the author can gain many skills and knowledge throughout the period and thus making this project to see its completion.

CHAPTER 2

LITERATURE REVIEW

This chapter reviews the development of membrane technology with the objective to enhance gas separation performances. Furthermore, literature studies on polymeric membranes and blend membranes that have been developed will be discussed in details. On top of that, materials for synthesizing polymeric blend membrane and methods of synthesizing membrane are reviewed. In the end of this chapter will cover the membrane characterization as well as the evaluation on the performances of membrane.

2.1 Membrane Separation Technology

Membrane technology has received significant attention especially gas separation technology on natural gas sweeting since the last few decades. Based on literature, there were many studies carried out by researchers for various gas separation mostly focus on natural gas purification. Specifically, membrane is defined as a thin semipermeable active or passive barrier and under certain driving force, which will separate two phases and permits preferential passage of one or more selected species or components (molecules, particles or polymers) in gaseous and/or liquid mixture solution in selective manner (J.-H. Kim & Lee, 1998). Figure 2.1 demonstrates the overall schematic diagram of gas separation through a membrane. Based on Figure 2.1, the primary species that are rebounded back by the membrane is called retentate whereas those species passing through the membrane is called permeate (Koros & Fleming, 1993).

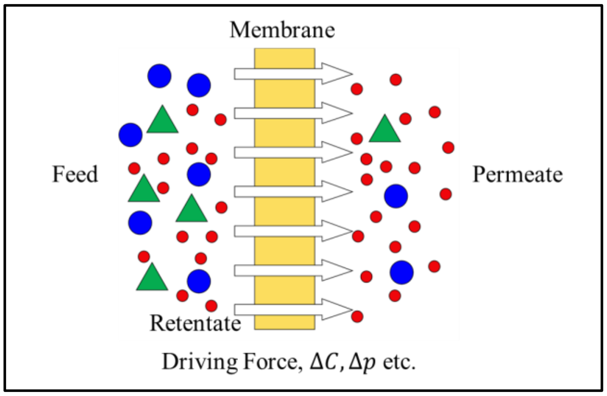

Figure 2.1: Schematic diagram of gas separation by a membrane (Mulder, 1996)

Development of membrane technology for CO_2/CH_4 separation has been started since early 1990's. There are several membranes were synthesized using various type of materials in the early state. The main objective is to produce a membrane which has the characteristic of great separation performance, robustness, mechanically, chemically and thermally good at rational production cost. In general, there are two types of materials which are polymeric membrane and inorganic membrane.

2.2 Polymeric Membrane

Gas separation using polymeric membranes has started its first commercial scale in late 1970's. Performances of polymeric membranes by different mechanisms which are based upon the properties of membrane means physical and chemical structure. It interacts between membrane, components and nature of gas (Duval, Folkers, Mulder, Desgrandchamps, & Smolders, 1993).

2.2.1 Classification of Polymeric Membrane

Polymeric membrane can be classified into porous and non-porous (Abedini & Nezhadmoghadam, 2010). A porous membrane has rigid and voided structure with random distribution of interconnected pores. Hence, separation of porous membrane is based on the molecular size of polymer as well as the distribution of pore size. This type of membrane will generate high fluxes but it is inherently low selective.

Non-porous membrane also known as dense membrane which consists of a dense film. Basically, permeate molecules will be first absorbed and followed by diffusing through polymer matrix under the driving force of concentration gradient or pressure. Dense membrane is highly selective but the transportation of gas through the polymer medium is very low. In dense membrane, permeate of similar sizes can be separated when there is significant different solubility in polymer.

2.2.2 Glassy and Rubbery Polymers

Polymers can be classified into glassy and rubbery polymers. In rubbery polymer, the polymer chains can move freely and limited rotation occurs around their chain backbone due to the thermal motion. This behaviors result the polymer to be soft and flexible. In addition, a significant high permeant diffusion coefficient is achieved by this thermal motion. In glassy polymer, the effect of steric hindrance along the polymer backbone restricts the movement of polymer chains. Since the thermal motion is limited in glassy polymer, thus the permeant diffusion coefficient is low. With that, glassy polymer is rigid, hard and brittle. When the temperature of a glassy polymer is increased until a point where the rise in thermal energy is able to overcome the effect of steric hindrance restricting rotation of polymer backbone segments. The temperature at this point is named glass transition temperature, Tg and the polymer will change from a glass state to a rubber state (Baker, 2004).

2.2.3 Performances of Polymeric Membrane

Polymeric membrane is extensively used for gas separations but its performance is limited by the upper bound trade-off discovered by Robeson in 1991. It is because glassy polymer generates high selectivity but low permeability and vice versa in rubbery polymer. This characteristics and behaviors can be explained in terms of structural properties of glassy and rubbery polymers. The rigid structures of glassy polymer will restrict the passage of particular gas molecules, consequently result in high selectivity. In rubbery polymers, polymer chains will be moving and rotating along their axis. Therefore, gas molecules transport at high rate, resulting in increased permeability but selectivity is sacrificed. Although polymeric membranes have high mechanical strength, economical processing capacity, it is still not much attractive because of the Robeson upper bound tradeoff between selectivity and permeability as shown in Figure 2.2.

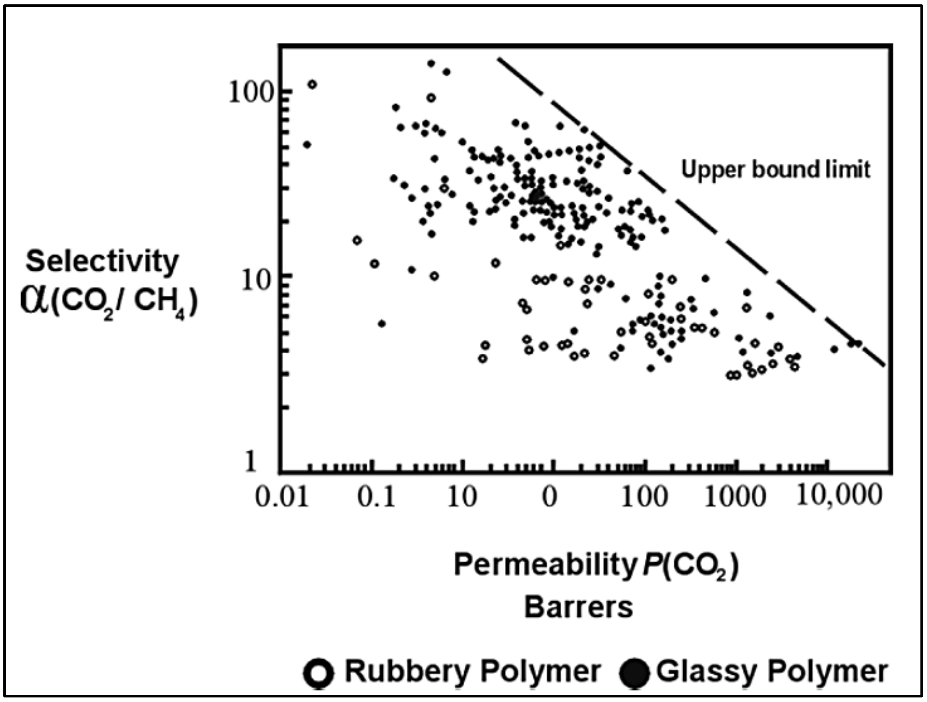

Figure 2.2: Robeson upper bound tradeoff (Maier, 1998)

Figure 2.2 illustrates the relationship between selectivity of CO_2/CH_4 and CO_2 permeability for all the membrane materials reported. Upper bound is the line that connects the most selective polymers at certain CO_2 permeability as shown in Figure 2.2. In addition, application of polymeric membrane is limited because those membranes are not able to withstand the chemical and thermal attacks (Goh, Ismail, Sanip, Ng, & Aziz, 2011).

Glassy polymeric membrane is often used for removal of carbon dioxide because it separates gas mixture based on molecular size of penetrating molecules since the molecular size of carbon dioxide is much smaller compared to methane (Mushtaq, Mukhtar, Shariff, & Mannan, 2013). Therefore, glassy membrane is selected when dealing with removal of carbon dioxide from natural gas.

2.3 Inorganic Membrane

Inorganic membranes refer to membranes which are made up of materials such as silica, zeolite, various oxides and metals such as palladium, silver and their alloys. They have been used and applied widely in gas separation technology. In term of performance, permeability and perm selectivity of inorganic membranes are thoroughly dependent on the structure of the membrane such as porosity, pore size and distribution as well as the affinity between permeating species and pore walls. However, there are many disadvantages reported in literature. One of the issue is the inorganic membranes are very sensitive to temperature gradient which will cause the membrane to crack easily due to the brittleness affected by high temperature. In addition, its application also having difficulty in proper sealing of the membrane operating at high temperature (Rizwan Nasir, Hilmi Mukhtar, Zakaria Man, & Dzeti F Mohshim, 2013a).

2.4 Polymeric Blend Membrane

Polymeric blend membrane is defined as the blend membranes which comprising of more than one polymer. The blending of polymers can be glassy-glassy, glassy-rubbery and rubbery-rubbery polymers. According to literature, polymeric blend membrane is very unique in nature. It has the ability to provide useful method to combine the benefits or advantages of each polymer into a newly developed membrane or product. Generally, a continuous range of performance is predicted by varying the composition of blend membrane (Mannan et al., 2013). This method offers a time and cost-effective combination of polymers with different separation and physicochemical properties in achieving desired superior properties which are not found in individual polymers (Kapantaidakis, Kaldis, Dabou, & Sakellaropoulos, 1996).

There are several methods can be used to prepare polymeric blend membrane such as solution mixing, melt mixing, molding processes and extrusion. The most important feature of polymeric blend membrane is its phase behavior related to gas separation. It can be categorized into miscible or phase-separated blends (immiscible and partially miscible blends) (Rowe, Robeson, Freeman, & Paul, 2010). When the polymers are dissolved completely in each other to produce homogeneous single-phase behavior solution, it is called miscible blends whereas phase-separated blends is when the polymers cannot dissolve in each other.

The phase behavior of blends can be determined by the glass transition temperature. Miscible blends will result single glass transition temperature whereas in a phase-separated blend, two distinct glass transition temperatures are observed. In gas separation application, partially miscible blends have been extensively applied and their performance is strongly dependent on membrane morphology, size and shape and specific volume fraction of the dispersed and continuous phase (Mannan et al., 2013).

2.4.1 Application of Polymeric Blend Membrane

Based on the literature, polymer blend membrane technology has been applied in gas separation for separating CO_2/CH_4, CO_2/N_2, CO_2/H_2, H_2/N_2 and N_2/O_2. It has been found that more attention is given to natural gas monetization and facilitated transport of CO_2 for CO_2 capture. This is due to the benefits and advantages it possess.

Polymeric blend membrane has the potential in lower down plasticizing behavior of polymers by blending with a less plasticizable polymer (Car, Stropnik, Yave, & Peinemann, 2008). It is also emphasized that it has the ability to improve mechanical and thermal properties. Facilitated transport of a specific gas can be obtained by changing the blend compositions and combinations (Shao, Low, Chung, & Greenberg, 2009). According to the literature, there are a few polymeric blend membranes have been developed and reported for gas separation application.

2.4.2 Previous studies on polymeric blend membrane

Based on the literature, many researches have been carried out in order to achieve the gas separation requirement. The deficiency of these membranes have driven the alternative materials by researchers which are much more mechanically stable, economic viable and having high efficiency in term of gas separation performances.

Different methods and techniques have been used with the objective to enhance the performance of polymeric membranes to fulfil the required duties. Table 2.1 summarizes the previous studies on polymeric blend membranes.

Table 2.1: Various researches on polymeric blend membrane

Year	Polymers	System	Remarks	References
1999	PEI/PVA (Glassy/Glassy)	CO_2/N_2	- The permeabilties of CO_2 and N_2 increased when PEI wt% increases. - Membrane was swollen at higher PEI wt%. - Highest selectivity was roughly 160 and was higher than that of the PVA membrane. - Selectivity increased when temperature is increased. - Selectivity achieved more than 230 by heat-treatment at 160 ℃.	(Matsuyama, Terada, Nakagawara, Kitamura, & Teramoto, 1999)
2002	PMMA/PVME (Glassy/Rubbery)	CO_2 /N_2	-Permeability coefficients of CO_2 and N_2 increased with, until it reached 5 phr with the coefficient of 1 and then leveled off.	(Moon, Yoo, Choi, & Kim, 2002)
2009	PVAm/PVA (Rubbery/Glassy)	CO_2/CH_4	- Selectivity of CO_2/CH_4 up to 45 and permeability of CO_2 up to 0.35 m^3 (STP)/m^2h bar in low pressure range (2–5 bar). - Addition of carbon nanotube (1.0 wt%), resulted better durability against compaction at elevated pressures.	(Deng, 2009)
2009	PVAm/PVA (Rubbery/Glassy)	CO_2/CH_4	- Membrane with 10 wt% PEG has the highest pure CO_2 permeation rate of 5.8×10−6 cm^3 (STP)/cm^2.s.cm Hg and the highest selectivity of 63.1 at 25 ℃ and 96 cm Hg of feed pressure. - CH_4 permeability increased when CO_2 partial pressure increases due to the coupling effects.	Deng, Kim et al. (2009)
2009	PVA/PEG (Glassy/Rubbery)	CO_2/CH_4	- Polar ether segments of PEG interact favorably with CO_2 and resulted in a high selectivity. - PVA provides a mechanically strong polymer matrix.	(Xing & Ho, 2009)
2010	Matrimid®/PSF (Glassy/Glassy)	CO_2/CH_4	- A membrane prepared from a 3:1 (Matrimid®:PSF) blend ratio showed consistent increase in selectivity at high CO_2 feed composition (90 vol%), elevated temperature of 95 ℃ and pressure of 14 bar.	(Basu, Cano-Odena, & Vankelecom, 2010)
2010	PEG/PDMS (Rubbery/Rubbery)	CO_2/CH_4, CO_2/N_2	-CO_2 permeability increased by a factor 5, about 530 barrer at 50 wt% PDMS–PEG loading. -The selectivity slightly decreases.	(Reijerkerk, Knoef, Nijmeijer, & Wessling, 2010)
2010	PSF/PI (Glassy/Glassy)	CO_2/CH_4	- Permeability increased with the increase in PI content and it decreased slowly with the increase in feed pressure in the range of 2-10 bar. - Membrane with 20% PI content produces maximum permeability and selectivity of 39.3 GPU and 28.69 respectively at 2 bar. - Improved chemical and thermal stability.	Rafiq, et al. (2011)

2011	ABS/PVAC (Glassy/Rubbery)	CO_2/CH_4, CO_2/N_2	- Permeability approximately decreased with the increase in pressure for PVAc at the content of 0–40wt.%, and it increased from 50–60wt.% - Highest CO_2 permeability of 5.72 Barrer for the membrane containing 10wt.% PVAC, the highest CO_2/CH_4 selectivity was 29 in 20wt.% PVAc and CO_2/N_2 was 40.41 in 30wt.% PVAc contents.	Sanaeepur, et al. (2011)
2012	PEI/PVP (Glassy/Glassy)	CO_2/CH_4, CO_2/N_2	-Fabrication of carbon hollow fibre membrane. -Presence of PVP caused slight decrease in thermal stability. -Polymer blends with 6 wt % PVP was the best composition with CO_2/CH_4, and CO_2/N_2 selectivities of 55.33 and 41.50.	(Salleh & Ismail, 2012)
2012	PU/PVAC (Rubbery/Rubbery)	CO_2/CH_4, CO_2/N_2	- Membranes with 2 to 4 phr pluronic will improve the selectivity of CO_2/CH_4 (33) and CO_2/N_2 (97)	(Semsarzadeh & Ghalei, 2012)
2012	PIM-1/Matrimid (Glassy/Glassy)	CO_2/CH_4, O_2/N_2	-The result showed increase in gas permeability and a slight decrease in selectivity. The additions of 5 and 10 wt% PIM-1 into Matrimid induce the permeability increments of 25% and 77%, respectively from the original 9.6 to 12 and 17 Barrer without compromising its CO_2/CH_4 selectivity. For O_2/N_2 separation, the incorporation of a small amount of Matrimid (e.g., 5–30 wt%) into PIM-1 promotes a fair increase in selectivity and drives the overall gas separation performance surpassing or close to the upper bound.	(Yong et al., 2012)

PMMA=polymethylmethacrylate, PVME=polyvinylmethylether, PDMS=polydimethylsiloxane, PEG=polyethylene glycol, PEI=polyether imide, PU=polyurethane, PI=polyimide, PIM-1=polymer of intrinsic microporosity, PSF=polysulfone, PVA=polyvinyl alcohol PVAC=polyvinyl acetate, PVAm=polyavinylamine, PVP= polyvinylpyrrolidone

2.5 Materials for Polymeric Blend Membrane

2.5.1 Polymer

Generally, polymeric blend membrane comprising of more than one polymer which can be either glassy polymer or rubbery polymer. In this project, the novel polymeric blend membrane is comprising of one glassy polymer and one rubbery polymer. There are many types of polymers that has been used for synthesizing membrane. Table 2.2 and Table 2.3 summarizes the common glassy and rubbery polymers respectively.

Table 2.2: Common glassy polymers used for membrane synthesis (Rizwan Nasir, Hilmi Mukhtar, Zakaria Man, & Dzeti F. Mohshim, 2013b)

No	**Polymer**	**Glass Transition Temperature, T_g (°C)**	**Operating Condition**		**Permeability**		**Selectivity**
			T (°C)	**P (Bar)**	**CO_2**	**CH_4**	**CO_2/CH_4**
1	Polyetherimide (PEI)	217	25	17	7.44E-4	0.12E-4	62
2	Polyimide (PI)	360-410	35	1	8.34	6.86	1.22
3	Polysulfone (PSF)	185	30	1	80.7	0.498	40.2
4	Poly(p-phenylene oxide) (PPE)	215	30	1	90	5.4	16.7
5	Acrylonitrile Butadiene Styrene (ABS)	105	30	37	3.43	0.17	20.2
6	Poly(aryleneether)s	138-158	35	1	30.3	1.9	16.13
7	Matrimid	325	35	10	7.26	0.23	31.6
8	Poly(vinyl pyrrolidone) PVP	150-180	50	26	0.02	1.69E-24	48.1

Based on Table 2.2, it is remarked that performance of glassy polymer is limited by tradeoff between selectivity and permeability. This characteristic can be explained based on upper bound trade-off discovered by Robeson in 1991. It can be seen that polymer such as PEI has the highest selectivity value compared to other polymers but at the same time it has low CO_2 permeability. PEI is selected as the glassy polymer for blend membrane in this project due to the highest selectivity it possess.

Table 2.3: Common rubbery polymers used for membrane synthesis

No	**Polymer**	**Glass Transition Temperature, T_g (°C)**	**Permeability**		**Selectivity**	**References**
			CO_2	**CH_4**	**CO_2/CH_4**	
1	Polyphosphazene (PPZ)	-66	9.3	0.62	15	(Nasir et al., 2013a)
2	Polyvinyl acetate (PVAc)	30	40.24	2.67	15.07	(Mushtaq et al., 2013)
3	Polydimethyl solaxane (PDMS)	-124.8	13	9	1.44	(Tremblay, Savard, Vermette, & Paquin, 2006)
4	Cellulose acetate (CA)	135.9	2.5	0.125	20	(Visser, Masetto, & Wessling, 2007)
5	Polyurethane (PU)	31	14	2.5	5.6	(Tremblay et al., 2006)

From Table 2.3, it can be seen that rubbery polymer generates high permeability but low selectivity which is inversely to glassy polymer. It is clear that PVAc rubbery polymer has the highest permeability of carbon dioxide in Table 2.3. Due to this reason, PVAc is finally chosen as the rubbery polymer for polymeric blend membrane in this project.

2.5.2 Solvent

In order to select the best suitable solvent for membrane fabrication, there are several factors that need to be considered. The most important factor is the solubility of polymers in solvent. The polymers must be able to dissolve completely in solvent to achieve homogenous solution. In addition, the simplicity for handling the hazards of solvent must be taken into consideration as well. Based on literature, there are a few solvents that have been widely used in synthesis of membrane as described below. The characteristics and physical properties of the solvents are outlined in Table 2.4.

Table 2.4: Different solvent characteristic and properties (Nasir et al., 2013a)

Solvent	MW [gmol^{-1}]	Density [g cm^{-3}]	B.P. [℃]	V.P. [kPa]	Solubility in water	Solubility parameter [J$^{1/2}$cm$^{-3/2}$]	Remarks
Dimethyl-acetamide (DMAc) C_4H_9NO	87.12	0.937	166	0.2	Soluble	22.1/22.8	It is polar and aprotic solvent. It is an excellent. It is an excellent solvent for high molecular weight polymers and synthetic resins (Nasirzadeh, Neueder, & Kunz, 2005).
Dichloromethane (DCM) CH_2Cl_2	84.94	1.336	39.8–40	46.5	Not soluble	19.9	It has a very low boiling point. Hence, its evaporation rate is shorter. Due to high volatility, the membrane can exhibit a wavy structure and therefore rapid evaporation can be avoided (WIRYOATMOJO, 2010).
N-Methyl-2-pyrrolidone (NMP) C_5H_9NO	99.13	1.028	202	0	Soluble	22.9	It is a very stable and powerful polar solvent. Besides, this solvent can replace hazardous solvents because of its low toxicity (Kusworo, Ismail, Mustafa, & Matsuura, 2008).
N-Dimethylformamide (DMF) C_3H_7NO	73.09	0.949	153	0.3	soluble	24.9	It is a polar solvent. Usually, it is highly suitable for salts or compound with high molecular weight owing to the combined action of its small molecules, high dielectric constant, electron donor properties, and can form complexes easily. It has high boiling point and miscible in water (Letcher & Whitehead, 1999).
Tetrahydrofuran (THF) C_4H_8O	72.10	0.888	64–66	19.3	Soluble	18.62	It is widely used as evaporative solvent which promoting the formation of skin and in membrane synthesis due to its high volatility. However, THF is very hazardous compared to other solvent (Hawley & Lewis, 1997).

MW: Molecular weight; B.P.: Boiling point; V.P.: Vapor pressure

2.6 Membrane Fabrication Techniques

2.6.1 Solution Casting Method

Solution casting method is suitable for small-scale membrane synthesis. In this technique, after preparing the dope solution, it is poured onto a clean glass plate. After that, casting knife is used to spread over the dope solution with particular thickness. The thin film membrane will be formed after it has been left for evaporation for two to three hours. Lastly, the final membrane will be crystalline and isotropic (Nasir et al., 2013b).

2.6.2 Phase-Inversion Method

Membrane for phase inversion can be synthesized from any mixture of polymers and solvent that forms a homogeneous solution under certain conditions of temperature and composition, but separate into two phases when these conditions are changed. For instance, phase inversion can be induced by vaporization of a volatile solvent from a homogeneous polymer solution, or by freezing a casting solution which is homogeneous only at high temperatures (Nasir et al., 2013b). This operation is very easy and simple. Besides, it does not require a very high cost for synthesizing the membranes.

Basically, there are numerous processes to synthesis membrane. The three main processes are (i) dry process, (ii) wet process and (iii) dry/wet process as shown in Figure 2.3. In dry process, it does not involve the immersion in coagulation bath and the rate of gas permeation is usually low due to a thicker selective layer. In wet process, the polymer solution composition is immersed into a coagulation bath, and phase separation phenomena occurs due to the diffusional exchange of solvent and non-solvent, but they are generally unstable and requires further treatment (Ronner, Wassink, & Smolders, 1989). The difference between dry and wet process is whether the outlet of the casting knife is submerged directly in a non-solvent coagulant.

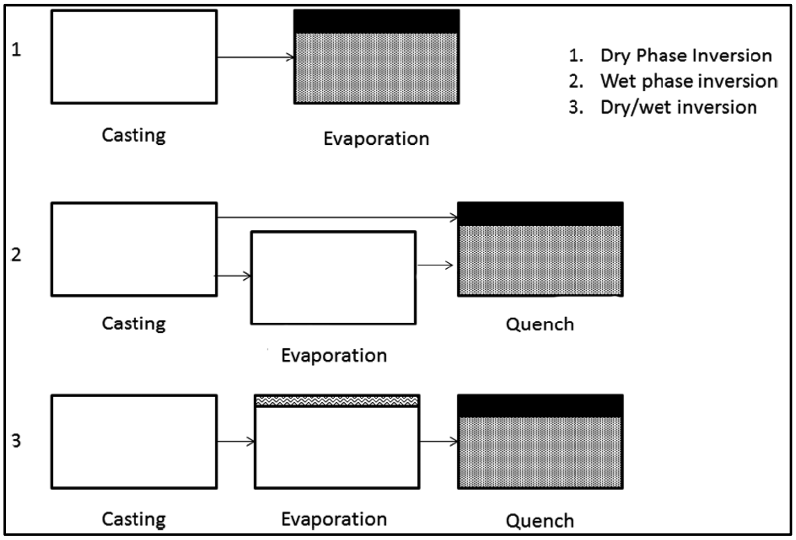

Figure 2.3: Phase inversion processes (Pinnau & Freeman, 2000)

2.7 Characterization of Membrane

Generally, membrane process covers a wide range of separation such as gas separation of carbon dioxide from natural gas. Hence, it will be different in their structure and consequently in their functionality or the performances. In order to identify the membrane required in particular separation process, different membranes must be characterized in terms of structure, physiochemical and thermal properties. Membrane characterization is one of the important parts in membrane research and development. This is because the design of membrane separation processes is depending on reliable data relating to its properties.

2.7.1 Morphology

Morphology can be defined as the identification, analysis, and description of the structures which commonly characterized by equipment such as Field Emission Scanning Electron Microscope (FESEM) and Scanning Electron Microscope (SEM). Both FESEM and SEM produces an image by using a microscope that uses electrons instead of light. From the equipment, some parameters such as surface area and cross sectional area of the membrane samples can be observed and measured (Li, 2007).

2.7.2 Glass Transition Temperature

Based on literature, glass transition temperature is defined as a range of temperature which the increase in thermal energy is sufficient to overcome the steric prevention restricting rotation of polymer backbone segments (Baker, 2004). It can also defined as the temperature region where the polymer transitions from a hard, glassy material to a soft, rubbery material. Generally, glass transition temperature indicates a qualitative measure of the flexibility of polymers. Glass transition temperature is determined by a number of factors such as the chemical structure of the epoxy resin, the type of hardener and the degree of cure. It is usually measured using Differential Scanning Calorimetry (DSC) (Vu, Koros, & Miller, 2003). The analysis of glass transition temperature is carried out based on the graph generated from DSC equipment. The graph shows the relationship between the heat flow response and temperature.

2.7.3 Thermal stability of membrane

In industry, Thermos Gravimetric Analysis (TGA) is the most common techniques that is used to characterize the thermal properties of samples. In membrane technology, thermal stability of membrane can be measured from TGA by determining the weight percent loss of the membrane with temperature change (Tutuk Djoko Kusworo, 2008). The heating temperature range can be varied from 20℃ up to 900℃ with nitrogen gas flow of 20℃/minute. Nitrogen is used to ensure inert environment around the samples. After that, the sample is cooled down to room temperature after been hold for 30 minutes at particular temperature to ensure the completion of the process (Mohamed, Yusup, & Maitra, 2012).

2.7.4 Miscibility of Blend Membrane

Thermodynamically there are two classes of blends which are miscible and immiscible blends. In immiscible blends the constituent polymers do not mix, but remain in separate phases, leading to the formation of a dispersion of one of the polymers in a continuous matrix of the other. Experimental evidence indicates that most polymer pairs are completely immiscible. It is important to take note that blends can exhibit complete immiscibility and partial immiscibility, just as in small molecule systems.

In miscible blends the constituent polymers mix on a molecular level, to form a homogeneous material equivalent to a polymer-polymer solution. The physical, chemical and mechanical properties are generally a weighted average of the mixture components. In this project, solution casting technique as described in chapter 2.6.1 is selected for synthesizing membranes.

Differential Scanning Calorimetry (DSC) technique can be used to make qualitative statements about whether or not polymer blend systems are miscible or immiscible, provided the inherent homopolymer transition temperatures of the blend components are sufficiently well separated. A description of the glass transition temperature characteristics of two different polymer blend systems evaluated by DSC will illustrate this point. In general, polymer blend systems which show two glass transition temperatures by DSC are recognized as being immiscible; those which show only a single glass transition temperature may or may not be miscible.

CHAPTER 3

MATERIALS AND METHOD

This chapter discusses the research methodology that are planned for the project. On top of that, this chapter also includes the discussion about the selection of raw materials and chemicals, technique which will be employed to synthesis, characterize as well as the experimental setup to evaluate the performance of novel polymeric blend membrane. Furthermore, the feasibility table and list of chemicals, glassware and equipment are summarized as well. Lastly, the key milestone and Gantt chart is also attached along in the end of the chapter.

3.1 Materials and Chemicals

In this project work, selection of materials are very important. They are listed as follows:

3.1.1 Polyetherimide (PEI)

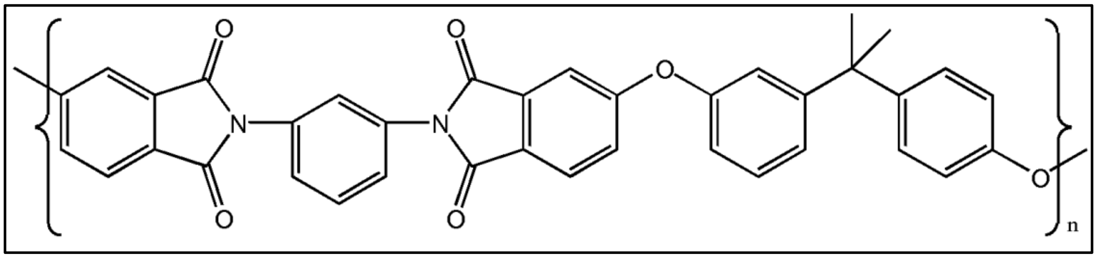

Figure 3.1: Molecular structure of polyetherimide (PEI)

Polyetherimide (PEI) is an amorphous and amber-to-transparent thermoplastic. It has the molecular formula of the repeating unit of PEI is $C_{37}H_{24}O_{6}N_{2}$. The glassy temperature, T_g of PEI is very high, 217°C and it will be glassy polymer at room temperature. The main reason PEI is selected is because of the imide functional group which has tendency to absorb more carbon dioxide and thus enhance the permeability and selectivity (Birbara, Filburn, & Nalette, 1999). On the other hand, high selectivity performance is also observed in PEI. Moreover, it is easy to handle, good mechanical strength and lower in term of cost (I.-C. Kim & Lee, 2004). Figure 3.2 shows the picture of PEI whereas Table 3.1 summarizes the physical properties of PEI.

Figure 3.2: PEI pellets

Table 3.1: Physical properties of PEI polymer

Properties	Details
Supplier	Sigma Aldrich
Type of polymer	Glassy polymer
Molecular formula	$C_{37}H_{24}O_6N_2$
Molecular weight of repeat unit	592.61 g/mol.
Glass transition temperature, T_g	217°C.
Density at 25°C	1.27 g/cm^3.
Shape	Pellet
Color	Amber

3.1.2 Polyvinyl Acetate (PVAc)

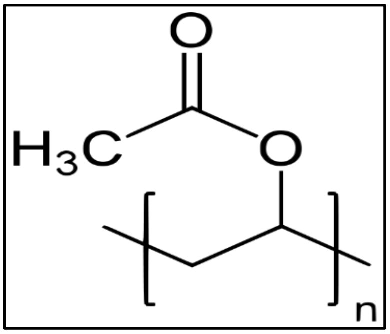

Figure 3.3: Molecular structure of polyvinyl acetate (PVAc)

Polyvinyl acetate (PVAc) is a rubbery polymer with the formula $(C_4H_6O_2)n$. Polyvinyl acetate can be prepared by polymerization of vinyl acetate monomer. It has a boiling point of 72.5 ℃. PVAc is selected as the rubbery polymer because its molecular structure contains C=O polar bonds which has the tendency to attract and absorb more carbon dioxide which is also a polar molecule. Hence, permeability and selectivity can be enhanced. In addition, the cost of PVAc is lower compared to other rubbery polymer (Steiner & Zimmerer, 2013). Figure 3.4 shows the picture of PVAc whereas Table 3.2 summarizes the physical properties of PEI.

Figure 3.4: PVAc pellets

Table 3.2: Physical properties of PVAc polymer

Properties	**Details**
Supplier	Sigma Aldrich
Type of polymer	Rubbery polymer
Molecular formula	$(C_4H_6O_2)n$
Molecular weight of repeat unit	86.09 g/mol.
Glass transition temperature, T_g	37^oC.
Boiling point	72.5^oC.
Density at 25^oC	1.19 g/cm^3.
Shape	Ellipsoid
Color	Colourless

3.1.3 N-Methyl-2-pyrrolidone (NMP)

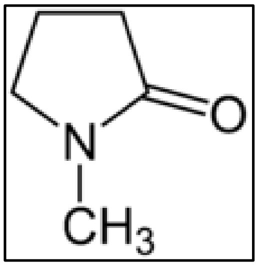

Figure 3.5: Functional group of N-Methyl-2-pyrrolidone (NMP)

N-Methyl-2-pyrrolidone (NMP) is an organic compound as well as the lactam of 4-methylaminobutyric acid. It is a colorless solvent but it will turn slightly yellowish in color due to the impurity. On top of that, it is a dipolar aprotic solvent which include dimethylacetamide, dimethylformamide as well as dimethyl sulfoxide. Thus, it is frequently used in a variety of chemical reactions (Moore & Koros, 2005).

NMP solvent is selected after performing initial miscibility study through different solvents including DMAc and DMF. The dope solution is stable when NMP solvent is used. NMP solvent is often used in membrane formation because it is a chemically stable and powerful polar solvent which has a lower volatility than most of the solvents used in membrane formation. Last but not least, it can replace other hazardous solvents because of its low toxicity (Nasir et al., 2013b). Table 3.3 summarizes the physical properties of NMP solvent used in this project.

Table 3.3: Physical properties of NMP solvent

Properties	**Details**
Supplier	Sigma Aldrich
Grade	Anhydrous grade with 99.5% purity
Molecular weight	99.13 g/mol.
Boiling point	202°C.
Density at 25°C	1.028 g/cm^3.
pH	7.7-8.0
Solubility in water	Soluble

Based on literature review, NMP is most suitable solvent for Polyetherimide (PEI) since it has been used as the solvent for membrane fabrication using polyetherimide. For instance, NMP solvent was selected to cast polyetherimide/ polyvinylpyrrolidone-based carbon hollow fiber membrane (A. F. Ismail & Salleh, 2013). Moreover, there was a research study on the preparation of ODPA-based polyetherimide polymer using NMP solvent (Simons et al., 2010).

3.2 Methods

3.2.1 Experimental Flowchart

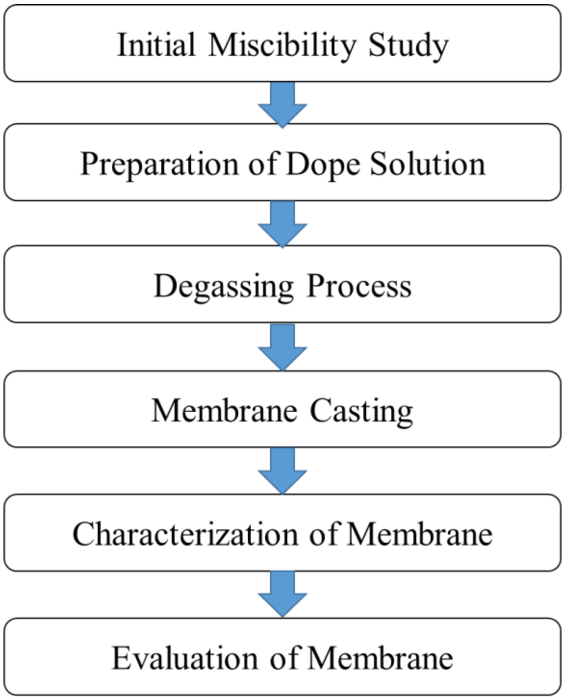

Figure 3.6: Experimental Flowchart

3.2.2 Project Design

The experimental work involved in this project is illustrated in the flowchart as shown in Figure 3.7.

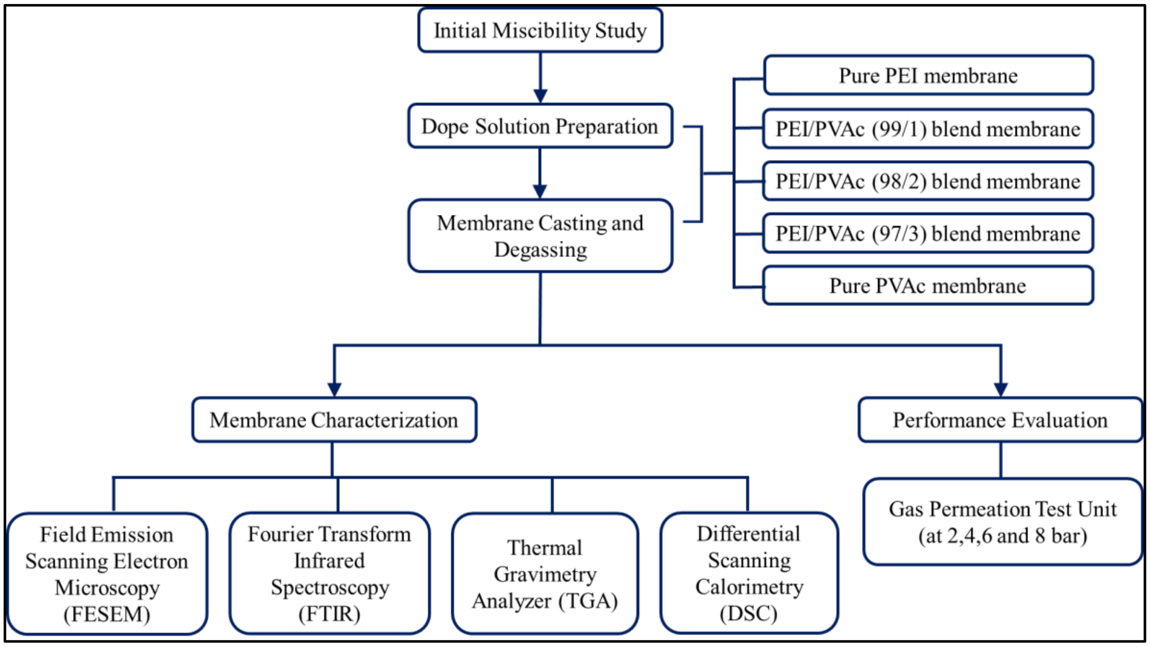

Figure 3.7: Overall experimental workflow of project

3.2.3 Synthesis of Membrane

3.2.3.1 Initial Miscibility Studies of Selected Polymers

Initial miscibility study is necessary to check the compatibility of PEI and PVAc so that the maximum composition of PVAc that is best suitable for the project can be determined.

i. Firstly, 8.3160 mL of NMP solvent was measured using pipette. Then, the solvent was poured into a glass bottle with cap.
ii. After that, 2.1158 g of PEI and 0.0214 g of PVAc were measured respectively using electrical balance.
iii. Next, PEI was dissolved in the solvent in one shot. A rotating magnetic bar was added into the mixture. The mixture was then stirred on a magnetic stirrer at 80 rpm and 50℃ for 48 hours.
iv. Once PEI has completely dissolved in solvent, PVAc was added into the solvent in one shot. The mixture was then left for continuous stirring for 24 hours at 50℃ and 80 rpm in close system.
v. Lastly, the miscibility between PEI and PVAc polymers in NMP solvent was checked by observing and determining the phase behavior of the solution.
vi. Step i to v were repeated with different composition of PEI and PVAc polymers at fixed total volume of solution (10 mL) and weight percentage of solution as illustrated in the Table 3.4.
vii. Lastly, effect of the solvent on the miscibility and stability between PEI and PVAc was studied as well by repeating step i to vi with DMF and DMAc solvent as shown in Table 3.5 and 3.6 respectively.

Table 3.4: Six samples test with variable amount of PEI and PVAc in NMP

Sample test	Ratio of PEI : PVAc		Weight percent of solution (wt %)		Amount			Total volume of solution (mL)
	PEI (wt) %	PVAc (wt) %	Polymers (PEI+PVAc)	Solvent (NMP)	PEI (g)	PVAc (g)	NMP (mL)	
1	99	1	20	80	2.1158	0.0214	8.3160	10
2	98	2			2.0942	0.0427	8.3151	
3	97	3			2.0726	0.0641	8.3141	
4	95	5			2.0294	0.1068	8.3123	
5	90	10			1.9215	0.2135	8.3076	
6	85	15			1.8138	0.3201	8.3029	

Table 3.5: Six samples test with variable amount of PEI and PVAc in DMF

Sample test	Ratio of PEI : PVAc		Weight percent of solution (wt %)		Amount			Total volume of solution (mL)
	PEI (wt) %	PVAc (wt) %	Polymers (PEI+PVAc)	Solvent (DMF)	PEI (g)	PVAc (g)	DMF (mL)	
1	99	1	20	80	1.9806	0.0200	8.4237	10
2	98	2			1.9604	0.0400	8.4228	
3	97	3			1.9402	0.0600	8.4219	
4	95	5			1.8998	0.1000	8.4201	
5	90	10			1.7988	0.1999	8.4156	
6	85	15			1.6980	0.2996	8.4112	

Table 3.6: Six samples test with variable amount of PEI and PVAc in DMAc

Sample test	Ratio of PEI : PVAc		Weight percent of solution (wt %)		Amount			Total volume of solution (mL)
	PEI (wt) %	PVAc (wt) %	Polymers (PEI+PVAc)	Solvent (DMAc)	PEI (g)	PVAc (g)	DMAc (mL)	
1	99	1	20	80	1.9577	0.0198	8.4419	10
2	98	2			1.9378	0.0395	8.4410	
3	97	3			1.9178	0.0593	8.4401	
4	95	5			1.8778	0.0988	8.4383	
5	90	10			1.7781	01976	8.4339	
6	85	15			1.6784	0.2962	8.4295	

3.2.3.2 Preparation of Dope Solution

Polymeric blend membranes were synthesized using solution casting and solvent evaporation method.

i. Firstly, PEI and PVAc polymers were preheated in the drying oven at 100℃ and 70℃ respectively for 8 hours to remove all the moistures content.
ii. Next, 33.26 mL of NMP solvent was measured using 50 mL measuring cylinder. The solvent was then poured into a glass bottle.
iii. The glass bottle was then close immediately with cap to prevent evaporation of the solvent.
iv. After that, 8.4634 g of PEI pellet was measured using electrical balance. It was then dissolved in the solvent in one shot. Next, a rotating magnetic bar was added into the glass bottle.
v. The mixture was then stirred on a magnetic stirrer at moderate speed, 80 rpm to prevent the formation of bubbles. The mixture was stirred continuously for 72 hours at 50℃ and 80 rpm.
vi. Then, 0.0855 g of PVAc pellet was measured using electrical balance.

vii. After that, it was added on shot into the mixture. The glass bottle must be closed immediately after adding the polymers into it.

viii. The mixture was then left for continuous stirring for about 24 hours at 50℃ and 80 rpm so that all the polymers were dissolved completely in the solvent.

ix. Step i to viii were repeated with different composition of PEI and PVAc polymers as shown in Table 3.4. For pure PEI and PVAc dope solution preparation, it involves only step i to v and step vi to viii respectively. Specifically, the total volume of solution for all membrane samples were fixed at 40 mL and weight percentage of solution for each sample was elaborated in the Table 3.7.

Table 3.7: Five membrane samples with different amount of PEI and PVAc in NMP

Sample test	**Ratio of PEI : PVAc**		**Weight percent of solution (wt %)**		**Quantity**			**Total volume of solution (mL)**
	PEI (wt) %	**PVAc (wt) %**	**Polymers (PEI+PVAc)**	**Solvent (NMP)**	**PEI (g)**	**PVAc (g)**	**NMP (mL)**	
1	100	0	20	80	8.5498	0	33.2678	40
2	0	100			0	8.4542	32.8956	
3	99	1			8.4634	0.0855	33.2641	
4	98	2			8.3769	0.1710	33.2603	
5	97	3			8.2905	0.2564	33.2566	

Figure 3.8 demonstrates the overall schematic diagram of preparing dope solution.

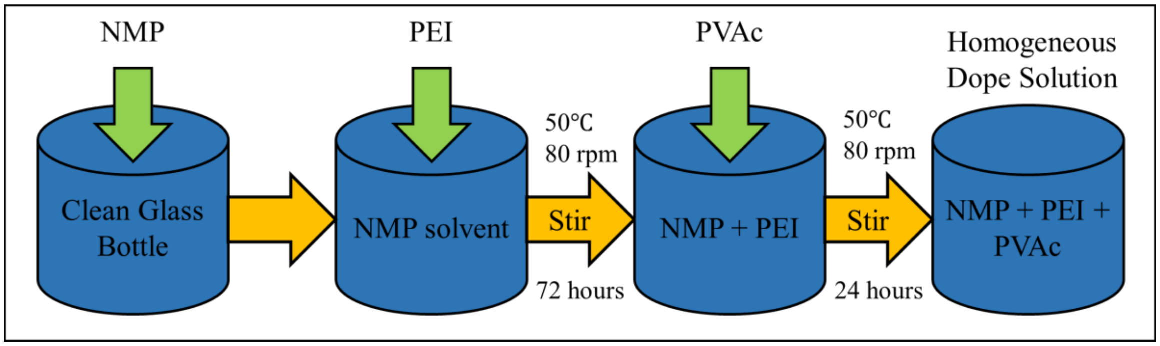

Figure 3.8: Schematic diagram of dope solution preparation

3.2.3.3 Degassing Process

Degassing process is a very crucial and important step to remove all the bubbles that might be formed during the stirring in membrane synthesis process. This step is to ensure zero defect on the membrane.

i. Firstly, the dope solution prepared (close system) was put into the ultrasonic sonication bath as shown in Figure 3.9.

Figure 3.9: Ultrasonic sonication bath ((Transonic Digital S, Elma®)

i. The parameters such as timer can be set for about one hour and temperature of 25℃.
ii. After degassing, the glass bottle with prepared dope solution was taken out from ultrasonic sonication bath and it was left for one hour to ensure all the bubbles were raised up to the surface of the solution before casting.

3.2.3.4 Membrane Casting

Figure 3.10: Membrane fabrication unit

In membrane casting process, there will be a glass plate which used for the template casting. Figure 3.9 shows the unit used for membrane casting.

i. Firstly, acetone was used to clean the glass plate to remove all the moistures and dust particles.
ii. Next, casting knife was adjusted to a thickness of 100 micron and it was ensured to be at the right position.
iii. After that, the dope solution prepared was poured on a flat glass plate (dimension of 148.5 mm x 210 mm). For pure PVAc dope solution, Teflon plate was used instead of glass plate. This is because PVAc rubbery polymer will stick to the glass plate and very hard to be peeled off from glass plate.
iv. The motor selector was then switched on and the casting knife will be moved automatically to cast the film.
v. Next, the casted film was covered with aluminum foil with a few holes on it. This step is important as it will reduce the evaporation rate of the solvent in the casted film. It was then left at room temperature for 4 hours.
vi. Finally, the casted film was undergo drying process in vacuum oven at 90℃ and 500mb for 24 hours.

3.2.4 Characterization of Membrane

The polymeric blend membrane that has been synthesized will be characterized to study its physicochemical and thermal properties. There are four important equipment are used in membrane characterization.

3.2.4.1 Field Emission Scanning Electron Microscopy (FESEM)

Figure 3.11: Field Emission Scanning Electron Microscopy (FESEM-ZEISS SUPRA^{TM} 55VP)

FESEM is used to investigate the physical properties by observing the morphology of the membranes. Besides, surface images will be employed to evaluate particles distribution and agglomeration in matrix. It has been widely used to obtain the morphology of a membrane.

In this project, FESEM is required to investigate and analyze the physical properties such as surface and cross sectional image, the thickness of the membrane, pores existence as well as the defect on surfaces of the flat sheet membrane.

Before FESEM analysis, the membrane samples were cut into the dimension of 0.5-1cm width and 3-5cm length. After that, the samples were fractured cryogenically in liquid nitrogen in order to get a clear cut of the cross-section. The samples were then mounted on a circular stainless steel sample holder with an electrically conductive double-sided tape. Next, the samples were sputter-coated by gold/palladium using Polaron Range SC7640 sputter coater to enable a conductive coating to increase the quality of images under FESEM. The membrane pieces were scanned for the morphology studies. In this project, FESEM micrograph were examined using an accelerating voltage of 5kV with a magnification of 500X and 1000X.

3.2.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3.12: Fourier Transform Infrared Spectroscopy (FTIR-Spectrum One, Perkin Elmer®)

FTIR is used to study the structural/compositional compounds substance qualitatively and quantitatively. It also provides details of chemical structure like bonding and functional group and as a characterization for sample mixture. Therefore, unknown materials can be identified through the quality or consistency of a sample and the amount of components in a mixture. In this project, it is used to study the chemical properties by determining the composition, chemical bonding and particular functional groups in membrane. Based on the developed membrane, the results should produce some peaks of related functional group in PEI, PVAc and NMP (if there is residue solvent).

In this project, all of infrared spectrums were recorded by using Perkin-Elmer® infrared instrument and analyzed by using Spectra One® software. Spectrums were achieved by co-condition of 200 scans at a resolution of 4 cm^{-1} in the range of 400-4000cm^{-1}.

3.2.4.3 Thermogravimetric analyses (TGA)

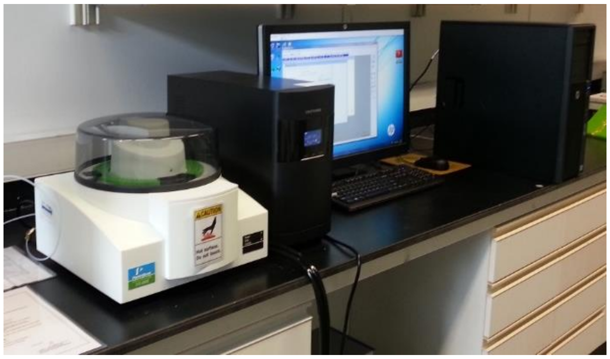

Figure 3.13: Thermogravimetric analyses (TGA-STA 6000, Perkin Elmer)

This analysis will measures changes of the weight of a particular material as a function of time or temperature under a fixed pressure. Based on the graph, information such as thermal stability of a materials, filler content in polymers, moisture and solvent content, and the percent composition of components in a compound. Therefore, the thermal property can be obtained by determining the weight change of synthesized membrane with temperature change. The tested sample were cut into pieces of about 10-20mg.

In this project, TGA analysis was used to study the thermal stability of polymeric blend membranes in the temperature range of 30℃ to 800℃ with heating rate of 10℃/minute under nitrogen gas atmosphere.

3.2.4.4 Differential Scanning Calorimeter (DSC)

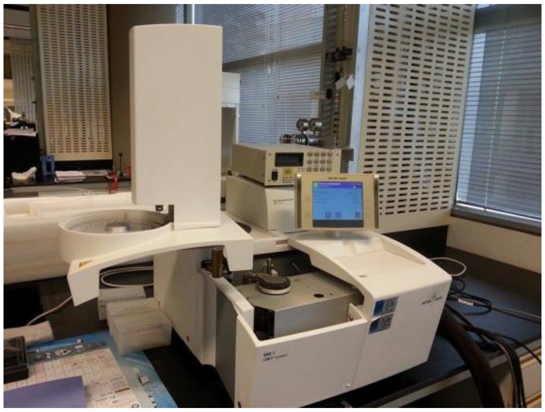

Figure 3.14: Differential Scanning Calorimeter (DSC1 STAR^e System, Mettler Toledo)

Differential scanning calorimetry is used to measure the difference of temperature and heat flow between a sample and a reference material respectively. The ability to determine transition temperatures and enthalpies makes DSC a valuable tool.

In this project, DSC was used to study the miscibility of the polymeric blend membrane. On top of that, it was used investigate the impact of polymeric blend membrane on the glass transition temperature. For pure PVAc membrane, the sample was heated from -10°C to 90°C and then from 90°C back to -10°C at heating rate of 10°C/min in two cycles. The rest of the samples were heated from 0°C to 250°C and then from 250°C back to 0°C at heating rate of 10°C/min in two cycles. Furthermore, the atmosphere was nitrogen gas at flowrate of 50 mL/min. The first cycle was aimed to remove all the thermal history and the glass transition temperature of the sample was determined in the second heating cycle (Liu, Lin, Yang, & Chen, 2005). The summary of DSC analysis procedure was described in Figure 3.15 and Figure 3.16.

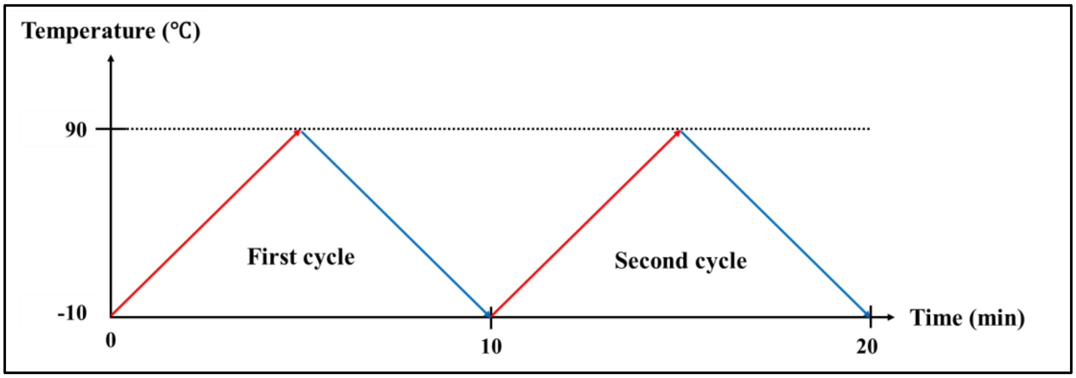

Figure 3.15: Temperature program diagram for pure PVAc membrane

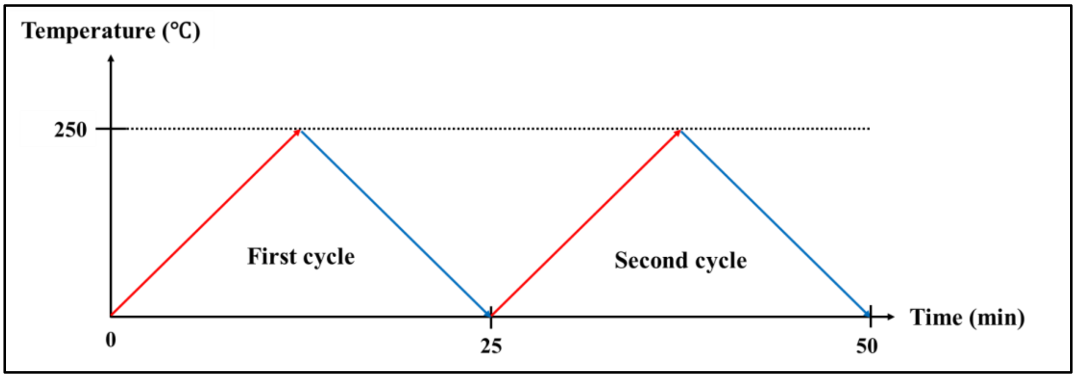

Figure 3.16: Temperature program diagram for pure PEI membrane and all polymeric blend membranes

3.2.5 Evaluation on Performance of Polymeric Blend Membrane

The gas separation performance of membranes were evaluated by using gas permeation test unit as shown in Figure 3.17. Figure 3.18 demonstrates the schematic diagram of gas permeation test unit. Generally, the permeation test depends on maintain both the pressure and area of membrane on the permeate phase. Pure CO_2 and CH_4 were employed as the test gases with different feed pressure of 2, 4, 6 and 8 bars. All tests were carried out at room temperature (25℃) condition.

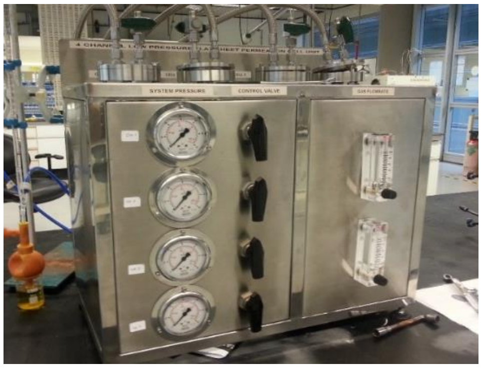

Figure 3.17: Gas permeation test unit

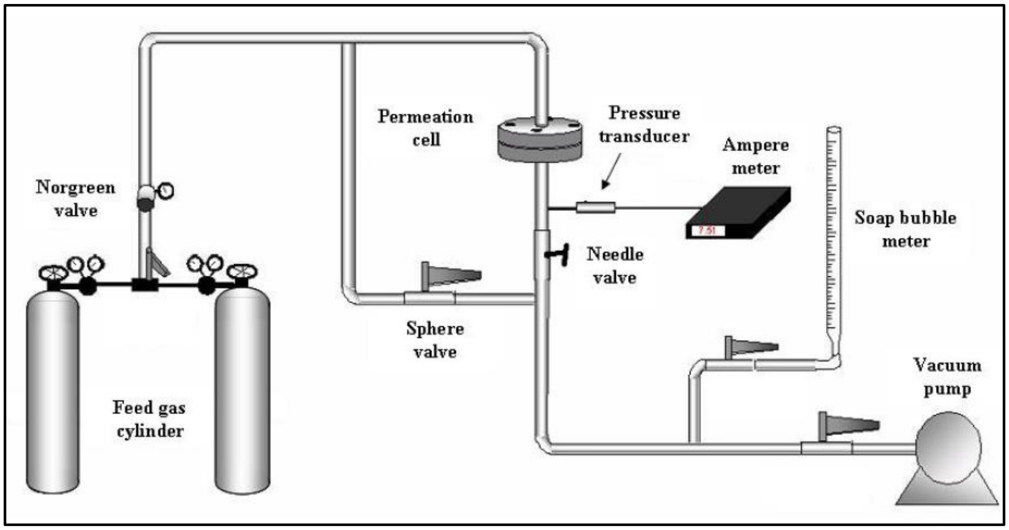

Figure 3.18: Schematic diagram of gas permeation test unit (Mohammadi, 2011)

i. Before the start of the experiment, the system was evacuated for 10 minutes to remove residual gases remaining in the system.

ii. The membrane was cut into a dimension of 4.8 cm diameter. It was then placed on the membrane module of the test unit.

iii. The feed gas was directly supplied from the gas cylinders that were equipped by a pressure gauge. A three-way valve was attached as the entry point of the system allowing only one pure gas stream enters at a time. Firstly, pure single carbon dioxide gas permeation system was introduced at feed pressure of 2 bar at room temperature (25℃). The permeate side of membrane was maintained at atmospheric pressure. Thus, pressure drop will be maintained at 2 bar.

iv. The permeation rate was measured by bubble flow meter. From the bubble flow meter, the time taken for the bubble to move from one initial set point to last set point was recorded.

v. Volumetric flow rate can be then calculated by measuring the total volume travelled by the bubble at specific time as recorded in step iv.

vi. Step ii to v were repeated by using pure single methane gas for the entire gas permeation system.

vii. The permeability of the membrane was calculated from the collected data by using equation 3.1 whereas equation 3.2 is used to calculate the selectivity of the membrane.

$$P_i = \frac{Q_i \cdot 273 \cdot l}{\Delta p_i \cdot T_i \cdot A} \tag{3.1}$$

$$\alpha_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}} \tag{3.2}$$

where P_i is permeability, Q_i is volumetric flow rate of gas (cm^3/s), l is the thickness of membrane (cm) Δp is the partial pressure driving force of gas component (cmHg), T_i is the absolute temperature (K), A is the surface area of membrane (cm^2), and α_{CO_2/CH_4} is ideal separation factor or selectivity. Permeability of the membranes were reported in the unit of Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm/cm^{2}s cm Hg).

viii. Step i to vii were repeated with feed pressure of 2, 4, 6 and 8 bars at ambient temperature.

ix. Plot of the pure gas permeability of CO_2 and CH_4 as well as the membrane ideal selectivity against operating pressure were drawn and presented in Chapter 4.

3.3 Project Feasibility Study

The expected experimental process flow are outlined in Table 3.8:

Table 3.8: Estimated duration for one trial

No.	Process	Duration
1	Initial miscibility study	72 hours
2	Preparation of dope solution	96 hours
3	Degassing and Membrane Casting	24 hours
4	Drying Process	24 hours
5	Characterization of membrane (FESEM, FTIR, TGA, DSC)	36 hours
6	Evaluation of membrane (Gas permeation test)	18 hours
	Total:	**270 hours**

The experiment will be carried out at least two times due to consideration of some errors that might occurred during the experiment. Therefore, it is important to understand and clear with every single procedure that involved in the experiment.

The project w expected to be completed within seven months period. Basically, it only involves simple experimental steps. However, time will be wasted in characterization and evaluation of developed membrane due to the limited equipment in UTP.

3.4 Chemical, Glassware and Equipment List

Table 3.9: List of chemicals, glassware and equipment

Type	No.	Name	Quantity	Location
Chemical	1	PEI polymer	250 g	Block 3-02-03
	2	PVAc polymer	50 g	Block 3-02-03
	3	DMAc solvent	450 mL	Block 3-02-03
	4	Acetone	350 mL	Block 3-02-03
Equipment	1	FESEM	1	Block P
	2	FTIR	1	Block 4
	3	TGA	1	Block 4
	4	DSC	1	Block 4
	5	Gas permeation test unit	1	Block 3-02-03
	6	Electric balance	1	Block 3-02-03
	7	Magnetic stirrer	1	Block 3-02-03
	8	Rotating magnetic stirrer	5	Block 3-02-03
	9	Vacuum oven	1	Block 3-02-03
	10	Drying oven	1	Block 3-02-03
	11	Ultrasonic degasser	1	Block 3-02-03
	12	Casting knife	1	Block 3-02-03
	13	Timer	1	Block 3-02-03
Glassware	1	Petri glass	2	-
	2	10 mL measuring cylinder	1	-
	3	50 mL measuring cylinder	1	-
	4	50 mL beaker	1	-
	5	100 mLglass bottle with cap	5	-
	6	Glass plate	4	-
	7	Teflon plate	1	
	8	Spatula	1	-
	9	Filter funnel	1	-

3.5 Gantt Chart and Planned Milestones

Table 3.10: Gantt chart with proposed milestones for FYP I

NO	DETAIL Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Title	🟥	🟥													
2	Meeting/Discussion with Supervisor	🟧	🟧													
3	Preliminary Research Work and Literature Review		🟨	🟨	🟨	🟨										
4	Submission of First Draft of Extended Proposal Defense					🟩										
5	Amendment on Extended Proposal Defense					🟦										
6	Submission of Chemical Request Form					🟪										
7	Submission of Finalized Extended Proposal Defense						●									
8	Slide Preparation for Oral Proposal Defense Presentation							🟥								
9	Slide Checking by Supervisor							🟫								
10	Oral Proposal Defense Presentation									●						
11	Detailed Literature Review									🟧	🟧	🟧	🟧	🟧	🟧	🟧
12	Booking of Laboratory											🟨				
13	Experimental Laboratory Briefing											🟩				
14	Experimental Laboratory Work												🟦	🟦	🟦	
	Initial Miscibility Studies												🟪			
	Preparation of Dope Solution													🟥		
	Casting of Membrane													🟫		

	Characterization of Membrane														🟥	
	Perform FESEM/FTIR/TGA/DSC														🟧	
	Perform Gas Permeation Unit														🟨	
15	Analysis and Interpretation of Results Obtained												🟦	🟦	🟦	🟦
16	Submission of Interim Draft Report														🟪 ●	
17	Submission of Interim Final Report															●

- Planned milestone

Table 3.11: Gantt chart with proposed milestones for FYP II

NO	DETAIL Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Meeting/Discussion with Supervisor	🟥	🟥	🟥	🟥	🟥	🟥	🟥		🟥	🟥	🟥	🟥	🟥	🟥	🟥
2	Project Work Continues		🟧	🟧	🟧	🟧	🟧	🟧		🟧						
	Preparation of Dope Solution		🟨	🟨	🟨	🟨										
	Casting of Membrane			🟩	🟩	🟩	🟩	🟩								
	Characterization of Membrane						🟦	🟦								
	Perform FESEM/FTIR/TGA/DSC							🟪		🟪						
7	Submission of Progress Report									●						
8	Pre-SEDEX												●			
9	Submission of Draft Report													●		
10	Submission of Dissertation (Soft Bound)														●	
11	Submission of Technical Paper															●
12	Oral Presentation															●
13	Submission of Dissertation (Hard Bound)															●

● Planned milestone

CHAPTER 4

RESULT AND DISCUSSION

In this project, polymeric blend membrane was synthesized using polyetherimide (PEI) and polyvinyl acetate (PVAc) polymers. In the first part of this chapter, miscibility between polymers in different solvents were discussed. Furthermore, all casted membranes will be presented and displayed. I, the morphology, bonding effect, thermal stability and miscibility of developed membrane characterized by FESEM, FTIR, TGA as well as DSC were discussed based on the outcomes of the analysis. Lastly, the gas separation performance of developed membrane was evaluated at the end of this chapter.

4.1 Initial Miscibility Study

Initial miscibility study between PEI and PVAc in solvent is very important so that the maximum composition of PVAc that is best suitable for the experiment can be determined. Table 4.1 presented all the results in terms stability or miscibility based on different solvent and ratio between polymers.

Table 4.1: Initial miscibility study between polymers in different solvent

Solvent	Polymer/Solvent Ratio	Polymer-Polymer Ratio (PEI/PVAc)					
		99/1	98/2	97/3	95/5	90/10	85/15
DMF	80/20	miscible	slightly miscible	not miscible	not miscible	not miscible	not miscible
DMAc	80/20	miscible	miscible	slightly miscible	not miscible	not miscible	not miscible
NMP	80/20	very miscible	very miscible	very miscible	slightly miscible	not miscible	not miscible

From Table 4.1, it was remarked that NMP was the most suitable solvent for PEI/PVAc blend membrane as the miscibility was much stable than DMF and DMAc solvent.

As stated in literature, NMP is a very stable and powerful solvent and it has been widely used in membrane preparation (Kusworo et al., 2008). When NMP solvent was used, there was no defect and voids on the membrane. However, phase separation was observed DMF and DMAc solvents were used. This scenario was reported in previous study as well (Bottino, Camera-Roda, Capannelli, & Munari, 1991). On top of that, it was found that PEI and PVAc were very miscible in NMP solvent at PEI/PVAc ratio of 99/1, 98/2 and 97/3 but the stability decreases as the composition of PVAc increases. Hence, based on the outcome of this study, NMP was selected as the solvent whereas the PEI/PVAc ratio were set at 99/1, 98/2 and 97/3 for this entire polymeric blend membrane project.

4.2 Synthesis of Membrane

Synthesis of membrane was one of the objectives of this project. There were total of five membranes with different composition were casted successfully using solution casting and evaporation method. Specifically, there were two pure polymeric membranes and three polymeric blend membranes using PEI glassy polymer and PVAc rubbery polymer in NMP solvent. The methodology of preparing membrane was described in chapter 3. Figure 4.1 presented the images of casted membranes that were cut into desired size for evaluating gas separation performance.

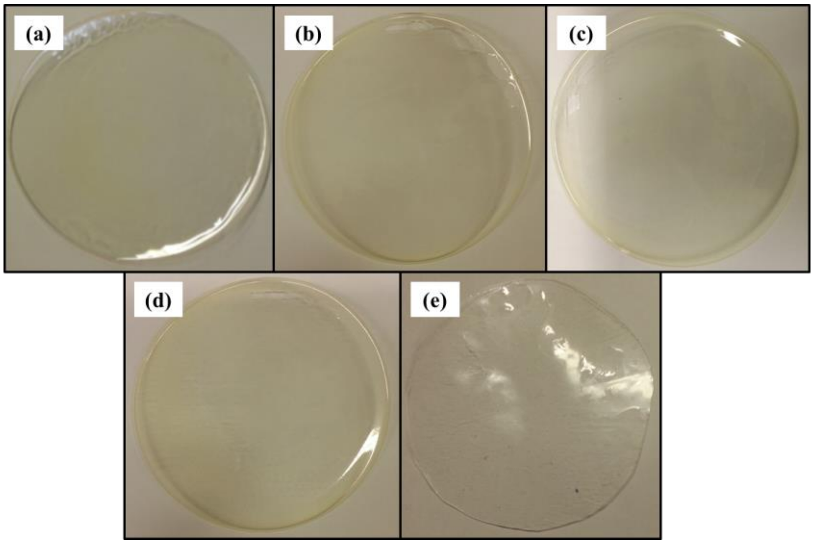

Figure 4.1: Images of all casted membranes (a) pure PEI (b) PEI/PVAc-99/1 (c) PEI/PVAc-98/2 (d) PEI/PVAc-97/3 (e) pure PVAc

Based on Figure 4.1, it can be observed that all five membranes were casted successfully. There was no defect and crack on the membranes. On top of that, top and bottom surface of all casted membranes were very smooth and the thickness of membranes were uniformly distributed. In terms of characteristics and behaviors, pure PEI polymeric membrane was hard and brittle whereas pure PVAc was soft and flexible. These characteristics and behaviors were corresponding to the theory of glassy and rubbery polymers behaviors as mentioned in literature (Baker, 2000). Besides, the results were also supported by a few studies (Landel & Nielsen, 1993; Van Krevelen & Te Nijenhuis, 2009). For polymeric blend membrane, the rigidity of the membrane decreases and it was becoming less brittle as the composition of PVAc increases.

4.3 Characterization of Membrane

4.3.1 Field Emission Scanning Electron Microscopy (FESEM)

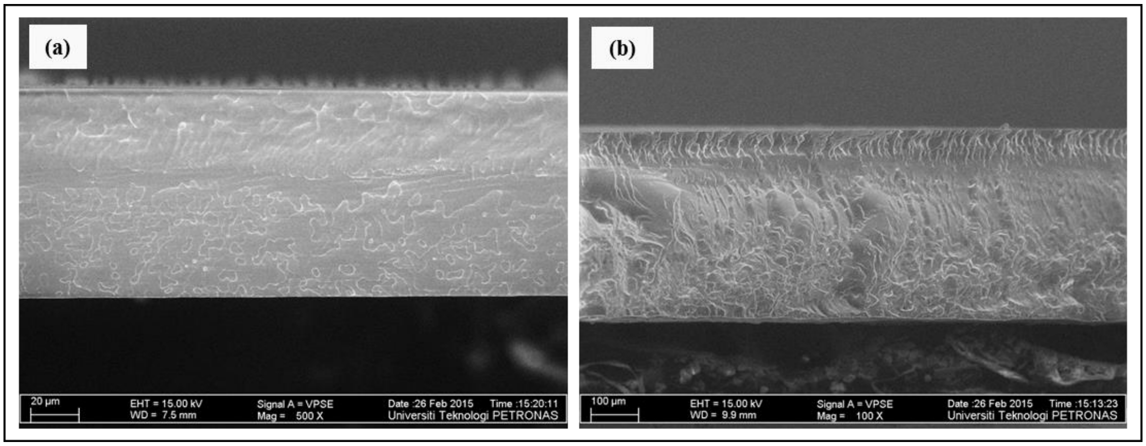

Figure 4.2: Cross sectional morphology of pure membranes at 500X. (a) Pure PEI polymeric membrane (b) Pure PVAc polymeric membrane

The FESEM images of cross sectional morphology of pure membranes were shown in Figure 4.2. In Figure 4.2a, cross sectional image of pure PEI polymeric membrane was shown. Based on the morphology, it was observed that the membrane was rigid and dense due to rigidity of PEI polymer chains. The morphology of pure PEI membranes was densely packed in structure as well in previous study (Park & Kim, 1996).

Figure 4.2b presents the cross sectional image of pure PVAc polymeric membrane. Again, rigid and dense structures can be seen on pure PVAc polymeric membrane. Besides, there was no agglomeration of polymer. Most importantly, the results obtained were matched with previous studies (Shieh & Chung, 1999).

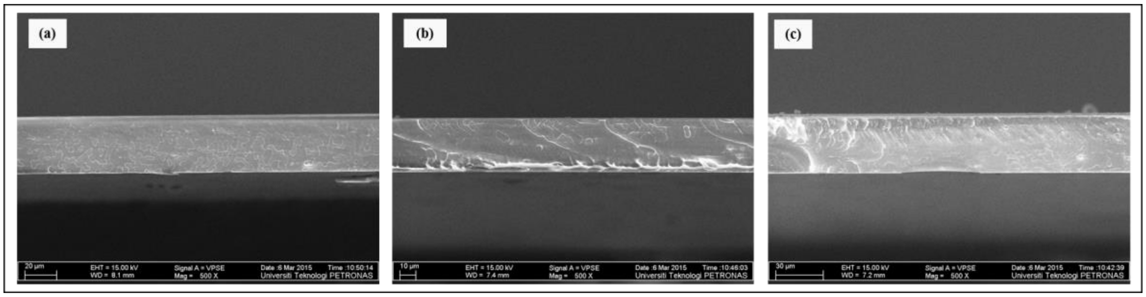

Figure 4.3: Cross sectional morphology of (a) PEI/PVAc-99/1 (b) PEI/PVAc-98/2 (c) PEI/PVAc-97/3 polymeric blend membranes at 500X

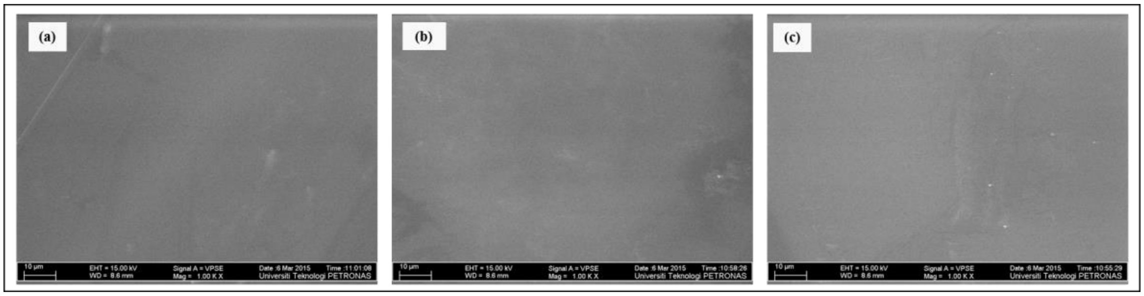

Figure 4.4: Top surfaces morphology of (a) PEI/PVAc-99/1 (b) PEI/PVAc-98/2 (c) PEI/PVAc-97/3 polymeric blend membranes at 1000X

Figure 4.3 illustrated the cross sectional image whereas Figure 4.4 reviewed the top surfaces morphology of polymeric blend membranes. The result showed that all membranes were casted successfully. All the membranes were homogeneous and there was no pores and voids observed in both cross sectional and top surfaces images. Furthermore, it was clear that no phase separation which confirmed the miscibility and compatibility polymers blending. Homogeneity of the membrane surface plays a very important role as it determines the compatibility of both polymers (Bos, Pünt, Strathmann, & Wessling, 2001; Chung, Guo, & Liu, 2006). Based on Figure 4.3, it was remarked that all the cross sectional images of polymeric membrane consisted of both the structure of PEI and PVAc by comparing to its pure structure as presented in Figure 4.2. Besides, it was also noticed that the intensity of turbulent-flow structure of PVAc increases from

Figure 4.3a to Figure 4.3c. This was because the composition of PVAc increases from 1% to 3%.

Most importantly, the analysis showed that no micro voids were observed and the cross sectional morphology was densely packed in pure polymeric membrane as reviewed in both Figure 4.2. Similarly, polymeric blend membrane was presenting the same packed cross section which indicating the good interaction and miscibility between PEI and PVAc as shown in Figure 4.3 and Figure 4.4. Lastly, polymer chains were regularly packed and miscibility was achieved at micro level.

4.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was required so that the functional groups and chemical bonding that were present in the membrane can be identified. FTIR analysis also managed to investgate the interaction betweeen two polymers in a membrane. Figure 4.5 illustrated the spectra of all five membranes.

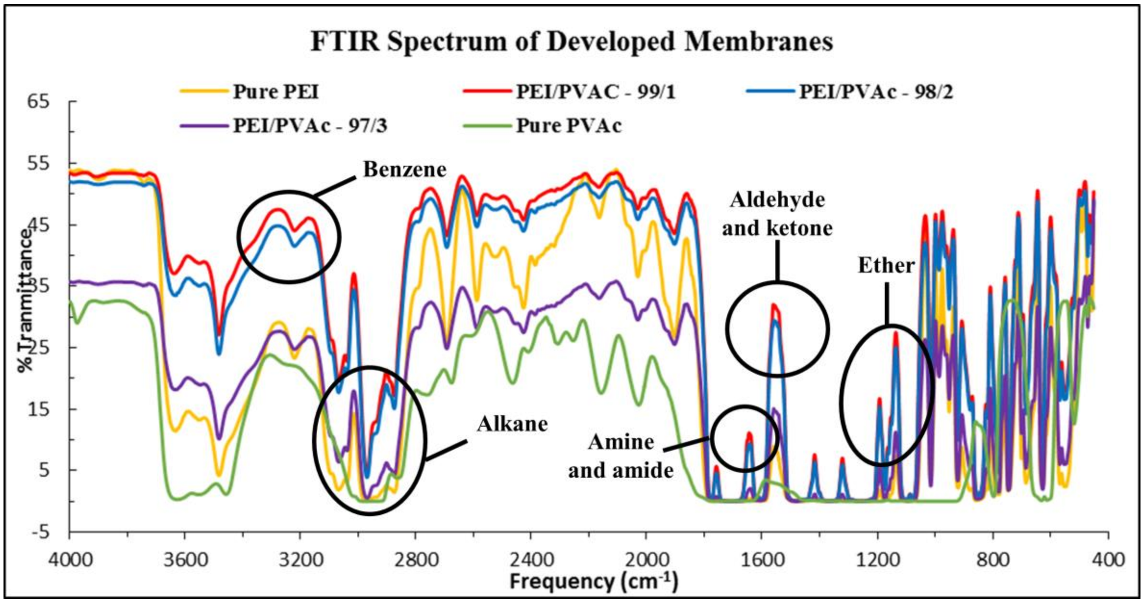

Figure 4.5: FTIR Spectrum of all developed membranes

Generally, there were several important functional groups that present in PEI molecular structure such as benzene, ethers, aldehyde, ketone, amine and amide functional groups (Chiang, Rommel, & Bode, 2009). Functional groups such as aldehyde, ketone and ethers can be found in PVAc structures (Ngai & Roland, 1993).

For pure PEI membrane, the benzene C-H aromatic rings structure was observed at 3220.36 cm^{-1}. However, no peak of C-H and C=C aromatic rings were found in pure PVAc membrane since it has no benzene ring structure. For both pure PEI and PVAc membranes, ether functional group was identified at 1096.03 cm^{-1} and 1228.22 cm^{-1} respectively. On top of that, aldehyde and ketone functional group was also appeared in the spectra for both pure membranes which were found to be at 1695.92 cm^{-1} and 1765.19

cm^{-1}. For pure PEI membrane, there were two additional functional groups (amine and amide) which appeared at 1248.33 cm^{-1}.

In polymeric blend membrane, a few shifts were observed in the spectra behaviour. For example, ether functional group was shifted from 1096.03 cm^{-1} to 1173.69 cm^{-1}, 1173.76 cm^{-1} and 1173.79 cm^{-1} for PEI/PVAc ratio of 99/1, 98/2 and 97/3 respectively. On top of that, the amine and amide functional groups were shifted as well originally from 1695.92.33 cm^{-1} up to 1707.37 cm^{-1} , 1707.68 cm^{-1} and 1708.03 cm^{-1} for PEI/PVAc ratio of 99/1, 98/2 and 97/3. This shift was quite significant and broad. Based on this observation, it can be analysed that these shifts might be due to the effect of hydrogen bonding between PEI and PVAc polymers (Abdul Mannan, Mukhtar, & Murugesan, 2014). In all membranes, C-C stretching peak was appeared in the range of 790 cm^{-1} to 1180cm^{-1}. Hydrogen bonding that occurred between two polymers indicated that PEI/PVAc blend was a compatible blend. Therefore, FTIR spectra of developed membrane further confirmed the macroscopic and microscopic observation of miscibility.

4.3.3 Thermos Gravimetric Analysis (TGA)

Thermal stability of polymeric blend membranes were analyzed using TGA. Figure 4.5 presented the result of TGA analysis. The graph showed the weight loss of sample over the temperature range from 30℃ to 800℃ at heating rate of 10℃/min (Abdul Mannan et al., 2014).

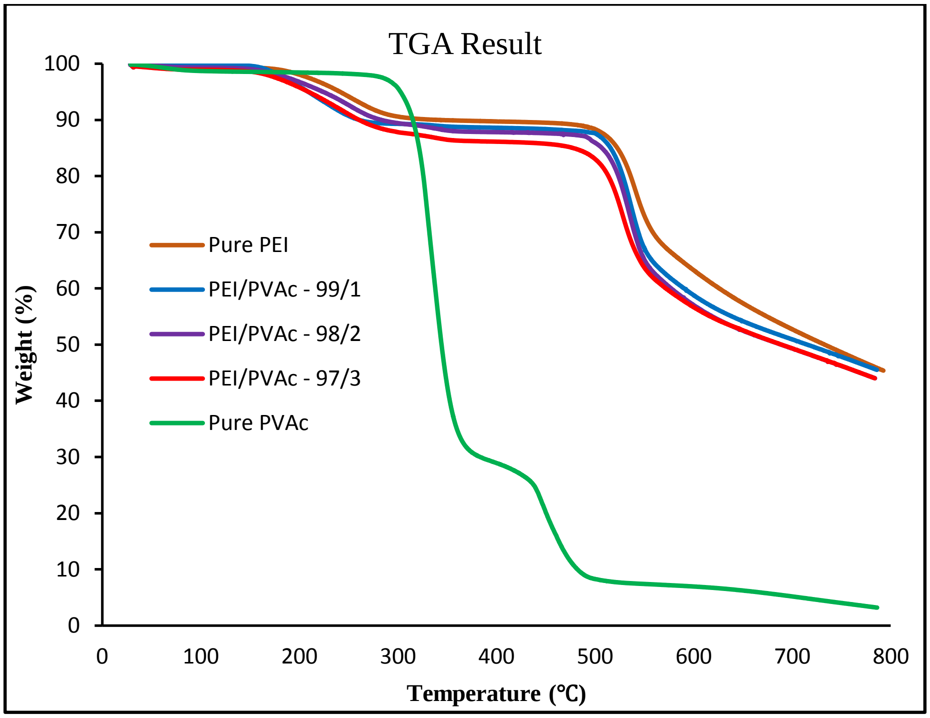

Figure 4.6: TGA curve of all developed membranes

Based on Figure 4.6, it was observed that all developed membranes were free from moisture as there was no weight loss up to 100℃. This observation indicated that the drying time in membrane preparation step was sufficient to remove all the moisture contents as reported in previous study (D. S. Kim, Park, Rhim, & Lee, 2004).

Moreover, two stages of weight loss can be noticed obviously from the graph. According to literature, the existence of first weight loss was usually due to the residue solvent in membrane which was NMP solvent in this case that occurred around 200℃. This scenario can be eliminated by extending the drying time in vacuum oven as described in literature (Mohshim, Mukhtar, Man, & Nasir, 2012). The second weight loss represented the degradation of membrane. The result showed that pure PEI membrane started to degrade at 499.01℃ and thermal degradation moving on till 561.77℃. The result obtained was liable as it was supported by previous study on pure PEI membranes (Wang, Jiang, Matsuura, Chung, & Goh, 2008). In pure PVAc membrane, it can be seen that the onset degradation temperature was lower than others which was 287.80℃ and its maximum degradation temperature was 376.77℃. Most importantly, the degradation temperature obtained for pure PVAc was also corresponding to the values as reported in literature (Rimez et al., 2008).

In polymeric blend membrane, two stages of weight loss can be observed. The first weight loss of 11.67 to 12.74% occurred at temperature range of 150 to 250℃ which indicated the residual NMP solvent left in the membrane while the second stage showed degradation behavior of blend membranes in between pure PEI and PVAc membranes. For instance, the degradation temperature started at 497.22℃, 496.75℃ and 494.71℃ for PEI/PVAc ratio of 99/1, 98/2 and 97/3 respectively. A summary weight loss in particular temperature range and degradation temperature for all membranes were summarized in Table 4.2 and Table 4.3.

Based on the observation, PEI/PVAc polymeric blend membrane has a lower thermal stability compared to pure PEI membrane. This was because PVAc membrane has a very low degradation temperature. However, the effect of PVAc loading on thermal stability was very small and insignificant (less than 0.86%). In overall, the results obtained from TGA were matched with previous studies (Hosseini & Entezami, 2005; Rimez et al., 2008; Wang et al., 2008).

In conclusion, TGA analysis reviewed that there were two stages of weight loss for all pure and blend membranes which indicated insufficient drying time during preparation of membranes. Most importantly, PEI/PVAc blend membranes reduced the thermal stability of pure PEI membrane because the degradation temperature of pure PEI membrane was slightly higher than blend membranes. However, the reduction in thermal stability was very small and almost negligible (less than 0.86%).

Table 4.2: Weight loss in particular temperature of all membrane samples

Membrane sample	Polymers		Percentage weight loss (%)			
	PEI [wt%]	PVAc [wt%]	150-250℃	250-400℃	400-800℃	450-800℃
1	100	0	10.42	-	-	45.43
2	99	1	11.67	-	-	44.23
3	98	2	12.08	-	-	43.81
4	97	3	12.74	-	-	43.17
5	0	100	-	68.33	26.25	-

Table 4.3: Onset and maximum degradation temperature of all membrane samples

Membrane sample	Polymers		Onset degradation temperature [℃]	Maximum degradation temperature [℃]
	PEI [wt%]	PVAc [wt%]		
1	100	0	499.01	561.77
2	99	1	497.22	560.97
3	98	2	496.75	560.02
4	97	3	494.71	559.01
5	0	100	287.80	376.77

4.3.4 Differential scanning calorimetry (DSC)

In this study, DSC analysis was performed to determine the effect of polymeric blend membrane on glass transition temperature. The rigidity of polymers were generally dependent on glass transition temperature. A greater glass transition temperature indicated the polymer was harder or more rigid (Robertson, 1966).

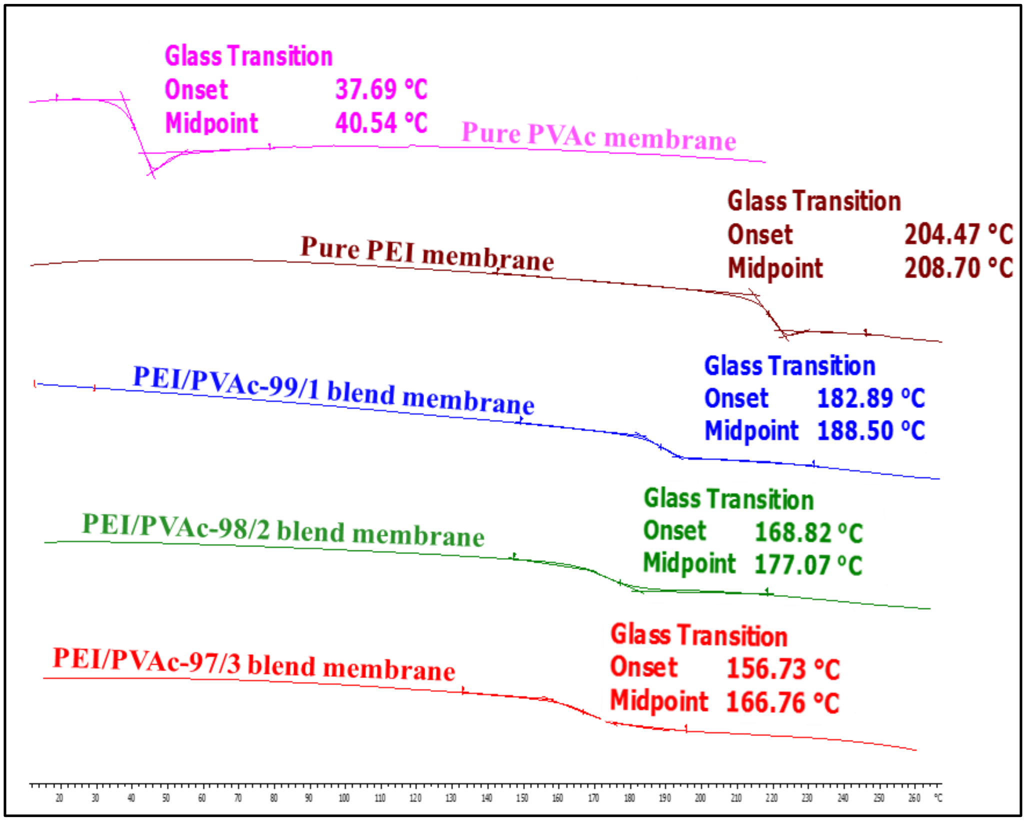

Figure 4.7: DSC analysis result

The result of DSC analysis was presented in Figure 4.7. Based on Figure 4.7, it was remarked that the glass transition temperature, T_g of pure PEI and PVAc membranes were found to be 208.7°C and 40.54°C respectively. The values obtained in this study were compared with the values of glass transition temperature as stated in previous studies. Glass transition temperature of PVAc was corresponding to the literature data but glass transition temperature of PEI was 9°C lower compared to literature (Koolivand et al., 2014).

It was important to take note that there were several aspects that might affect the glass transition temperature of membranes. Aspects such as plasticizers, co-polymer and melting point were needed to be taken into consideration (Ceccorulli, Pizzoli, & Scandola, 1993). In this present study, the aspect that might cause the reduction of glass transition temperature was plasticizer.

Generally, plasticizer is a non-volatile substance that has a low molecular weight. It is usually added into the polymer to enhance the process ability and flexibility. Plasticizer will reduce the glass transition temperature by weakening the force of cohesion between polymer chains. Moreover, a polar attractive force between the molecule of plasticizer and polymer chains will be formed and these forces will reduce the glass transition temperature by weakening the cohesive forces between polymer chains. As a matter of fact, low molecular weight solvent such as water has been reported in previous studies that these solvents have the tendency to exert a plasticizing effect on polymers and hence decreasing the glass transition temperature (Ceccorulli et al., 1993).

In another word, water and NMP solvent could be the plasticizers which reduced the glass transition temperature of membranes. In the previous discussion, TGA analysis indicated that no moisture content was noticed but there were some NMP solvent residuals left in the membranes. Since the molecular weight of NMP solvent (99.1g/mol) was relatively lower than PEI (592.6 g/mol). It was corresponding to the properties of plasticizer and this factor explained a lower glass transition temperature was obtained in pure PEI membrane.

In polymeric blend membrane, a miscible blend membrane was achieved by the present of single glass transition temperature. According to the result obtained, there was only one glass transition temperature which indicated the compatibility and miscibility of PEI and PVAc (Abdul Mannan et al., 2014).

However, the effect of blending between PEI and PVAc has reduced the glass transition temperature. For example, blending of PEI and PVAc at weight composition ratio of 99 to 1 has reduced the glass transition temperature of pure PEI membrane significantly from 218.7℃ to 188.5℃. This was because PVAc polymer has a very low glass transition temperature compared to PEI polymer. However, a continuous increment of PVAc loading in PEI membrane did not cause a substantial fall in glass transition temperature. A linear decline in glass transition temperature at about 11℃ was noticed from blend ratio of 99/1 to 98/2 and then 97/3. A summary of glass transition temperature for all prepared membranes were tabulated in Table 4.4.

Table 4.4: Glass transition temperature of all prepared membranes

Membrane sample	Polymers		Glass Transition Temperature, T_g [℃]
	PEI [wt%]	PVAc [wt%]	
1	100	0	208.70
2	99	1	188.50
3	98	2	177.07
4	97	3	166.76
5	0	100	40.54

In short, single glass transition temperature of blend membrane from DSC analysis has confirmed the miscibility and good interaction between PEI and PVAc. However, the present of PVAc in PEI polymer has reduced the glass transition temperature of pure PEI membrane. It was also remarked that the glass transition temperature of blend membrane was lied in between PEI and PVAc polymers. Lastly, factor such as plasticizer was also taken into the consideration as the cause of reduction in pure PEI glass transition temperature.

4.4 Gas Separation Performance

In the present study, gas permeability of developed membranes were evaluated using pure CO_2 and CH_4 in the feed pressure of 2, 4, 6 and 8 bars at ambient temperature. Figure 4.8 described the graph of CO_2 permeability against feed pressure.

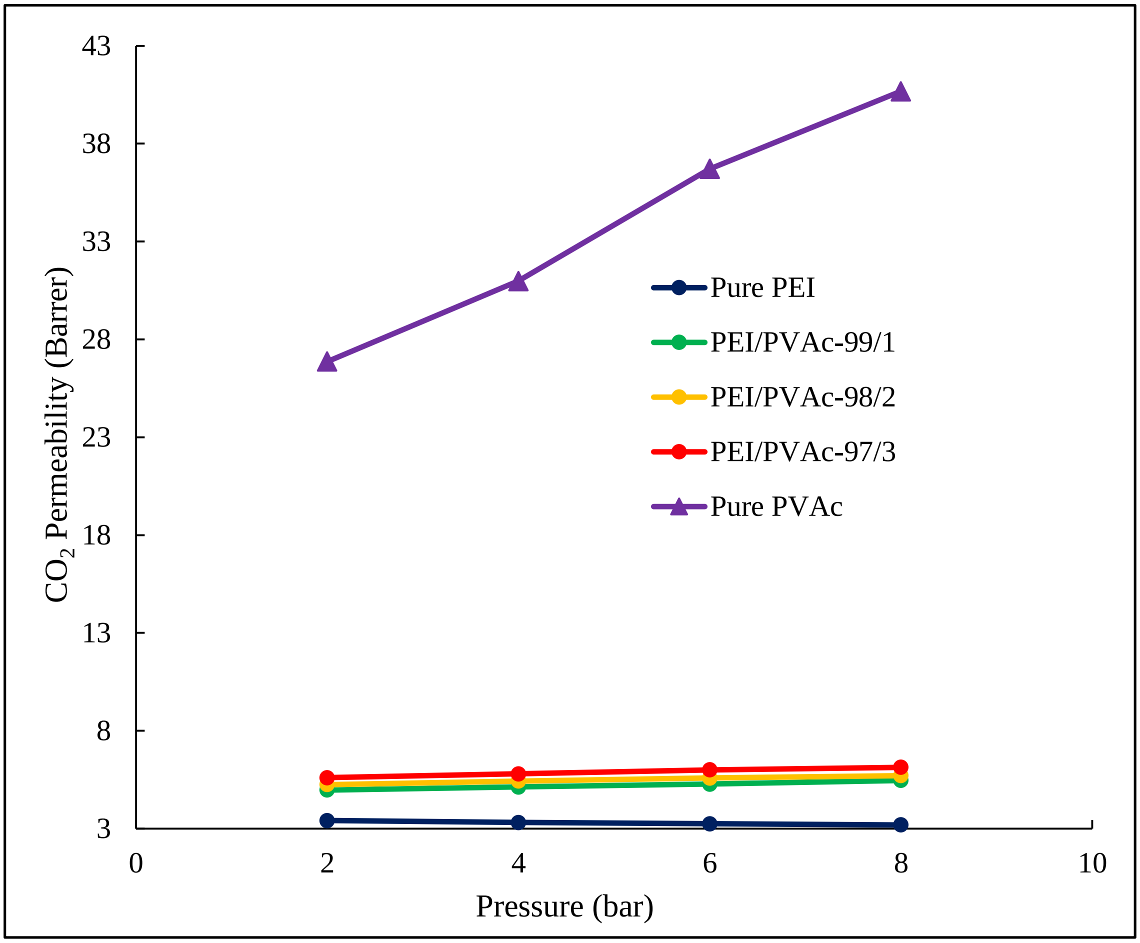

Figure 4.8: Permeability of CO_2 against feed pressure

For pure PEI membranes, it was remarked that the permeability of CO_2 decreases as the feed pressure increases. This decreasing trend was theoretically correct because glassy polymer will result a decreasing trend in CO_2 permeability with respect to feed pressure (Baker & Lokhandwala, 2008). This was also supported by previous study on pure PEI gas separation performance (Bos et al., 2001).

On the other hand, increasing trend of CO_2 permeability was observed with respect to feed pressure in pure PVAc membranes. This result was also corresponding to the theory of rubbery polymer gas separation performance as stated in the literature (Baker & Lokhandwala, 2008). Besides, same trend of pure PVAc graph was achieved in previous study (Mushtaq, Mukhtar, & Shariff, 2014).

For polymeric blend membrane, it was noted that permeability of CO_2 increases linearly as the feed pressure increases. Based on the result obtained, PEI/PVAc blend membranes have achieved a better CO_2 permeability which was up to 95% higher compared to pure PEI membrane.

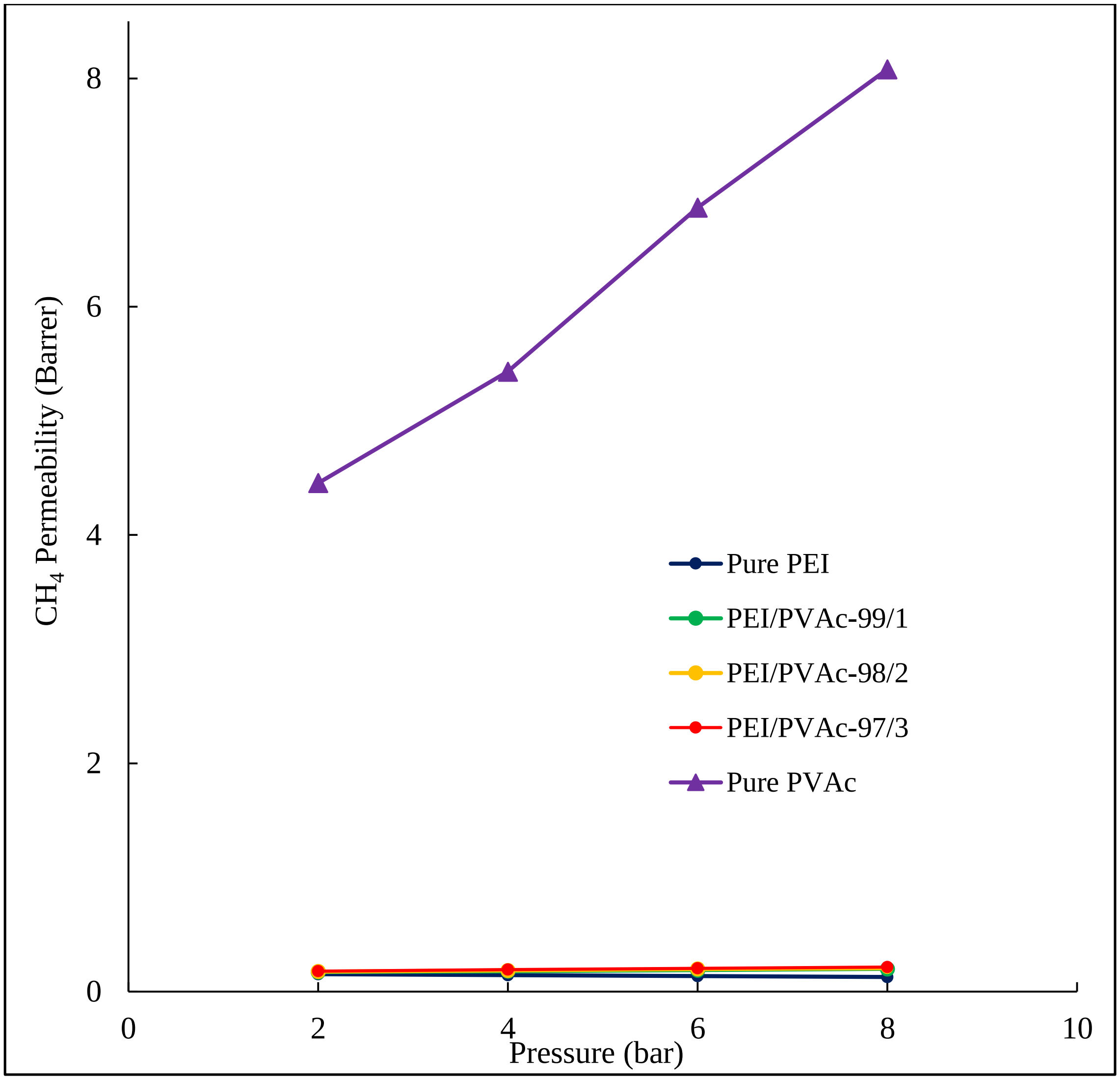

Figure 4.9: Permeability of CH_4 against feed pressure

Furthermore, permeability of CH_4 against feed pressure was recorded as well. For pure PEI membranes, a rise in feed pressure resulted a decrease in CH_4 permeability and vice versa trend of CH_4 permeability in pure PVAc membranes. These trends were similar as described in literature and previous studies (Baker & Lokhandwala, 2008; Bos et al., 2001; Sanaeepur, Amooghin, Moghadassi, & Kargari, 2011). For PEI/PVAc blend membranes, similar increasing trend was observed in Figure 4.9. However, it was important to take note that the increment in CH_4 permeability was relatively slower compared to CO_2 permeability. Based on Figure 4.8 and Figure 4.9, permeability of CH_4 was lied in between pure PEI and PVAc membranes. In overall, blend membranes have increased the CH_4 permeability but the improvement was not significant as shown Figure 4.9.

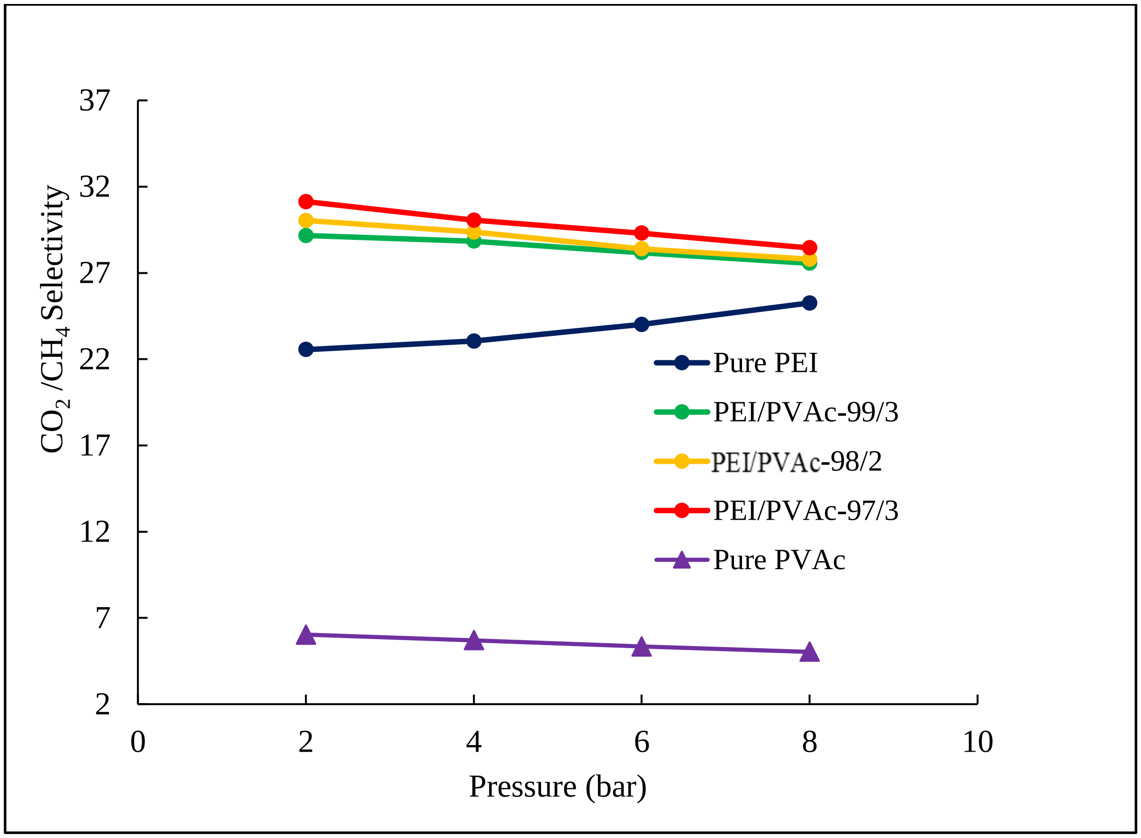

Figure 4.10: Selectivity against feed pressure

Lastly, ideal selectivity of pure PEI and blend membranes were compared in Figure 4.10. Basically, ideal selectivity was defined as the ratio of CO_2 to CH_4 permeability. The result showed an increasing trend in selectivity for pure PEI membranes with respect to feed pressure. In addition, gas separation performance of pure PEI was also found in previous study and same trend of plot was obtained (Bos et al., 2001). On the other hand, selectivity of PVAc membranes decrease as the feed pressure increases. This result was also matched and in agreement with literature data (Mushtaq et al., 2014). According to the gas separation performance as illustrated in Figure 4.10, selectivity of pure PEI membrane was relatively higher compared to pure PVAc membrane. This statement was also supported by literature and previous studies in membrane technology (Amo et al., 1995; Lokhandwala et al., 2007; Mannan et al., 2013; Nasir et al., 2013a).

For polymeric blend membrane, the selectivity was found to be higher than both pure PEI and PVAc membrane. This observation indicated that polymers composition will affect the behavior of CO_2 permeability. Specifically, an increasing in the weight composition of PVAc in PEI matrix has enhanced the overall performance of pure PEI membrane. Based on the FESEM image of pure PVAc in Figure 4.2b, it has a less tightly packed internal structure compared to pure PEI membrane as shown in Figure 4.2a. Hence, the transport of gas molecules through the membrane were less hindered due to the internal structure of PVAc and eventually generating a higher permeability. By comparing the permeability of CO_2 and CH_4, CO_2 permeability was enhanced significantly compared to the increment in CH_4 permeability. Therefore, the overall ideal selectivity was improved and higher than both individual polymers. Statistically, improvement of 40% in ideal selectivity was achieved in blend membranes compared to pure PEI membranes. In overall, this polymeric blend membrane can be considered as a new product in optimizing the cost and separation efficiency of PEI membrane.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

In conclusion, all pure and blend membranes were developed and synthesized successfully within the time frame given. Firstly, miscibility study between PEI and PVAc were carried out and it was remarked that NMP was the most suitable solvent for PEI/PVAc polymeric blend membrane. The dope solution and membranes with different composition achieved stability in NMP solvent.

On top of that, characterization of membrane by FESEM, FTIR, TGA and DSC were conducted as well. The result in FESEM showed that all the membranes were homogeneous and densely packed in structure. This observation has confirmed the miscibility of polymers blending. In addition, FTIR analysis was conducted and it showed that the functional groups of individual polymers such as aldehyde, ketone and ether were remained in the structure of blend membranes which indicated no alternation and changes of chemical structure in blend membranes. Furthermore, TGA result presented that a slightly lower degradation temperature in blend membranes and this reflected that thermal stability of blend membrane has been reduced compared to pure PEI membrane but the effect was almost negligible. On top of that, a single and lower glass transition temperature were found in DSC analysis which confirmed the miscibility and good interaction between PEI and PVAc. However, the present of PVAc in PEI polymer has reduced the glass transition temperature of pure PEI membrane.

Last but not least, gas separation performance was carried out and the result showed a decreasing trend in CO_2 permeability with respect to feed pressure for pure PEI membranes. For pure PVAc and blend membranes, permeability of CO_2 increases as the feed pressure increases. In overall, an impressive result with up to 95% improvement in CO_2 permeability was achieved in polymeric blend membranes. In term of selectivity, it was observed that the trend was increasing for pure PEI membranes but decreasing for both pure PVAc and blend membranes. Besides, it was noticed that pure PEI membranes has higher selectivity compared to pure PVAc membranes. Nevertheless, selectivity of blend membranes were found to be 40% higher compared to pure PEI membranes.

In short, this present study showed that casted polymeric blend membranes have improved the overall performances of polymeric membrane and it has a great potential to be used for natural gas purification application.

5.2 Recommendations

The present work has shown that polymeric blend membranes synthesized could improve the overall performance of gas separation. However, further researches are necessary to investigate the overall performance in different process conditions. Besides, computational software modelling should be developed to study the passages of gas molecules within the membranes so that the feasibility and efficiency of polymeric blend membranes can be estimated.

5.2.1 Gas permeability studies using mixture of CO_2 and CH_4 and different process conditions

In the present study, polymeric blend membranes have demonstrated its separation performance towards pure feed gases such as CO_2 and CH_4 at various pressure. Since the industrial application of membranes are not ideal applications, therefore further investigation on feed gas composition and process temperature are necessary. The non-ideal environment of the mixture of gases will provide information on the effect of feed gas composition to the separation mechanism and properties. The effect of feed composition will provide information on the competition between CO_2 and CH_4 within the membrane, and its effect to membrane selectivity. Different process temperature will definitely provide a better understanding in membrane stability in various process conditions.

5.2.2 Development of computational software modelling of gas transport within the membrane

This study could be further extended by developing a computational model of gas transport within the temperature. The outcomes of this model can be used to estimate the feasibility and efficiency of gas separation in polymeric blend membranes.

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APPENDIX A: GAS PERMEABILITY CALCULATION

Permeability of a membrane is measured by considering the volumetric flow rate of certain gas through the membrane. Gas permeation measurement is performed using has permeation test unit. Pure CO_2 and CH_4 are employed as test gases. Membrane is cut into a circular with effective area of 16.62 cm^2 and mounted into the module. Before measurement, the system is evacuated to remove any gases remaining in the system. Pure CO_2 and CH_4 are employed as the test gases with different feed pressure of 2, 4, 6 and 8 bars. All tests are carried out at room temperature (25℃) condition.

For instance, in 25℃ and feed pressure of 2 bar, a 66μm of pure PEI membrane is able to permeate 0.1cm^3 CO_2 gas in 710.6 seconds with permeate in atmospheric pressure. The permeability of CO_2 gas can be determined as follows:

Firstly, the volumetric flow rate of CO_2, Q, s calculated as below:

$$Q_i = \frac{\Delta V_i}{\Delta t_i} \text{……………………….. ….Equation B-1}$$

$$= \frac{0.1\text{cm}^3}{710.6\text{ s}}$$

$$= 1.407 \times 10^{-4}\text{cm}^3/\text{s}$$

Secondly, the volumetric flow rate is then corrected to standard pressure and temperature condition (1 atm, 0℃), Q_{STP} as follows:

$$Q_{STP} = Q_i \times \frac{T_{STP}}{T_i} \text{ ……………….Equation B-2}$$

$$= 1.407 \times 10^{-4}\text{ cm}^3/\text{s} \times \frac{273\text{ K}}{293\text{ K}}$$

$$= 1.311 \times 10^{-4}\text{ cm}^3(\text{STP})/\text{s}$$

Next, CO_2 flux is expressed as the volumetric flow rate of CO_2 gas per unit membrane area, calculated as follows:

$\mathrm{J_i} = \frac{\mathrm{Q_{STP}}}{\mathrm{A}}$……………………….Equation B-3

$$\mathrm{J_{CO_2}} = \frac{1.311 \times 10^{-4}\ \mathrm{cm^3(STP)/s}}{16.62\ \mathrm{cm^2}}$$

$$= 7.889 \times 10^{-6}\mathrm{cm^3(STP)/cm^2s}$$

CO_2 permeability is a pressure and thickness-normalized flux of the gas through the membrane and defined by:

$\mathrm{P_i} = \frac{\mathrm{J_i l}}{\Delta \mathrm{p_i}}$………………………Equation B-4

Since $\mathrm{P_{CO_{2,feed}}} = 2\ \mathrm{barg} = 150.0128\ \mathrm{cmHg} + 76.0002\ \mathrm{cmHg} = 226.013\ \mathrm{cmHg};$
and $\mathrm{P_{CO_{2,permeate}}} = 1\ \mathrm{atm} = 76.0002\ \mathrm{cmHg}$

$$\mathrm{P_{CO_2}} = \frac{(8.560 \times 10^{-6}\mathrm{cm^3(STP)/cm^2s})(66 \times 10^{-4}\mathrm{cm})}{(226.013\text{-}76.0002)\ \mathrm{cmHg}}$$

$$= 3.471 \times 10^{-10}\mathrm{cm^3(STP)cm/cm^2s\ cmHg}$$

Permeability is often expressed in customary unit of Barrer, which:

$$1\ \text{Barrer} = 1 \times 10^{-10}\mathrm{cm^3(STP)cm/cm^2s\ cmHg}$$

Therefore, $\mathrm{P_{CO_2}}$= 3.471 Barrer

By repeating the same procedure, permeability of CH_4 gas can be calculated. For the same experiment conditio, permeability of CH_4 is obtained 0.1512 Barrer. Therefore, the ideal selectivity can de determined by taking the ratio of permeability of one penetrant over another as follows:

$$\alpha_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}}$$

$$= \frac{3.471}{0.1512}$$

$$= 22.96$$

APPENDIX B: GAS PERMEATION RESULTS

Table B.1: Summary of gas permeation results

Membrane	Pressure (bar)	Time (CO_2) (s)	Time (CH_4)(s)	Vol (CO_2)	Vol (CH_4)	Thickness for PCO_2 (μm)	Thickness for PCH_4 (μm)	PCO_2	PCH_4	Selectivity
Pure PEI	2	71.06	1700.12	0.01	0.01	66	70	3.47	0.1512	22.96
	4	36.59	894.51	0.01	0.01	66	70	3.31	0.1438	23.05
	6	24.92	634.57	0.01	0.01	66	70	3.24	0.1351	24.01
	8	18.99	508.67	0.01	0.01	66	70	3.19	0.1264	25.26
99/1	2	472.73	1184.72	0.1	0.01	64	55	4.97	0.1706	29.16
	4	229.51	568.94	0.1	0.01	64	55	5.12	0.1776	28.85
	6	148.54	359.62	0.1	0.01	64	55	5.28	0.1873	28.17
	8	107.66	255.01	0.1	0.01	64	55	5.46	0.1981	27.56
98/2	2	621.15	1471.52	0.1	0.01	88.75	70	5.25	0.1748	30.04
	4	300.21	695.41	0.1	0.01	88.75	70	5.43	0.1849	29.37
	6	194.51	435.62	0.1	0.01	88.75	70	5.59	0.1968	28.39
	8	142.87	313.21	0.1	0.01	88.75	70	5.71	0.2053	27.79
97/3	2	590.65	1225.98	0.1	0.01	90	60	5.60	0.1798	31.13
	4	285.11	571.21	0.1	0.01	90	60	5.80	0.1930	30.05
	6	183.77	359	0.1	0.01	90	60	6.00	0.2047	29.30
	8	134.78	255.63	0.1	0.01	90	60	6.13	0.2156	28.45
Pure PVAc	2	451.26	272.14	0.1	0.01	330	330	26.87	4.4553	6.03
	4	195.67	111.62	0.1	0.01	330	330	30.98	5.4312	5.70
	6	110.09	58.84	0.1	0.01	330	330	36.71	6.8687	5.34
	8	74.51	37.51	0.1	0.01	330	330	40.68	8.0810	5.03