Development of polysulfone/polyetherimide blend membrane for removing carbon dioxide from methane

by

Do Minh

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

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CERTIFICATION OF APPROVAL

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Approved by,

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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.

(DO MINH)

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ABBREVIATIONS AND NOMENCLATURES

MMM	Mixed matrix membrane
PSU	Polysulfone
PEI	Polyetherimide
NMP	N-Methyl-2-pyrrolidone
Tg	Glass transition temperature
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermo gravimetric analysis
DSC	Differential scanning calorimetry

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ABSTRACT

Monitor of high CO_2 content natural gas is very important issue. The content of CO_2 in the natural gas will cause the lower of calorific value which effects to the value of the oil. In order to remove CO_2, membrane is one of the best options in term of economy. However, the membrane has low selectivity and is not able to apply in industry. The development membrane selectivity is necessary. During this project, two materials used are polysulfone and polyetherimide. The main objective for this study is to develop polymeric membrane for removal of high CO_2 at the platform. The method used for drying is solvent evaporation. After drying process, the membrane needs to be characterized. The synthesized membranes will be used for the performance test by using pure CO_2 and CH_4 gases. The outcome of the project is a membrane which has high selectivity to remove $CO_{2.}$

CHAPTER 1: INTRODUCTION

This chapter discuss about the background, problem statement and objectives of project

1. BACKGROUND

1.1.Natural gas

Natural gas is an important source of energy for industry. It is a non-renewable resource. Like other non-renewable fossil fuels (Biruh Shimekit & Mukhtar, 2012). Natural gas is a hydrocarbon gas mixture. The detail of composition of natural is shown in the below table 1.1

TABLE 1.1 Composition of natural gas(Mushtaq, Mukhtar, Shariff, & Mannan, 2013)

Chemical name	Composition
CH_4	70-90%
C_2H_6	0-20%
C_3H_8	
C_4H_{10}	
CO_2	0-30%
O_2	0-0.2%
N_2	0-5%
H_2S	0-5%

There are sour gas and sweat gas. Sour gas is natural gas contain a significant amount of hydrogen sulphide . Sweet gas is natural gas contain less amounts of hydrogen sulphide. Most of the current natural gas from the reservoir is sour gas so gas separation and treatment sour gas is very important in gas industry. Every country has some criteria to evaluate the quality of natural gas. One of the criteria is the calorific value. It is the amount of energy release when the natural gas burns. The calorific value depends on the composition of the natural gas. If the content of

CO_2 in natural gas is high, the calorific value will be lower. From this reason, CO_2 needs to be removed to increase the value of natural gas.

1.2.Separation process

In a normal process, the first treatment process needs to be done in platform. The gas has been pumped from the reservoir to the platform. After that, gas will go through the acid treatment. The purpose for this treatment is removing the chemical which has the properties of acid such as CO_2 or H_2S. In this separation, CO_2 needs to be eliminated from the natural gas. With the current technology, there are 4 methods to remove CO_2(Rao & Rubin, 2002) They are adsorption, absorption, membrane and cryogenic. Each method has their advantages and disadvantage stated in the below table.

TABLE 1.2 Comparison of gas separation techniques
(Biruh Shimekit & Mukhtar, 2012)

Technology	Advantages	Disadvantages
Absorption	This separation process is necessary for large quantities	The solvent react with some corrosion inhibitors, it will cause erosion of the unit and reduce CO_2 solvent loading. All of the solvents cannot be recycled back to the absorber column; the disposal of the solvents causes environmental hazards.
Adsorption	The major advantages of using adsorption processes are simplicity of operation and low energy requirement for the regeneration of the sorbent material with short period of time.	This separation process requires high transfer rates and high capacity
Membrane	The general advantages of the membranes process and mainly for the removal of CO_2 from natural gas includes are low energy requires, low capital cost and easy to setup.	This separation process has some limitations for the separation at low pressure, it needs additional energy for compression of the feed gas to and meet pipeline pressure standard.
Cryogenic	The advantage of this process is suitable for liquefying and purifying the feed gas with high concentration of CO_2 and it does not require compression	The main disadvantage of cryogenic separation is highly energy intensive for regeneration and can significantly decrease the overall plant efficiency when applied to streams with low CO_2 concentration.

2. PROBLEM STATEMENT

Among the current technologies, membrane is the method which is economic and easy to operate. More than that, in gas treatment process of offshore, membrane is the most suitable method to be used in gas separation in offshore because the area of the platform is limited and membrane does not require a big area to setup.

With the high content of CO_2, the calorific value of the natural gas is reduced. That is the reason why CO_2 separation process needs to be optimized. Nowadays, current membranes are not good enough in term of selectivity to apply in industry (ref). Development of membrane is required to enhance the selectivity of membrane. In this project, PSU has been chosen as main material because it has good chemical resistance, mechanical stability, and thermal stability, low cost with the high CO_2 permeability. In order to reduce the lost amount of CH_4 in gas treatment and optimize the separation, it is necessary to add another minor material in membrane. PEI is suitable for this requirement because the selectivity of CO_2/CH_4 is high. For the properties of two materials, they will be discussed later in the material and method part.

3. OBJECTIVES

- To synthesize the blended membrane by PSU and PEI
- To characterize physicochemical properties of the polymer blend membrane
- To evaluate the gas separation performance of the polymer blend membrane in two criteria: selectivity and permeability

4. SCOPE OF STUDY

- In this study, the main subjects under investigation are material and characterization of the membrane. The polymer used in this study is PSU and PEI. NMP is used as solvent.
- Next step, the membrane need to be characterized its properties and morphology. The membrane will be characterized by using the following equipment: FESEM

inspects the morphology of prepared membranes. TGA determines the mass loss and the moisture content in membrane. FTIR gives information on the molecular interaction of the molecules and functional group of the membrane. DSC gives information about the transition temperature of the membrane. From that, the properties of the membrane will be predicted.

- The performance of the prepared membranes will be tested using the gas membrane permeation unit. The prepared membranes will be tested on the pure CO_2 and CH_4 permeability and selectivity at variable pressure

CHAPTER 2: LITERATURE REVIEW

This chapter discuss about the previous study and research about the membrane

1. DEFINITION OF MEMBRANE

Membrane is a thin layer of semi permeable material which separates two phases and controls the movement of solutes across it in a specific manner, a selective barrier that permits the separation of certain species in a fluid by combination of sieving and sorption diffusion mechanism(Malek & Rusydi, 2009).

Morphology is one of the important properties of membrane. There are two typical types of membrane morphology: symmetric and asymmetric. With the different morphology, membrane has different structure and different mechanism. Typically, the porous membrane has a lot of large voids and the voids connect to each other to let the gas pass through it. The separation of porous membrane depends on structure and distribution of the pore. From this reason, the porous membrane has been used as a bulk separation and the material of porous membrane is depends on the requirement of the process (Davis, 2002)

In the opposite side, the dense membrane has fewer voids. Its mechanism is based on the diffusion and the intrinsic properties of the material. The diffusivity depends mainly on its molecular size and the operating condition such as pressure and temperature. Non-porous membranes have high selectivity.

2. PREVIOUS STUDY

The concept of a membrane has been known since 1800. In 1850, Graham had found the law of diffusion. Law of diffusion shows the relationship between the concentration and length of the diffusion flux. After the law of diffusion, a lot of research has been done to find the configuration, material and the synthesis membrane method. Five years after end of World War II, the first unit to measure permeability of the membrane has been invented. In 1961, first anisotropic membrane had been made. In 1980, the first use of membranes in industry was with micro-filtration and ultra-filtration technologies(Bernardo & Clarizia, 2013). In 1982, the first separation gas by using membrane has been produced. After that, the membrane for gas separation had been developed. Until 1897, advanced membrane materials for O_2/N_2; H_2/N_2 and H_2/ CH_4 separations had been launched. During 1988, the first commercial vapor separation plants installed membrane. From 1990 to 2000, the membrane is developed to separation for the different specific gas: CO_2/CH_4 or C_3H_6/N_2. During 1994, the first polyimide hollow fiber membrane for CO_2/CH_4 separation was installed. After two years, first C_3H_6/N_2 separation plant was installed. Nowadays, membrane is still continuing to be developed to meet the requirement of the market. (Bernardo & Clarizia, 2013)

3. CLASSIFICATION

There are two types of membranes: natural membranes and synthetic membranes. The natural membranes can be collected in the nature and the most common materials are rubber, wool and cellulose. The synthetic membranes are synthesized from polymeric and inorganic. In order to increase the quality of separation process, composite membranes have been used. Composite membranes which made from polymer are the blend polymer membrane. Another side, composite membrane made from both polymer and inorganic material is the MMM.

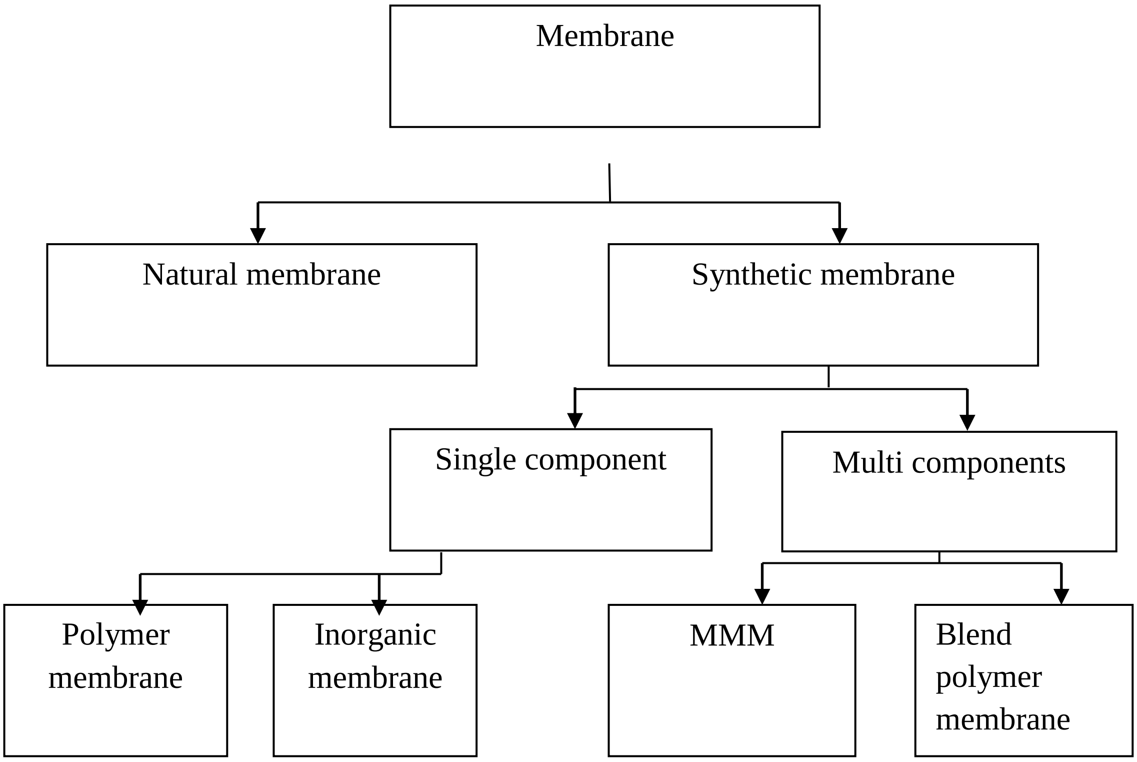


FIGURE 2.1 Classification of membranes (Grossniklaus & Gass, 1998)

3.1. Polymer membrane

The polymeric membrane is applicable for offshore because it is high adaptability to variation off CO_2 easy to combine with other separation processes. No moving parts make the process more flexible for operating, controlling and easy to scale up with low maintenance requirement. It reduces energy consumption unless compressor is used and low capital costs(Biruh Shimekit & Mukhtar, 2012). However, it has some limitations as the separated of CO_2 at low pressure and requires of additional energy for the feed gas to provide the driving force for permeation and to meet pipeline pressure (Biruh Shimekit & Mukhtar, 2012).

Polymer membrane has been divided into two groups: glassy polymer membrane and rubbery polymer membrane. The glassy polymer membrane and rubbery polymer membrane can be differential by Tg. If the temperature of membrane is lower than Tg; it will transform to glassy state. The glassy state can be considered as a super cooled liquid where the molecular motions have been frozen in(Mushtaq et al., 2013). It is brittle, hard and rigid like a crystalline solid, but it retains the molecular disorder of a liquid(Biruh Shimekit & Mukhtar, 2012). If the temperature of membrane is higher than Tg; it will transform to rubbery state. When an amorphous polymer is in rubbery state, it is soft and flexible(Mushtaq et al., 2013).

Permeability and selectivity are the two main parameters that characterize the performance of membrane material. There is a general trade-off between permeability and selectivity for polymeric membranes with rubbery polymeric membranes with high permeability and low selectivity for glassy polymeric membranes(Bernardo & Clarizia, 2013). The relationship between the permeability and selectivity has been found by Robeson in 1991. In the graph of Robeson, the glassy polymer is always in the left of the graph. It has less permeable and high selectivity. Mostly, rubbery polymers show a high permeability, but a low selectivity, whereas glassy polymers exhibit a low permeability but a high selectivity.

Usually glassy polymeric membranes are preferred for CO_2 separation because glassy polymers separate gas mixture base on the differential diffusion ability. In this project, one of material has been chosen is PEI which has the amine group in its molecular. The amine solution has the capability to purify the natural gas having CO_2. Amine group has an affinity for passing CO_2 easily.

3.2. Inorganic membrane

In the other side, the inorganic membrane is made from inorganic material. The most common inorganic membranes are carbon molecular sieves membranes and metal organic framework membranes (He & Hägg, 2012). Inorganic membrane performance in gas separation is quite good and their selectivity is high. Its function is removing the particular from the steam of the gas by its size. Apart from stability at high temperature and large pressure gradient, inorganic membranes are also known to be invulnerable to be attacked by chemically active mixture (Othman, Mukhtar, & Ahmad, 2004). These favourable attributes have been identified to have brought about an acceptance level of inorganic membranes by industries(Othman et al., 2004). Due to the imposing efficient as illustrated in many technical journals and reports, the use of inorganic membranes for air filtration or air cleaning from particulate matters has been made more prevalent today than in the past. However, due to the lack of technology to form continuous and defect-free membranes, high cost of production and handling issues, the commercial applications of inorganic membranes are still limited(Othman et al., 2004).

3.3. Mixed matrix membrane

One of the other alternatives is the development of MMM. MMM contains inorganic fillers such as rigid molecular sieving materials (B Shimekit, Mukhtar, & Maitra, 2010). The molecular sieve filler used in MMM are capable to discriminate between different molecules present in the feed mixture based on the basic of size and shape of molecules(Biruh Shimekit & Mukhtar, 2012).

3.4. Blend polymer membrane

Blend polymer membrane is the unique membrane which is made from two or more polymers. It has the properties of the polymer components. The purpose of blending two materials is making a better membrane in gas separation by making the higher permeability and the higher selectivity. However, there are a lot of choices for the synthesis method. The blend may be prepared by solution mixing. In fact, the most important feature of polymer blend membrane separation is its structure and its morphology. With the blend polymer membrane, there are two types of membrane structures. They are the porous membrane and the dense membrane. The porous membrane separates based on the size of the molecular because it has a lot of void during synthesis process. By the interconnection in the porous membrane, the gas which has smaller particles will pass through it. In the opposite, the dense membrane is non-porous membrane. The morphology of the dense membranes is homogenous and no micro voids are seen on surface and cross sections are symmetric porous (Li, Wang, Lu, & Xiao, 2008)

CHAPTER 3: MATERIALS AND METHODS

This chapter discuss all the materials used and the details of procedures

1. MATERIAL

1.1. Polysulfone

The purity of used polysulfone for this project is 99%

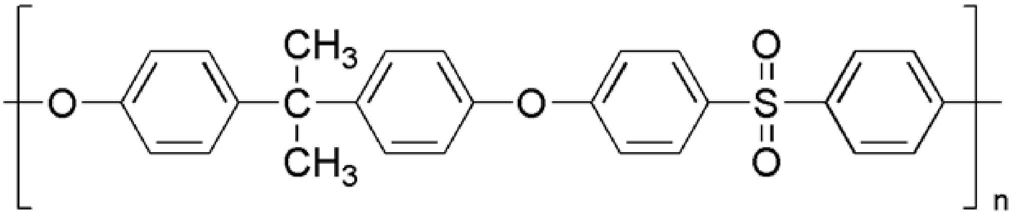
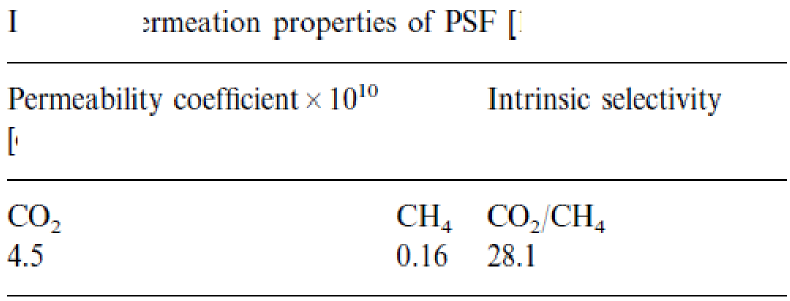


FIGURE 3.1 PSU molecular structure (Aitken, Koros, & Paul, 1992)

Polysulfone polymers are rigid, high-strength, and transparent. Its glass transition temperature is 185°C. It is highly resistant to mineral acids, alkali, and electrolytes, in pH ranging from 2 to 13(Celebi, Kaya, Altikatoglu, & Yildirim, 2013).

PSU polymer membrane is a glassy polymer membrane and has high selectivity. The selectivity between CO_2 and CH_4 is increasing when the pressure is increasing. It will be an advantage in gas separation because the operation pressure in industry is very high. However, its permeability is low and the gas is difficult to pass. The below data shows the detail of the permeability and the selectivity of the membrane based on a previous study about PSU membrane.

TABLE 3.1 Intrinsic permeation properties of PSU(Ismail & Lorna, 2003)



I ermeation properties of PSF [

Permeability coefficient × 10^{10} [		Intrinsic selectivity
CO_2	CH_4	CO_2/CH_4
4.5	0.16	28.1

PSU polymer membrane is stable in the high pressure. With the effect of the pressure, the gas separation becomes more efficiency. At 2 bars, the permeability of CO_2 is 15 and the permeability of CH_4 is 0. At higher pressure, the permeability of CO_2 and CH_4 is higher. It means more of CH_4 will be lost during the gas separation. The relationship between pressure and permeability of single gas has been shown in the below graph.

1.2. Polyetherimide

The purity of used polyetherimide for this project is 99%

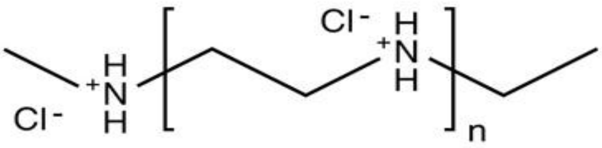


FIGURE 3.2 The molecular structure of PEI (Fuertes & Centeno, 1998)

PEI polymer membrane is the glassy polymer membrane. It has a melting point of 73-75° C. In molecular of PEI, there is an amine. The amine group will attract the other entire polar molecular have properties of acid such as CO_2.

1.3. N-Methyl-2-pyrrolidone

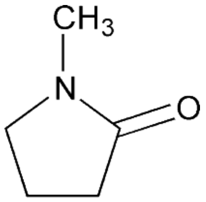


FIGURE 3.3 NMP molecular structure

(J.-Y. Niu, Wei, Wang, & Dang, 2003; J. Y. Niu, Wei, Wang, & Dang, 2004)

NMP is an organic compound consisting of a 5-membered lactam. It is a colourless liquid, although impure samples can appear yellow. It is miscible with water and with most common organic solvents.

TABLE 3.2 Properties of NMP(Brandrup et al., 1999)

Properties	
Melting point	−24 °C
Boiling point	202 °C
Solubility in water	Miscible

The solvent chosen based on the polymer material and the polymer needs to be soluble in the solvent. For synthesis PSU polymer membrane, a lot of solvent can be chosen. However, the minor material affects to the selection of the solvent. With the second material is PEI, the suitable solvent for this synthesis process is NMP. However, NMP solutions are toxic solvents. From this reason, it needs to be proceeding with precaution and it is requirement to wear the personal protection equipment before proceeding.

2. METHOD

2.1. Chemical and equipment

TABLE 3.3 Chemical and equipment need to use for the experiment

Type	Number	Name	Amount	Location
Chemical	1	PSU		Block 3
	2	PEI		Block 3
	3	DMAC		Block 3
Equipment	1	Mixing breaker	2	Block 3
	2	Hot plate stirring	1	Block 3
	3	Casting machinery	1	Block 3
	4	Casting knife	1	Block 3
	5	Glass plate	1	Block 3
	6	Sonication	1	Block 3
	7	Dedicator	1	Block 3
	8	Drying	1	Block 5
	9	FESEM	1	Block P
	10	FTIR	1	Block 4
	11	TGA	1	Block 4
	12	DSC	1	Block 4

2.2. Selection method

For the first step of synthesis membrane process, it was choosing the correct method for synthesis membrane. From the previous study, there were a lot of methods to synthesize membrane: sintering, stretching, leaching out and track – etching techniques. Each method has their advantages and disadvantages.

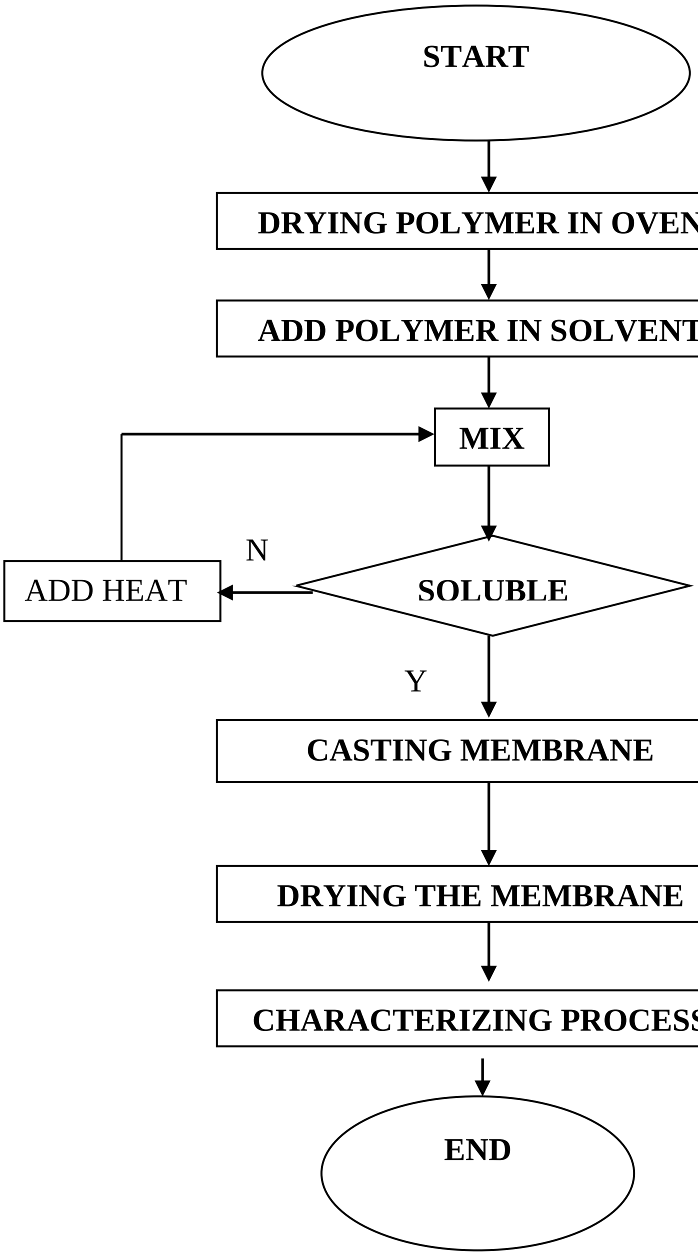
- For the sintering method, the material has been melt to become membrane.
- In leaching out process, an amount of heat needs to be supplied to the material. The polymer will leach out from the mixture of the polymer from 3 phases to 2 phases.

- With the stretching, a mechanical force has been used to stretch the polymer to make the membrane.
- In track – etching, laser and coagulation bath has been used to make the membrane.

However, all these methods had been used to synthesize the porous membrane. The blended membrane PSU – PEI was dense membrane. The most conventional way to synthesize non porous membrane is using the phase inversion method.

2.3. Sketching the procedure

FIGURE 3.4 Systematic diagram of synthesis process



2.4. Preparation step

The synthesis process had been started with the calculation the amount of the requirement chemical. Based on the previous research, the suitable ratio between polymer and total solution was from 18 % to 23 % weight of total solution. In this project, the chosen ratio between polymer and total solution was 20% weight of total solution. With data in material safety data sheet, it was possible to calculate the amount of each chemical has been used in this project.

In the previous study about membrane, to test the effect of the minor material, the ratios between the main material and the minor material should be used are 1%, 2% and 3%. The mass of the polymer for each sample was 8 grams. Below is the detail of each component in the other trial membranes:

TABLE 3.4 Ratio between PSU/PEI in different sample -Based mass is total mass of the polymer

No	**Membrane type**	**Membrane name**	**Wt% PSU**	**Wt% of PEI**
1	Polymer membrane	Sample 1 pure PSU	100%	0%
2	Polymer membrane	Sample 2 pure PEI	0%	100%
3	Blend membrane	Sample 3 99% PSU + 1% PEI	99%	1%
4	Blend membrane	Sample 4 98% PSU + 2% PEI	98%	2%
5	Blend membrane	Sample 5 97% PSU + 3% PEI	97%	3%

TABLE 3.5 Amount of PSU/PEI for each sample

Trial number	Mass of PSU	Mass of PEI
1	0g	8g
2	8g	0g
3	7.92g	0.08g
4	7.84g	0.16g
5	7.76g	0.24g

2.5. Compatibility study

It was necessary to study about the compatibility of blending polymer because it was one of the most important properties of polymer that need to be understood fully before mixing two polymers. In fact, the best way to study the compatibility was conducting the experiment. For the first step of the compatibility, the composition between the solvent and polymer should be found. In this project, the solvent had been used is NMP and the main polymer had been used is PSU. Based on two materials have been chosen, the best composition of PSU in the NMP solvent need to be found before the starting the next step is calculation the minor material. In the previous study, the best composition between PSU and total mixture of solvent and polymer was 20% of weight total solution (Mulder, 1996). The mass of the mixture was 10 grams. This amount could guarantee to have a good result and reduced the error during the experiment because of the error in system. In this project, 5 membranes should be synthesized with the different composition of PSU and PEI. There were 2 polymer membranes. The rest of them were blend polymer membranes with the different composition of PEI starting from 1% to 3% weight percentage based on total solution.

1. First step would be measuring the amount of solvent. 40 grams of NMP would need to put into 5 containers; each container has 8 grams NMP.
2. One magnetic bar would be putted in each container. The requirement of each magnetic bar was able to mix the mixture, inert with the chemical and the size of it must be suitable for the size of the container. The selection of magnetic bar was very important because if the magnetic bar was too short,

the mixing time would be longer. If the magnetic bar was too long, it may cause the mixing speeding too high and it would cause the void in the membrane. The void would cause the dense membrane defect.

3. After the magnetic bar would be putted in the container, the next step was turning on the switch of the hot stir and the magnetic bar began stirring.
4. After 15 minutes, the entire PSU amount would be putted in the solvent. In the first container. The mixture would be stirred during 12 hours at 180 rpm.
5. After 12 hours the mixture was homogenous. Then the second component would be putted in the container and the mixture was mixed during next 12 hours at 55^{0}C

2.6. Synthesizing membrane

The next step was measuring the mass of each material. PSU had been put in the container and after that NMP had been put. Magnetic bar was put in the container. Next, the containers were closed to avoid the moisture and the hot stirring plate was turned on.

FIGURE 3.5 Container, Mass measurer and hot plate in block 3

After 12 hours, when the PSU was totally solved in the solvent then minor material was put in the same container with PSU and the hot plate continue to stir until the mixture was miscible. After that, the sonication had been used the for the purpose of degassing.

FIGURE 3.6 Sonication machine

FIGURE 3.7 Glass plate and casting machine

Next step was casting membrane by the casting machine. The casting plate was glass plate and membrane was casted by casting knife. The chosen thickness was 300 micrometers. After thickness of the knife was chosen, membranes were casted manually by casting knife. The high speed of the casting knife need to be avoided because it would cause the membrane has hollow pin and it would cause to the quality of the membrane. For the first 48 hours, the membranes were isolated in the vacuum oven at 25^{o}C. For the next 24 hours, the temperature was increasing 20 ^{0}C for each 2 hours. Until the temperature reaches 65 ^{0}C, the temperature was maintained for 20 hours. After 72 hours of drying process, membranes could undergo the entire characterizing test and the performance test. If the characterize equipment was not available, membrane would be put in the desiccator to prevent the moisture from the atmosphere.

FIGURE 3.8 Vacuum oven

2.7. Process flow time

TABLE 3.6 Process flow time

No	Step	Duration
1	Experiment setup preparation	30 minutes = 0.5 hours
2	Membrane solution preparation	1 hours
3	Stirring	24 - 48 hours
4	Degassing	24 hours
5	Casting	30 minutes = 0.5 hour
6	Evaporation	30 seconds
7	Drying	72 hours
Total		120 – 144 hours

2.8. Evaluate the blended membrane

2.8.1. Field emission scanning electron microscopy

FESEM is an analytical technique used in materials science to investigate molecular surface structures and their electronic properties. In the first step, membrane needs to be dipped in nitrogen liquid. After that, membrane needs to be broken and the sample is putted in FESEM. FESEM test gives the information about morphology of the surface and structure of the membrane based on cross surface.

2.8.2. Fourier transforms infrared spectroscopy

FTIR is a technique which is used to obtain an infrared spectrum of absorption and emission. The result of the Fourier transform infrared spectroscopy will show composition and the structure of the molecular.

2.8.3. The thermal gravimetric analysis

TGA instrument continuously weighs a sample as it is heated to temperatures of up to 800° C to test any moisture content in the membrane. Next, the result will show the temperature where the membrane changes to ashes.

2.8.4. Differential scanning calorimetry

DSC is equipment to test the glassy transition temperature, melting temperature and crystallization temperature. Its result will show the role of each polymer in the membrane. The transition temperature of membrane may change compare with the polymer membrane or each component in the membrane has its own role, so the transition temperature remains.

2.9. Gas permeability test

The gas test permeability will determine the permeability and the selectivity. From that permeability and selectivity data, the separation ability of a membrane will be determined. Permeability is a quantitative measure of the transport flux of a gas component through a membrane. The permeability is calculated by the below formula:

$$P = \frac{J*L}{\Delta P}$$

- The unit to measure gas permeability is barrer.

- J is the flux
- L is the thickness of the membrane.
- ΔP is the difference between the pressure before passing through the membrane and the pressure after passing through the membrane

The gas permeability has been conducted with the single gas permeability test at room temperature and pressure from 6 to 10 bars. CO_2 and CH_4 pass through the membrane at different pressure. After the test finish, the flux and different pressure data are ready to calculate for the permeability. Selectivity is the value to determine the quality of gas separation. Selectivity of CO_2 / CH_4 separation is determined by the formula

$$S = \frac{P\ carbon\ dioxide}{P\ methane}$$

- P CO_2 is the permeability of CO_2
- P CH_4 is the permeability of CH_4

However, before the gas permeability test has been conducted, membrane needs to be cut to a circle which has 5 cm diameter.

CHAPTER 4: RESULT AND DISCUSSION

This chapter discuss about the results of this project

1. SYNTHESIS OF MEMBRANE

FIGURE 4.1 Sample 1 pure PSU

FIGURE 4.2 Sample 2 pure PEI

FIGURE 4.3 Sample 3 99% PSU + 1% PEI

FIGURE 4.4 Sample 4 98% PSU + 2% PEI

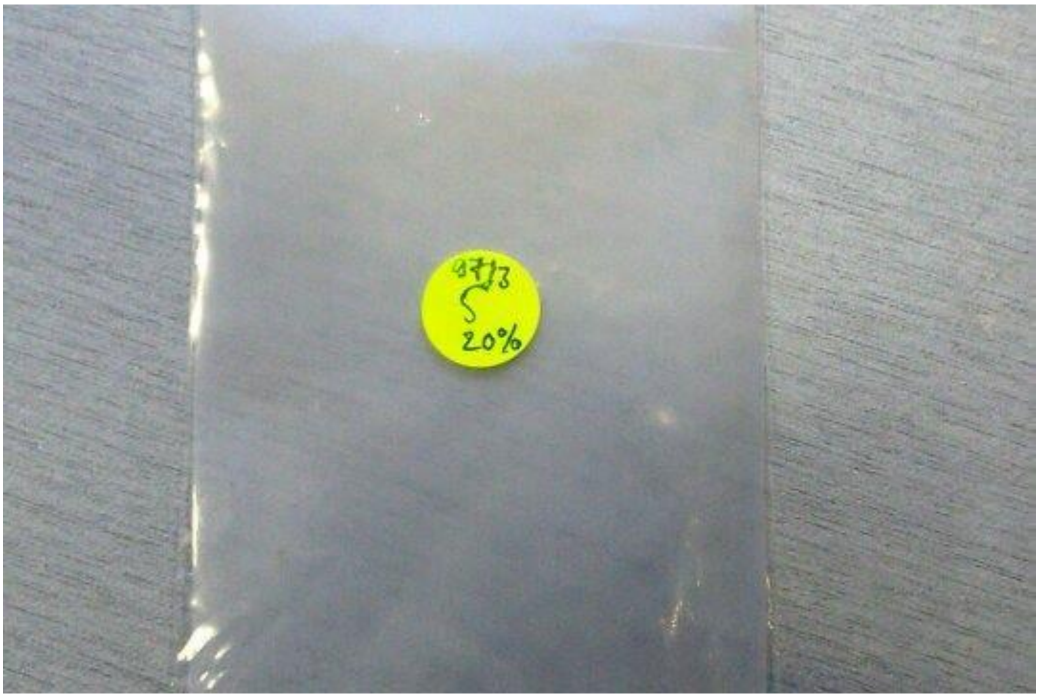


FIGURE 4.5 Sample 5 97% PSU and 3% PEI

All membranes have been fabricated according to the compositions provided before. The following figures show the picture taken for each membrane that has been synthesized.

- Fig. 4.1 shows the picture of polymeric membrane sample 1 made from 8 g PSU and 32 g NMP
- Fig. 4.1 shows the picture of polymeric membrane sample 2 made from 8 g PEI and 32 g NMP
- Fig. 4.2 shows the picture of polymer blend membrane sample 3 made from 0.08 g PEI, 7.92 g PSU and 32g NMP
- Fig. 4.2 shows the picture of polymer blend membrane sample 4 made from 0.16 g PEI, 7.84 g PSU and 32g NMP
- Fig. 4.3 shows the picture of polymer blend membrane sample 5 made from 0.24 g PEI, 7.76 g PSU and 32g NMP

Five membranes will the smooth surfaces and defect-free have been synthesized in time. When the observation by eyes, it can be seen clearly that the sample 1 and the sample 2 are transference, no colour and sample 3,4 and 5 have the white colour. Based on the properties of polymer membrane, there will be no phase separation in sample 1 and sample 2. That is the reason they are transference. However in sample

3, sample 4 and sample 5, the phase separation happens. However, by adjusting the speed of magnetic bar in mixing step, the blend will be more homogenous. During the synthesize process, there are three parameters need to be avoided. First is the speed of the magnetic bar when the hot plate stirs. The speed cannot too high to avoid the pores of the membrane. Secondly, the operating temperature of the hot stir needs to be lower than 55^{o}C to prevent the viscosity of the mixture reduces. If the temperature of the hot plate is more than 55^{o}C, the mixture will reduce its viscosity and it is very difficult to cast it. Thirdly, drying protocol is very important and it will affect to the surface of the membrane. If the evaporation is too fast, it will cause the surface of membrane is not smooth and has the defects on the surface. From this reason, high temperature is avoided in this protocol. For the first step of drying protocol, membrane is put in the vacuum oven to isolate with the air for 48 hours. In the condition of the lab, the air has a lot of moisture and it will cause the defects of the membrane. However, the oven is not turned on because the vaporization process needs to be slow. After 48 hours, the oven starts to be turned on and membrane is dried by the heat supply from the oven. The temperature is increasing 20 ^{o}C in each 2 hours and it reaches to 65 ^{o}C, the temperature is maintained for 24 hours before membrane is taken out from vacuum oven.

2. CHARACTERIZATION PROCESS

2.1.FTIR results

From the FTIR graph obtained by analysis, we can recognize the absorption band at several points shows the functional groups in the membrane. For the fabricated membranes, FTIR spectra were focused on some pronounced peaks of the main functional groups in PC. Therefore, we can see that this analysis is corresponding to the structure of membrane as we expected.

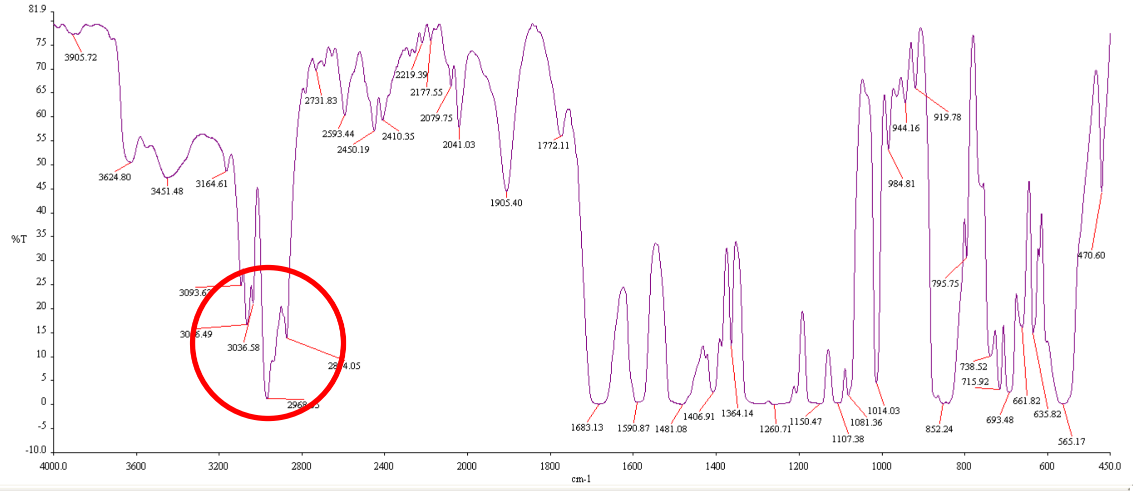


FIGURE 4.6 FTIR pure PSU

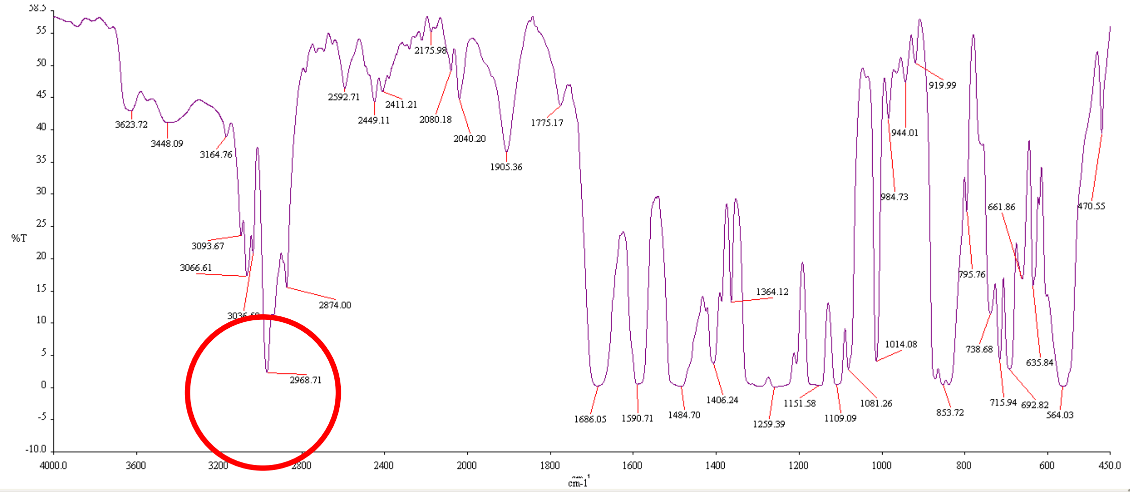


FIGURE 4.7 FTIR pure PEI

From figure 4.6 to 4.10, it can be seen that all the FTIR results are almost the same because the concentrations of the PSU and PEI in the mixed blend are not changed much. More than that, all the sample has the peak from 2800 cm^{-1} to 3200 cm^{-1}. With each peak, it presents for a chemical group in the sample. In this case, this peak presents for the double connection between oxygen particle and carbon particle. This group has an important role in removal CO_2 process

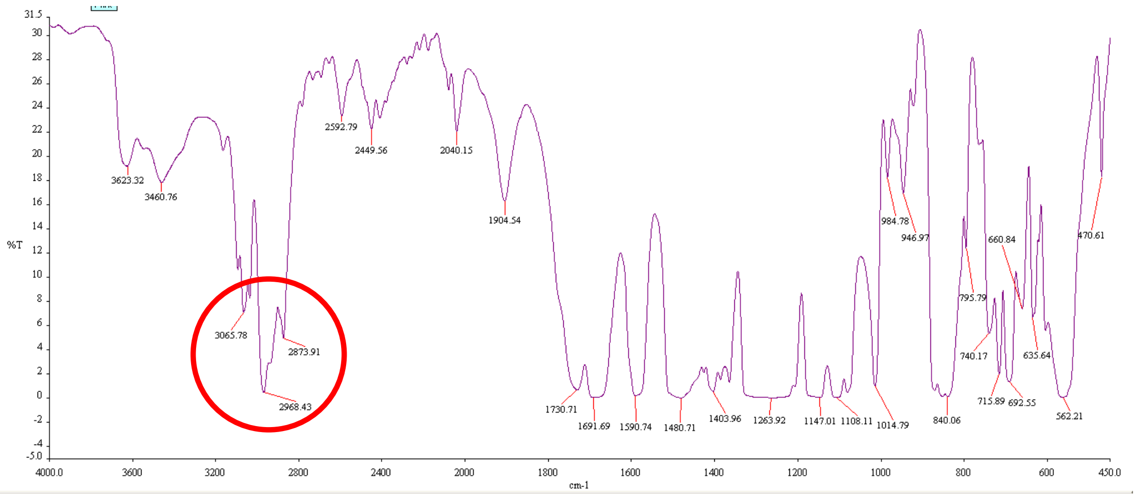


FIGURE 4.8 FTIR 99% PSU + 1 % PEI

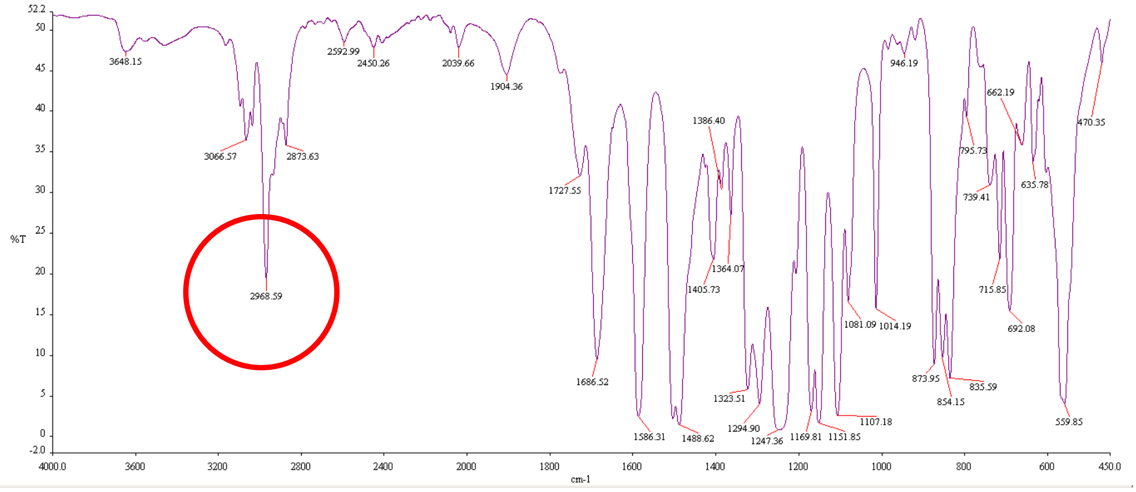


FIGURE 4.9 FTIR 98 % PSU + 2% PEI

From 450 cm^{-1} to 1800 cm$^{-1,}$ there are a lot of peaks. These peaks present for the C-O group, N-H group and the other groups. In conventional, polymers always have all these peaks.

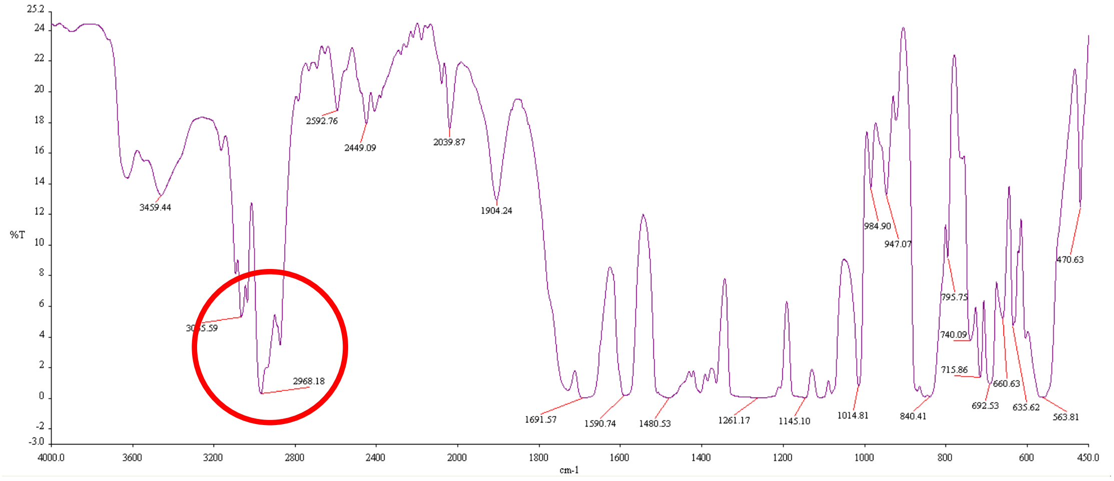


FIGURE 4.10 FTIR 97 % PSU + 3% PEI

2.2.TGA results

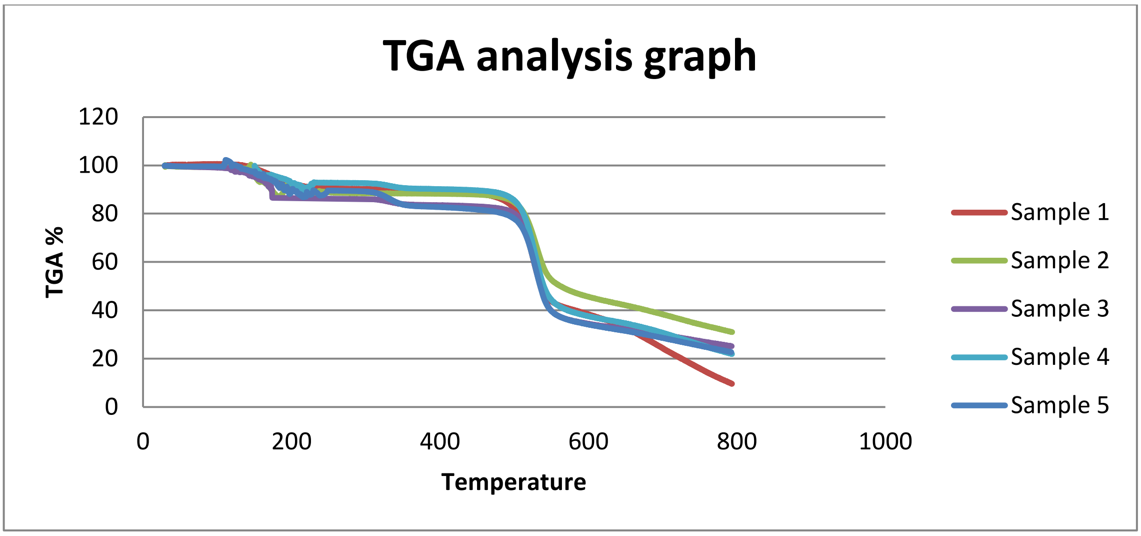


FIGURE 4.11 TGA analysis graph

Figure 4.9 in appendices shows TGA analysis for fabricated polymeric membrane. TGA provides measurement of mass change in materials that are associated with transition and degradation due to change in temperature or thermal change. Through this TGA analysis, we can determine the maximum mass loss is 20% when the temperature is raised to 500^{o}C. Therefore, it can be seen that blend polymer membrane can withstand relatively high temperature, which is suitable for processes which require high temperatures

2.3.FESEM results

Different magnifications of membranes were captured at 100x – 1000x. Surface images of membrane show that this type of membrane is a dense membrane. Small pores are observed on the surface. Cross sectional images are also captured in this case. The typical thickness of membrane is 50 μm as shown in the figures below.

- From figure 4.12, it can be seen that, polysulfone pure membrane is dense membrane. There are no defection, no porous and no pin hole. NMP is a suitable solvent for this membrane because polysolfone is solved in NMP completely. The mixture is transference and it will cause a good results for this membrane
- From figure 4.13, it can be seen that, polyetherimide pure membrane is dense membrane. There are no defection, no porous and no pin hole. NMP is a suitable solvent for this membrane because polyetherimide is solved in NMP completely. The mixture is transference and it will cause a good results for this membrane
- From figure 4.14, it can be seen that, PSU/PEI membrane is dense membrane. The surface of this membrane is not smooth because of the defections. NMP is a suitable solvent for this membrane because polysolfone and polyetherimide is solved in NMP completely. The mixture after mixing is cloudy and stable.
- From figure 4.15, it can be seen that, PSU/PEI membrane is dense membrane. The surface of this membrane is not smooth because of the defections. NMP is a suitable solvent for this membrane because polysolfone and polyetherimide is solved in NMP completely. The mixture after mixing is cloudy and stable.
- From figure 4.16, it can be seen that, PSU/PEI membrane is dense membrane. The surface of this membrane is not smooth because of the defections. NMP is a suitable solvent for this membrane because polysolfone and polyetherimide is solved in NMP completely. The mixture after mixing is cloudy and stable.

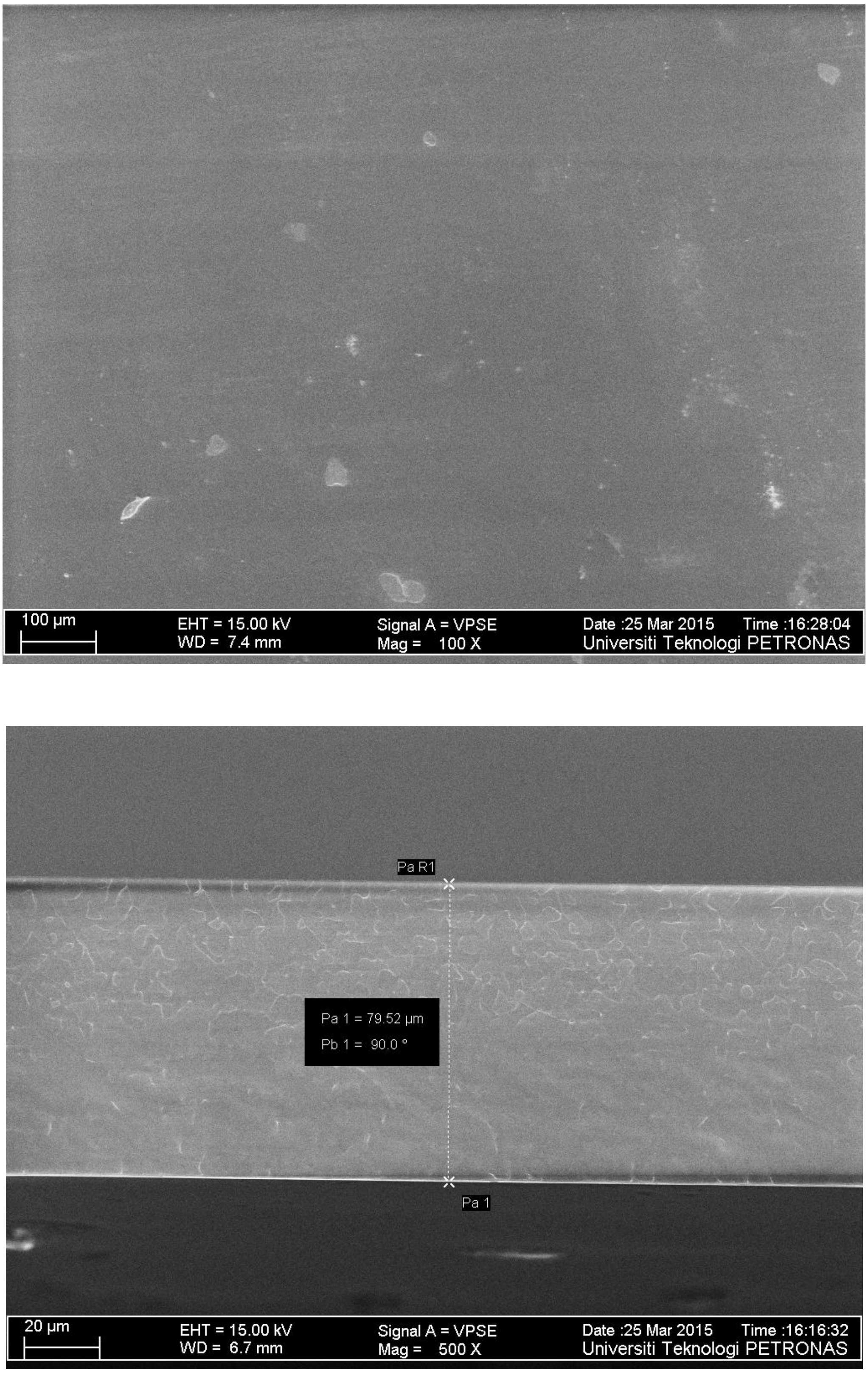


FIGURE 4.12 FESEM surface and cross section of pure PSU membrane

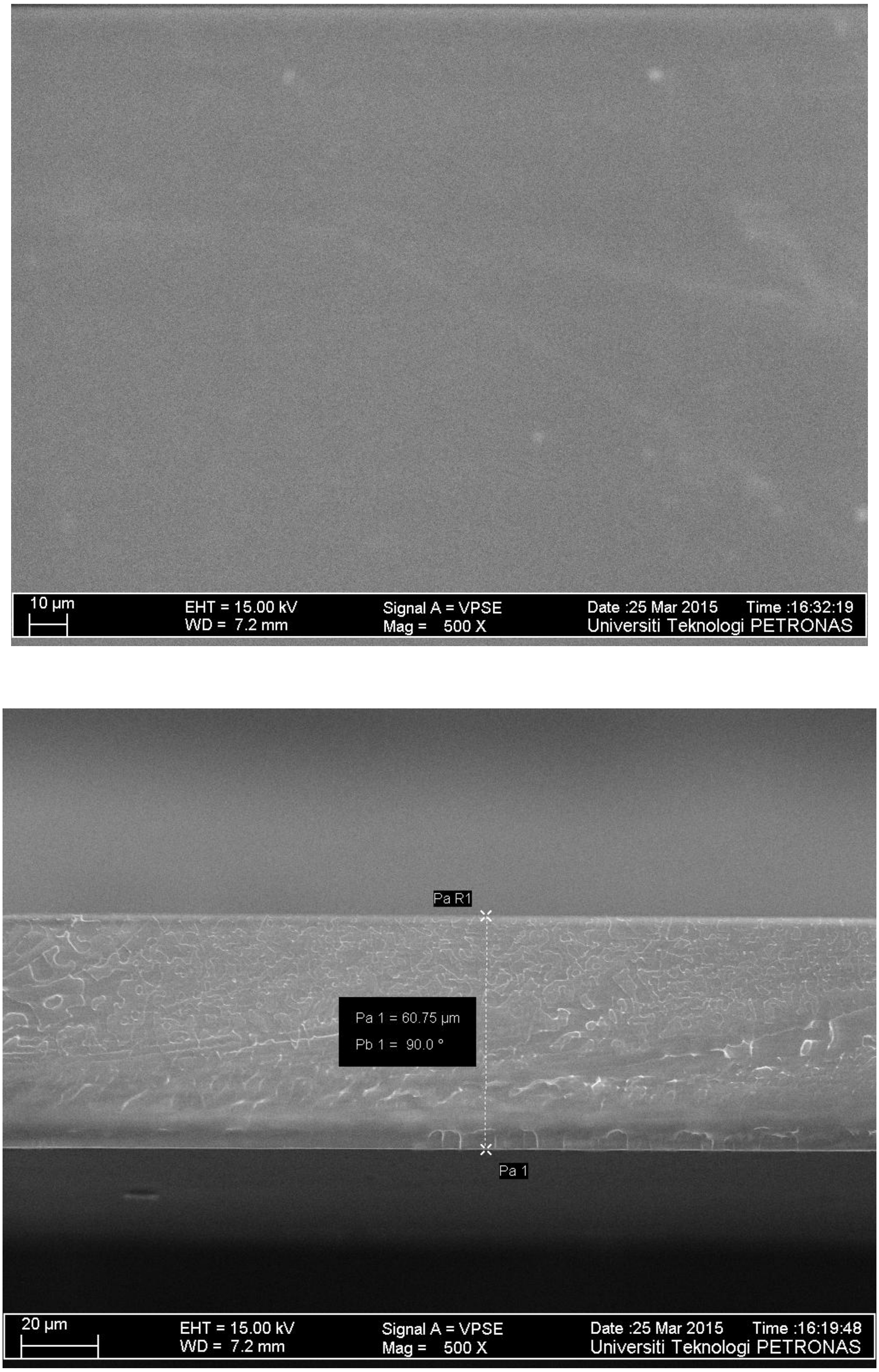


FIGURE 4.13 FESEM surface and cross section of pure PEI membrane

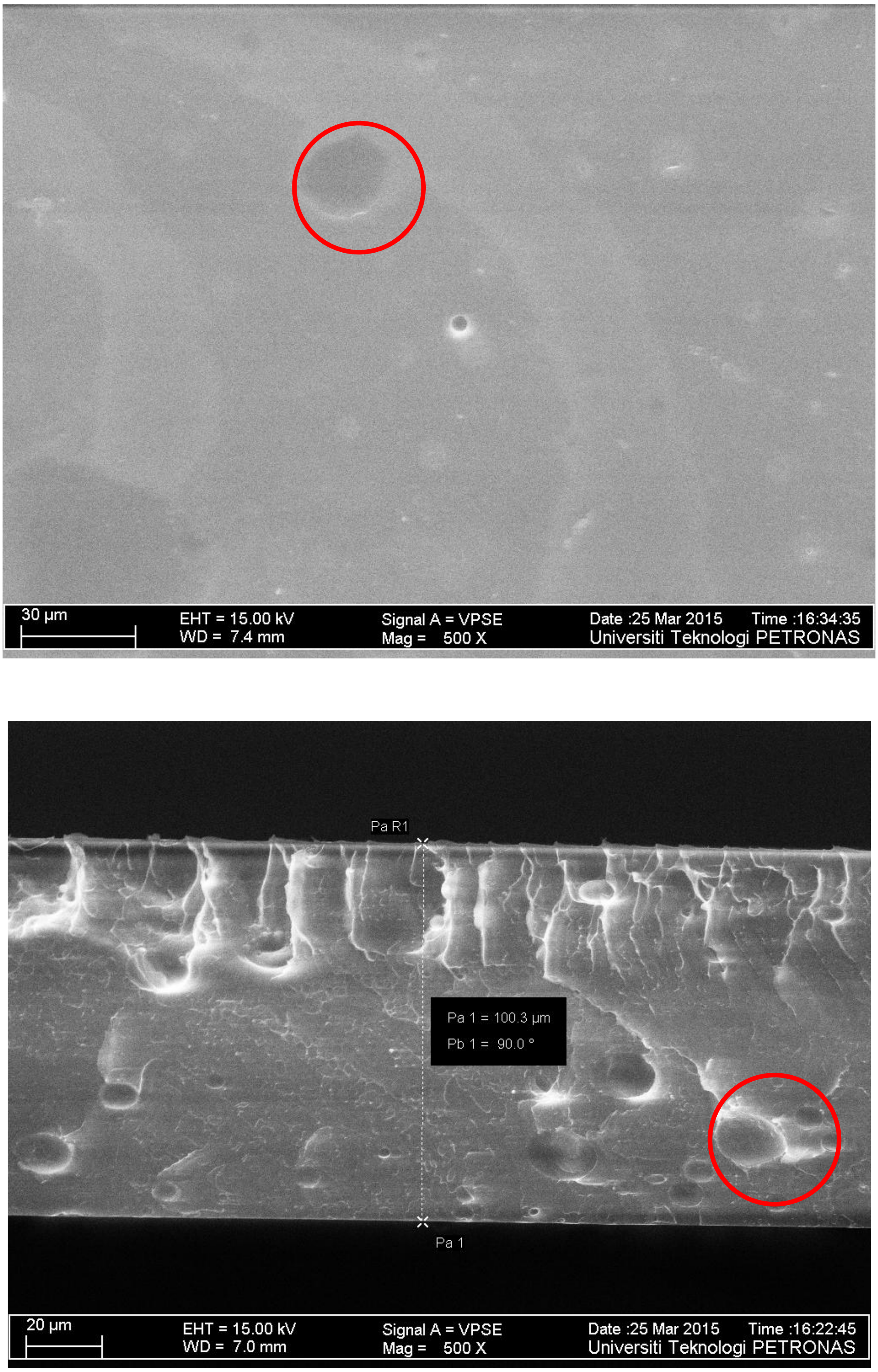


FIGURE 4.14 FESEM surface and cross section of 99% PSU + 1 % PEI membrane

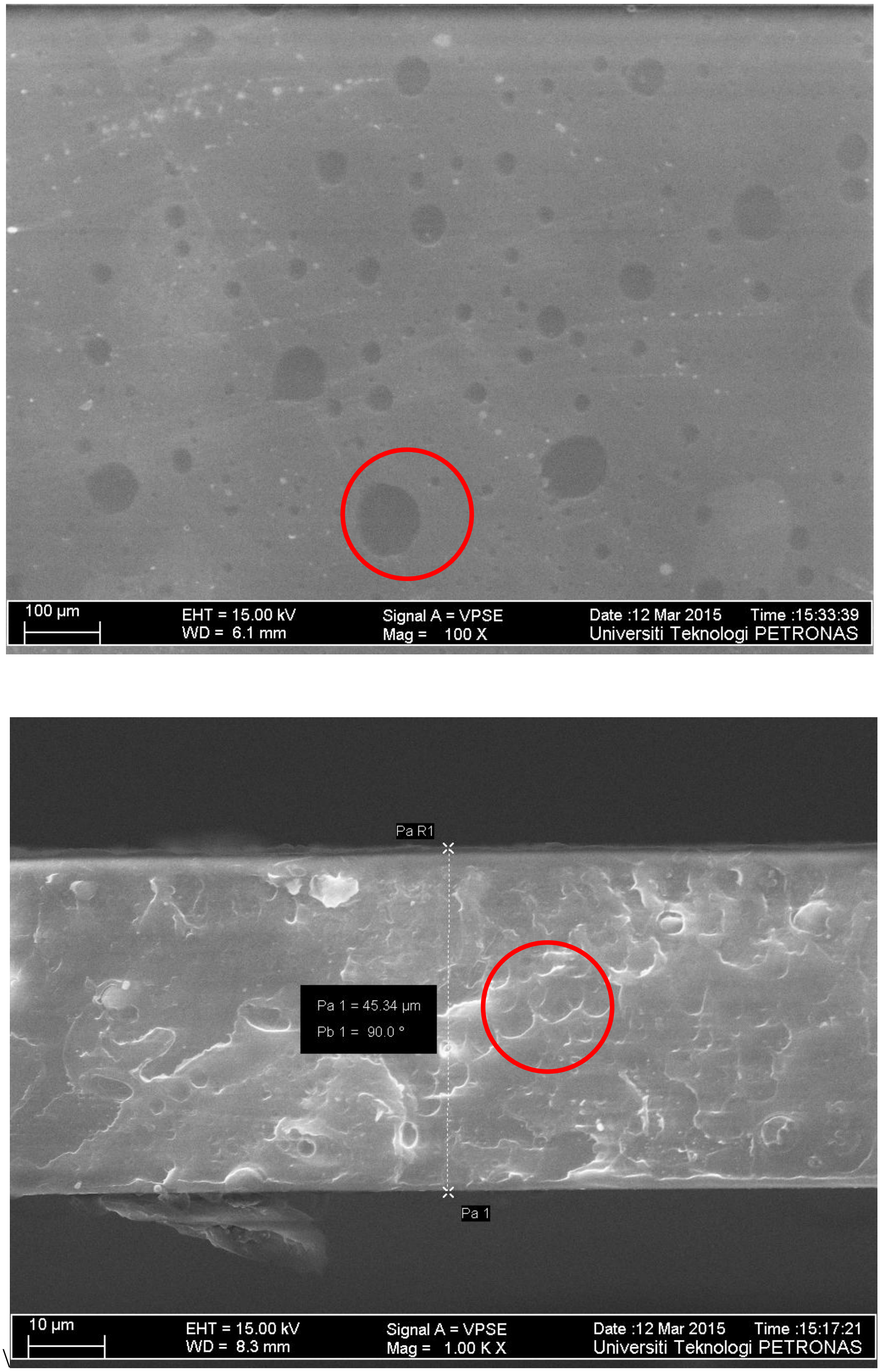


FIGURE 4.15 FESEM surface and cross section of 98% PSU + 2 % PEI membrane

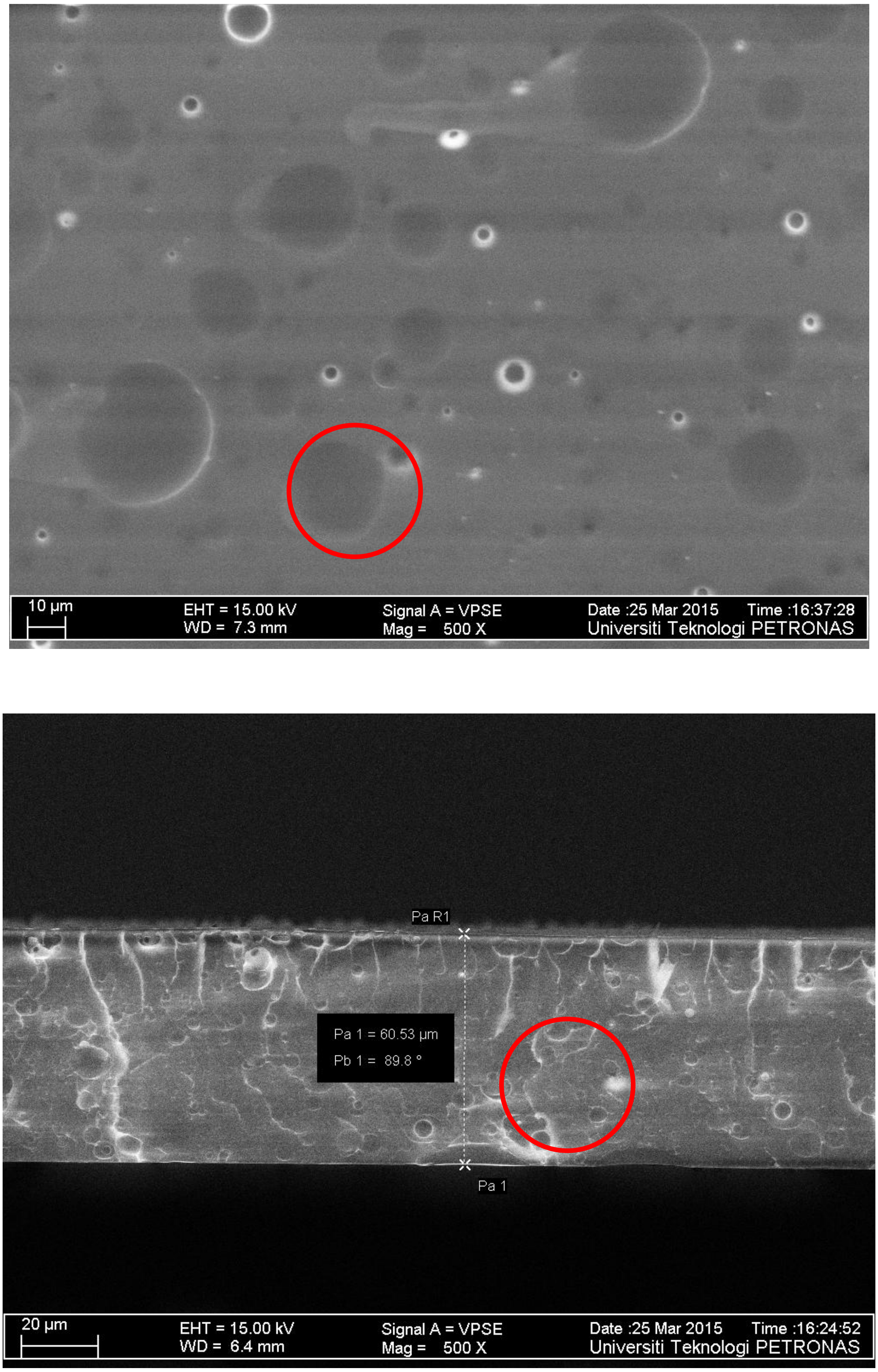


FIGURE 4.16 FESEM surface and cross section of 97% PSU + 3 % PEI membrane

3. GAS PERMEABILITY

From the first sample to the fifth sample, the compositions between PSU and PEI change. However, the major component in the membrane is PSU and the membrane will be affected by the properties of PSU more than PEI. It can be seen through the performance of gas separation test

TABLE 4.1 Permeability of CO_2

	6 bar	8 bar	10 bar
Sample 1	5.355343	4.566546	4.066542
Sample 2	1.336475	1.272343	1.166476
Sample 3	5.028678	4.338768	3.836456
Sample 4	4.793425	4.134575	3.612374
Sample 5	4.568769	3.878763	3.377567

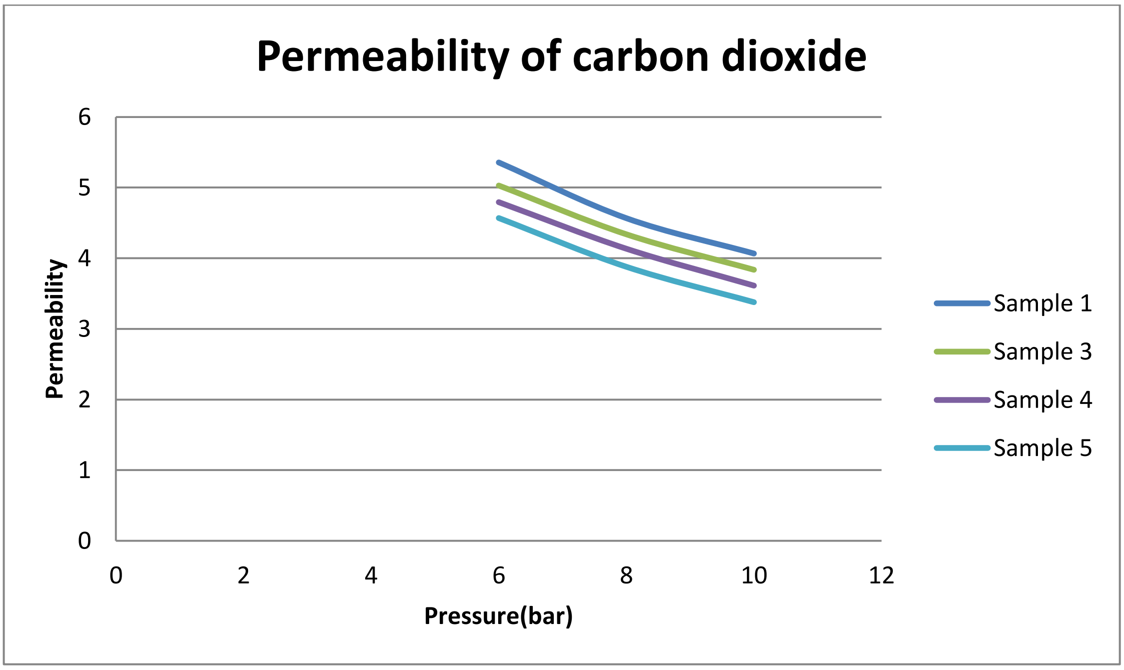


FIGURE 4.17 Permeability of CO_2

TABLE 4.2 Permeability of CH_4

	6 bar	8 bar	10 bar
Sample 1	0.593457	0.457567	0.367582
Sample 2	0.036563	0.027567	0.016546
Sample 3	0.468567	0.383453	0.324326
Sample 4	0.435345	0.346573	0.286542
Sample 5	0.398568	0.309345	0.258567

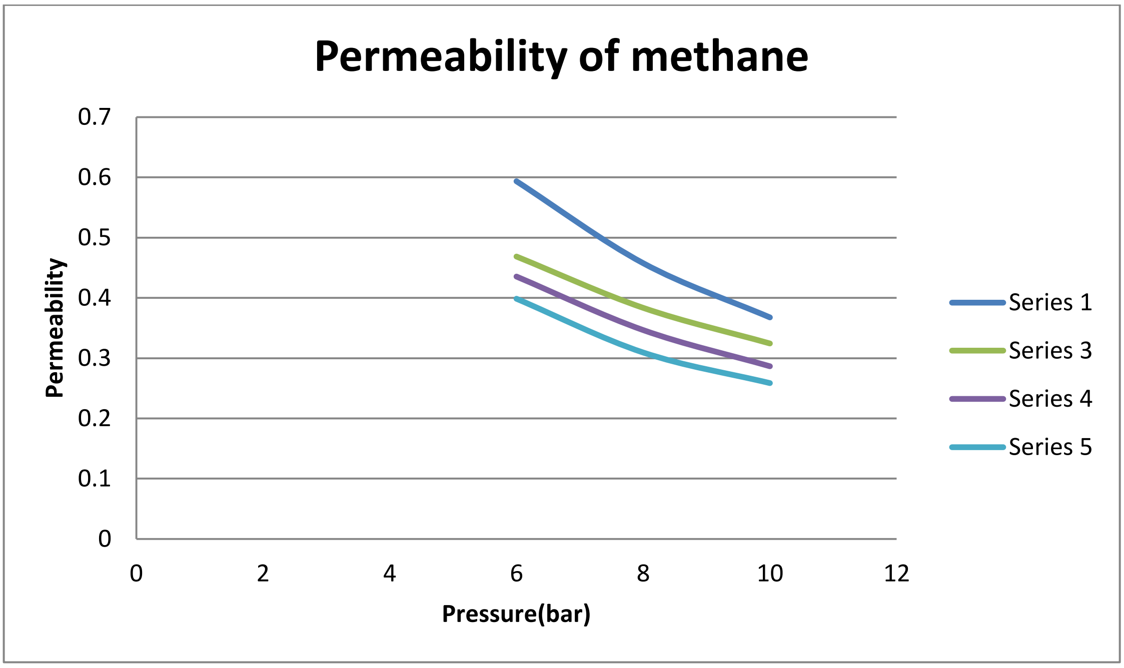


FIGURE 4.18 Permeability of CH_4

TABLE 4.3 Selectivity of membrane

	6 bar	8 bar	10 bar
Sample 1	9.023978	9.98006	11.06294
Sample 2	36.55266	46.15405	70.49895
Sample 3	10.73204	11.31498	11.82901
Sample 4	11.01064	11.92988	12.60679
Sample 5	11.46296	12.53863	13.06262

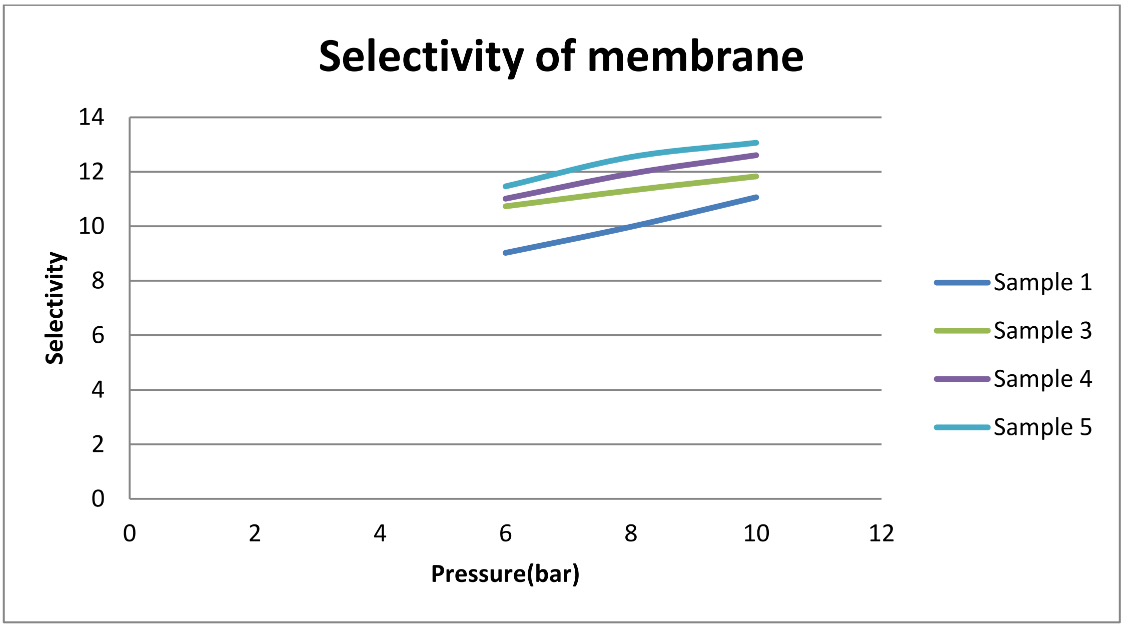


FIGURE 4.19 Selectivity vs. Pressure

The selectivity of the blend membrane is in the range of the PSU polymer membrane selectivity and PEI selectivity. When the second component is added in the mixture of membrane, the selectivity of the membrane is increasing. From the result of permeability test, it can be seen that the blend membrane has the selectivity in the range between the selectivity of the pure PSU membrane and the pure PEI membrane. Pressure is an important factor in this performance test. When the pressure is low, the permeability of CO_2 and CH_4 is high. However, the selectivity is low. When the pressure is high, the permeability of CO_2 and CH_4 reduces. However, the selectivity increases significant.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

This work about synthesizing five membranes with different composition of PSU and PEI in NMP solution is completed. From the research, we concluded that membrane synthesized from PSU and PEI has a good selectivity to remove CO_2 in natural gas. Several factors that have been studied in the research such as polymer concentration, speed of magnetic bar and the drying protocol have shown their effects on the membrane synthesized. FTIR analysis has also shown the functional groups in these synthesized membranes which are corresponding to structure. These groups can be used to explain some characteristics of the membrane synthesis. TGA analysis has also been carried out and ensures that the synthesized membrane has high heat resistance and is suitable to be used for high temperature process. FESEM, in addition, has shown clearer images to the morphology of membrane after synthesis.

Gantt chart for FINAL YEAR PROJECT II

Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Fyp 2 briefing	🟧													
Meeting with supervisor			🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	
Research work			🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧
Submission draft proposal												🟥		
Pre SEDEX												🟥		
Final submission													🟥	

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