CHAPTER 1

INTRODUCTION

1.1 Background

Membrane technology has been actively practiced for many years in the separation of CO_2 and CH_4 as it offers numerous advantages over other techniques (S.L Wee 2008). Membrane separation processes consume less energy, with the possibility of continuous operation (Uemiya 2004). Artificial membrane, or synthetic membrane, is a synthetically created membrane which is usually intended for separation purposes in laboratory or in industry. Synthetic membranes have been successfully used for small and large-scale industrial processes since the middle of the twentieth century (Pinnau 1999). Most of the commercially utilized synthetic membranes in separation industry are made of polymeric structures. Polymeric membranes lead the membrane separation industry market because they are very competitive in performance and economics. Owing to their strength, reproducibility, and low cost, they are suitable for various applications in science and technology and for research purposes. In the last two decades significant improvements in the performance of polymeric membranes for gas separation have been made (W. Koros 2002) and resulting from the research and development, the understanding of the relationships between structure, permeability and selectivity of polymeric membranes has been greatly advanced (P. Pandey 2001).

1.2 Problem Statement

One of the major problems related to the use of polymeric membranes is the strong trade-off between permeability and selectivity (Stern 1991)as most desirable gas separation membrane materials should have high permeability and high perm-selectivity besides high mechanical and thermal stability properties. Thus, these parameters are given great attention during fabricating (C.A. Scholes 2008) andthe control of gas permeability and permselectivity of polymer membranes has become a subject of strong research with worldwide participation in both industrial and academic laboratories because of its importance for the improvement of membrane separation processes as well its economic aspects (Stern 1991). The properties of the membrane greatly depend on the material and the related parameters such as types and concentration of polymer.

Thus, this paper will attempt tostudy the effect of different concentration of polysulfone polymer and solvent in synthesizing polymeric membrane with respect to membrane's properties such as the morphology, porosity and glass transition temperature.

1.3 Objectives

1. To study the effect of different concentration of polysulfone polymer and solvent in the casting solution towards the membrane properties.
2. To characterize the fabricated membrane by using scanning electron microscope (SEM) and Thermogravitmetry Analysis (TGA).

1.4 Scope of study

This paper will cover several stages. Figure 1.1 below shows the stages in completing the project.

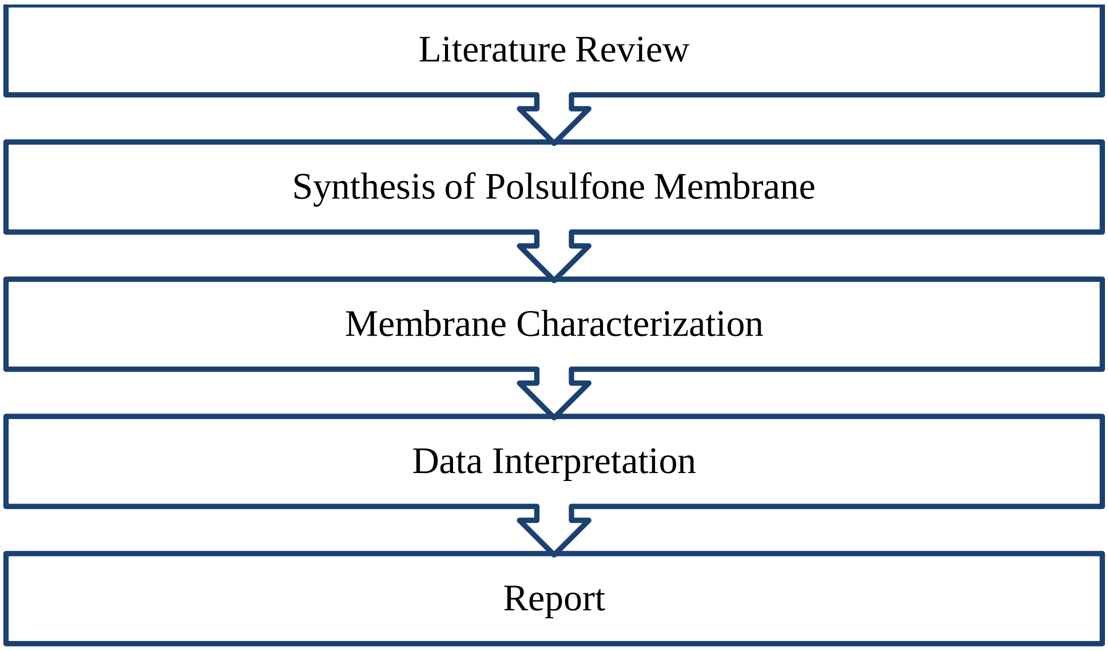


Figure 1.1: Scope of study

The very first stage is the understanding process and data collection fromprior art. The second and third stage is the experimental work, where the second stage where polysulfonemembrane is synthesizedby using dry-wet phase-inversion technique.

The main focus is during preparation of the casting solution where different concentration of polymer and solvent based on the weight percentage is manipulated. The third stage is the on membrane characterization which is used to study application-related properties of the membrane for use in gas separation. Among the proposed characterization process is scanning electron microscopy, viscosity measurement and differential scanning calorimeter. The next scope to be covered is the data interpretation where the properties of the membrane are discussed based on the data from the membrane characterization. Last stage is report writing on the findings from the experiment.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane technology for gas separation

Membrane can be defined as a selective barrier between two phases, the ‘‘selective’’ being inherent to a membrane or a membrane process (Mulder 1996). In the concept of membrane science, a synthetic membrane behaves as a thin barrier between two phases through which differential transport can occur. The membrane gas separation technology is over 15 years old and is proving to be one of the most significant unit operations as the technology inherits certain advantages over other methods that include compactness and light weight, low labour intensity, modular design permitting easy expansion or operation at partial capacity, low maintenance, low energy requirements, low cost, and environmental friendly. The progress in membrane science and technology was accelerated during the 1980s by the development and refinement of synthetic polymeric membranes. Membrane gas separation emerged as a commercial process on a large scale during the 1980s. During this period, significant progress was made in virtually every aspect of membrane technology, including improvements in membrane formation process, chemical and physical structures, configurations and applications.

Membrane can generally be classified into two; synthetic and biological membrane. Synthetic membrane can be made up by large numbers of different materials and further classified into two classes; organic (polymeric) and inorganic membrane. In any type of separation including gas, the membrane acts as a selective boundary that exists in between two heterogeneous fluids. For a normal membrane process, high pressure feed gas is supplied at one side of the membrane and it flows in plug flow and parallel to the membrane, permeate will leave in a direction normal to the membrane due to the concentration and pressure gradient. Particles which are allowed to pass through the membrane will move into permeate stream while the retained particles will stay in retentate stream. Figure 2.1 show the feed supplied at high pressure as it passes through the membrane. Particles which pass through the membrane move into the permeate stream while the retained particles will move into the retentate stream (Nadine Schmeling 2010).

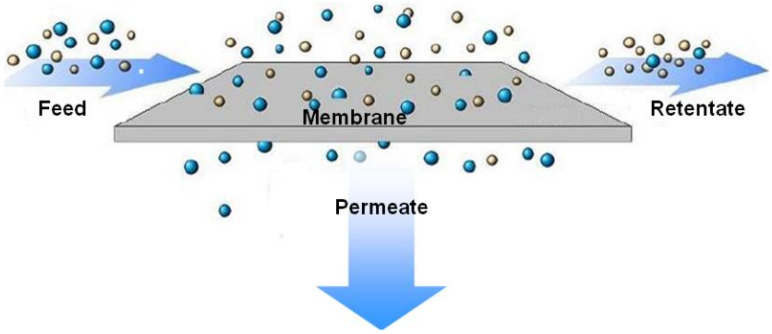


Figure 2.1: The movement of particles from feed into retentate and permeate streams.

Driving forces that facilitate this transport are pressure, concentration, and electrical potential across the medium (W. J. Koros 1996). The transport itself is a non-equilibrium process and the separation of chemical species results from differences in transport rates through the membrane. For different driving force, different separation processes and operations can be distinguished. Table 2.1 shows the different separation applications based on different type of driving force.

Table 2.1: Table shows type of different driving force and its examples of applications

Driving Force	**Example**
Pressure	Micro, Ultra and Nano-filtration, Reverse osmosis, Gas separation
Concentration	Dialysis, Osmosis
Electrical Potential	Electro dialysis, Membrane electrolysis, Electrophoresis
Temperature	Membrane distillation

2.2 Polymeric Membrane

Chemical structures coupled with subtle physical properties of the membrane material influence the permeability and selectivity of a gas. The responses of a polymeric material to permeation are strongly influenced by the polarity and steric characteristics of the polymer and permeate. The size and shape of bulky groups in both the polymer main chains and side chains determine certain fundamental properties like packing, density, and rigidity. These, in turn, influence the accessibility. An absence of such groups tends to increase the structural regularity, which favours increased density. The effect of lateral substituents on the backbone of aliphatic polyamides has a strong bearing on the gas separation properties. Bulky hydrocarbon groups force parallel chain segments further apart, thereby increasing free volume and diminishing hydrogen bonding and rigidity, and increasing the permeability (Pandey 2001).

A porous membrane is a rigid, highly voided structure with randomly distributed inter-connected pores. The separation of materials by porous membrane is mainly a function of the permeate character and membrane properties, such as the molecular size of the membrane polymer, pore-size, and pore-size distribution. A porous membrane is very similar in its structure and function to the conventional filter. In general, only those molecules that differ considerably in size can be separated effectively by microporous membranes. Porous membranes for gas separation do exhibit very high levels of flux but inherit low selectivity values. Microporous membranes are characterized by the average pore diameter, the membrane porosity, and tortuosity of the membrane.

There are several ways to prepare porous polymeric membranes, such as solution casting, sintering stretching, track etching, and phase separation. The final morphology of the membrane obtained will vary greatly, depending on the properties of the materials and the process conditions utilized. Nonporous or dense membranes have high selectivity properties but the rates of transport of gases through the medium are usually low. An important property of a nonporous dense membrane is that even permeates of similar sizes may be separated if their solubility in the membrane differs significantly.

A dense membrane can be prepared by melt extrusion, where a melt is envisioned as a solution in which the polymer in both solute and solvent. In the solution-casting method, dense membranes are cast from polymer solutions prepared by dissolution of a polymer in a solvent vehicle to form a sol. This is followed by complete evaporation of the solvent after casting. Polymer membranes have gained popularity in isolating carbon dioxide from other gases (Gramain March 2002). These membranes are elastomers formed from crosslinked copolymers of high molecular weights. They are prepared as thin films by extrusion or casting. They demonstrate unique permeability properties for carbon dioxide together with high selectivity towards H2, O2, N2, and CH4.

2.3 Polysulfone Polymer (PSf)

Polymer is a high molecular weight component which is built up from a repeating basic unit known as monomer. The polymer molecular weight depends on the degree of polymerization of the monomer and the molecular weight of the monomer.

Polysulfone (PSf), or also known as udel or ultrason is a family of sulfur-containing thermoplastics closely related to polyethersulfone (PES). The structure of the polysulfones is aromatic groups, generally with more than one benzene ring, joined by a sulfone group. Figure 2.2 shows the repeating unit of polysulfone polymer.PSf was selected because of its satisfactory gas permeability and acceptable permselectivities, and widespread use as a commercial polymer. Its relative low cost and mentioned properties established PSf as the choice for use as a proper glassy polymer for the fabrication of CO2 or H2 separation membrane (Kapantaidakis GC 1996).

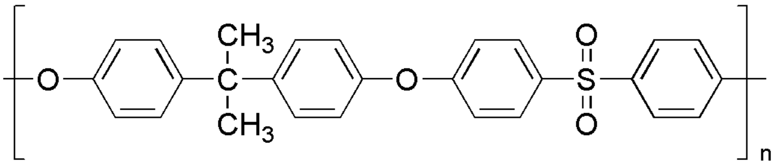


Figure 2.2: Molecular structure of polysulfone monomer

Generally, PSfis an amorphous material with low moisture absorption. Reinforcement improves toughness and further enhances dimensional stability, but turns materials opaque. In addition, PSf are characterized by high strength, very high surface-temperature limits, low creep, good electrical characteristics, transparency, self-extinguishing ability, and resistance to greases, many solvents, and chemicals. Polysufones may be processed by extrusion, injection molding, and blow molding. Table 2.2 below are the properties of PSf;

Table 2.2: Properties of PSf

Properties	**Value**
Density	1.24 g/cm^3
Young Modulus	3.2 GPa
Tensile Strength	10200lb/in^2
Elongation	50%
Melting Point	375°F

2.4 Solvent: N-Methylpyrrolidone (NMP)

NMP is the lactam of 4-methylaminobutyric acid and a very weak base. It is a clear to slightly yellow liquid miscible with water and solvents like ethyl acetate, chloroform, benzene and lower alcohols or ketones. It also belongs to the class of dipolar aprotic solvents which includes dimethylformamide, dimethylacetamide and dimethyl sulfoxide. These characteristics are highly useful in a variety of chemical reactions where an inert medium is of concern. Despite the stability of NMP, it can also play an active role in certain reactions: hydrolysis, oxidation, condensation, conversion with chlorinating agents, polymerization and o-alkylation, and related reactions.Other names for this compound are 1-methyl-2-pyrrolidone, N-methyl-2-pyrrolidinone, N-methylpyrrolidone, N-methylpyrrolidone and pharmasolve.

NMP is a chemically stable and powerful polar solvent. Figure 2.3 below shows the functional group of NMP;

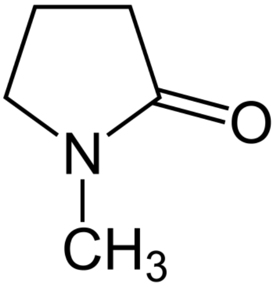


Figure 2.3: Functional group of NMP

2.5 Polymeric Membrane's Preparation Technique

If material selection affects the membrane morphology and performance, so do the preparation technique. The material selection limits the employable techniques, thus it is crucial to use a proper technique in order to produce a membrane structure with suitable morphology for specific separation, for this case, gas separation. There are few numbers of preparation techniques that can be used to prepare synthetic membranes including polymeric membrane such as sintering, stretching, track-etching, solution coating, phase inversion, sol-gel process and vapour deposition.

2.5.1 Phase Inversion Technique

Most commercial membranes are prepared by using phase inversion technique. The technique has been widely used for the preparation of asymmetric membrane since Loeb and Sourirajan successfully developed cellulose acetate membrane from seawater desalination in the 1960s (S. Loeb 1962). Phase inversion technique is a technique where a polymer is transformed from liquid to solid state in controlled manner. The solidification process is often getting started by the transition from one liquid state into two liquids, in other word liquid-liquid demixing. At a certain period or stage of the demixing process, one of the liquid phases with the higher polymer concentration will solidify, forming solid matrix. By controlling the initial stage of the phase transition, the membrane morphology can be controlled including the membrane porosity.

The concept of phase inversion covers a range of different techniques including precipitation by solvent evaporation, precipitation from the vapour phase, precipitation by controlled evaporation, thermal precipitation and immersion precipitation. Majority of phase inversion membranes are prepared by using immersion precipitation technique. Immersion precipitation or known also as dry/wet phase inversion is suitable to prepare polymeric membranes from a variety of polymer as long as the polymer is soluble in the solvent. Basically, the parameters which influence the membrane properties and performance can be controlled prior to or during the experiment such as polymer concentration, evaporation time, humidity, temperature and the composition of the casting solutions.

2.5.2 General Procedure of Dry/Wet Phase Inversion

The polymer is dissolved in a suitable solvent mixture. Additives are optional. The selection of the material including the polymer, solvent and additives will affect the viscosity of the solution. The polymer solution or also known as casting solution is cast on a supporting layer, known as casting plate by using casting knife. The cast solution or film is then immersed in the non-solvent bath to allow the interaction between solvent and non-solvent and eventually, the polymer will precipitate. So generally, the phase inversion method could be described in the figure 2.4 where there are five major steps in the technique.

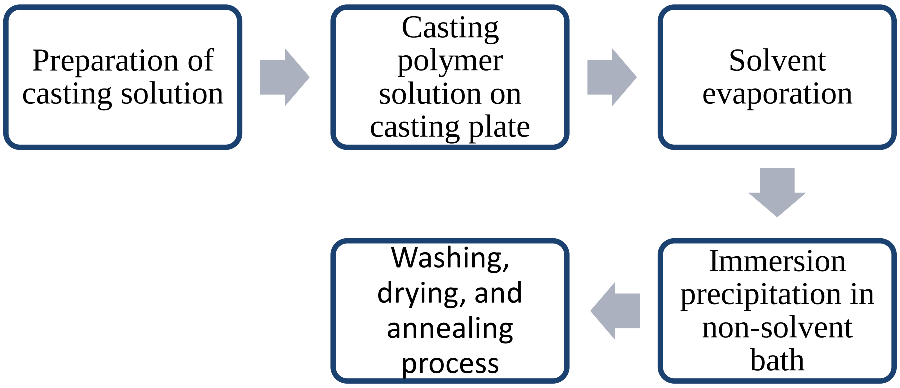


Figure 2.4: Diagram shows that basic step in dry/wet phase inversion method

CHAPTER 3

METHODOLOGY AND PROJECT WORK

3.1 Phase Inversion Set Up and Experiment

There will be three experiments on investigating the effects of solvent and non-solvent towards membrane properties and performance. Figure 3.1 below illustrates the whole experiments in general.

3.2 Experiments

3.2.1 Apparatus and Materials

For the experiment, the required glassware, apparatus and chemicals are listed in table 3.1 and 3.2.

Table 3.1: Glassware for phase inversion process

No	Glassware
1	500 mL beaker
2	Casting plate
3	250 glass bottle with cover

Table 3.2: Apparatus for phase inversion process

No	Apparatus
1	Electronic weighing machine
2	Magnetic stirrer and bar
3	Casting knife
4	Ultrasonic degasser device
5	Spatula
6	Stopwatch
7	Plastic tray

Below are the materials which are used in the experiment.

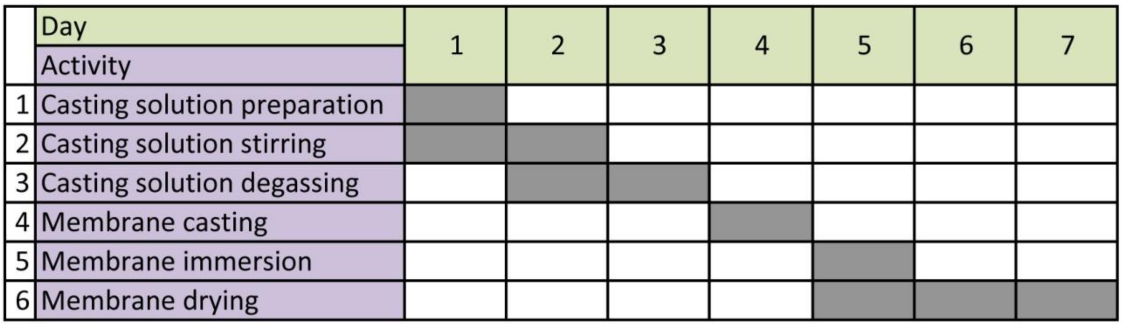
Table 3.3: Solvent and Non-solvent for the experiment

No	Chemicals	Remarks
1	N-Methyl-2-pyrrolidone (NMP), purity 99%	Solvent
2	Dionized water, purity 99%	Coagulation Bath
3	Polysulfone polymer	Polymer

3.2.2 Procedure

1) Polysulfone polymer is dried 24 hours before the experiment
2) Casting solutions are prepared by mixing 15wt% of polysulfonepolymer with 85wt% solvents. The solution is then stirred for 24 hours by using magnetic stirrer at room temperature. Ensure that the
3) The casting solution is degassed by using an ultrasonic degasser machine for 3hours to remove trapped air bubbles in the solution. The solution is let for 24 hours for further degassing.
4) After degassing, the solution is then castby using casting machineat ambient temperature on the casting plate.
5) After the solution is cast, the cast film is let for 5 minutes.
6) The film is then immersed in deionized-water bath until the cast film is detached from the casting plate.
7) The detached film is then air-dried for 24 hours and later dried at drying oven for 3 days.
8) The experiment is repeated by using different concentration of polymer and solvent at ration 20: 80 and 25: 75.

3.2.3. Gantt Chart formembrane synthesize



	Day Activity	1	2	3	4	5	6	7
1	Casting solution preparation	▨						
2	Casting solution stirring	▨	▨					
3	Casting solution degassing		▨	▨				
4	Membrane casting				▨			
5	Membrane immersion					▨		
6	Membrane drying					▨	▨	▨

Figure 3.1: Gantt Chart

3.3 Thermogravimetry (TGA) analysis

3.3.1.1 Apparatus and materials

Table 3.4: Apparatus for TGA Analysis

No	Apparatus
1	Thermogravimetry analysis device

Table 3.5: Chemical for TGA Analysis

No	Materials
1	Membrane samples

3.3.1.2 Procedure

1) Membrane samples are cut into 2 cm X 1 cm square shape. Then, the sample is further cut into very small pieces.

2) The samples are then put into the TGA device and the temperature is set from room temperature until 800°C

3) The result is plotted to evaluate on the outcome.

3.3.2 FESEM

3.3.2.1 Apparatus and materials

Table 3.6: Glassware for FESEM Analysis

No	Apparatus
1	FESEM device

Table 3.7: Chemical for FESEM Analysis

No	Materials
1	Membrane samples
2	Liquid nitrogen

3.3.2.2 Procedure

1) Membrane samples are cut into 2 cm X 1 cm square shape. Then, the sample is further cut into very small pieces.

2) The samples are then put into the TGA device and the temperature is set from room temperature until 800°C

3) The result is plotted to evaluate on the outcome.

3.4. Results and discussion.

3.4.1.1 Thermogravimetry Analysis

Sample A (15wt% Psf, 85 wt% NMP)

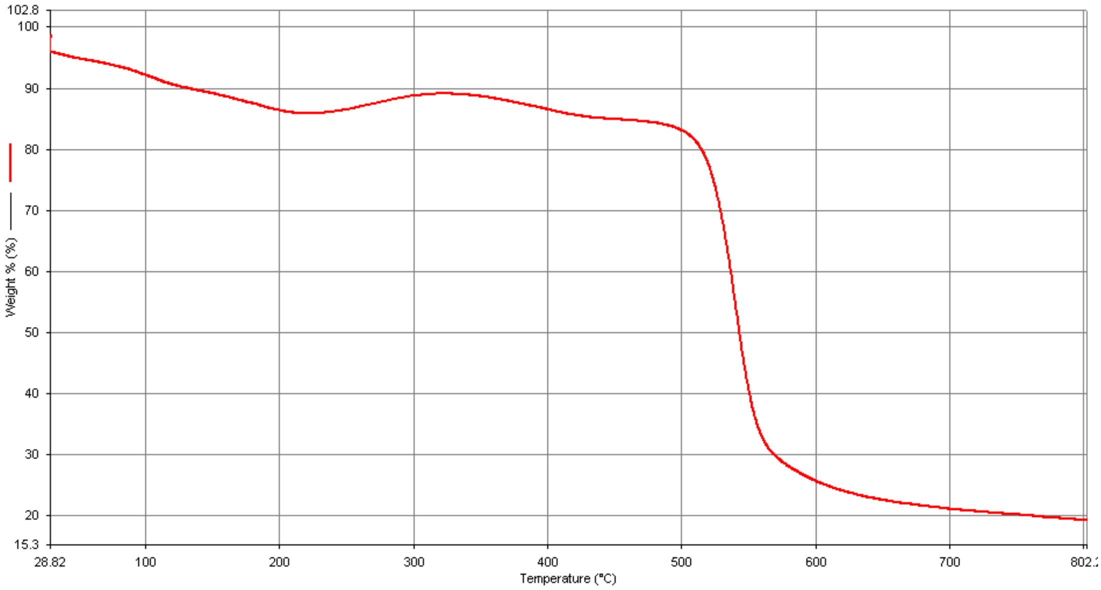


Figure 3.2 : Sample A (15wt% Psf, 85 wt% NMP)

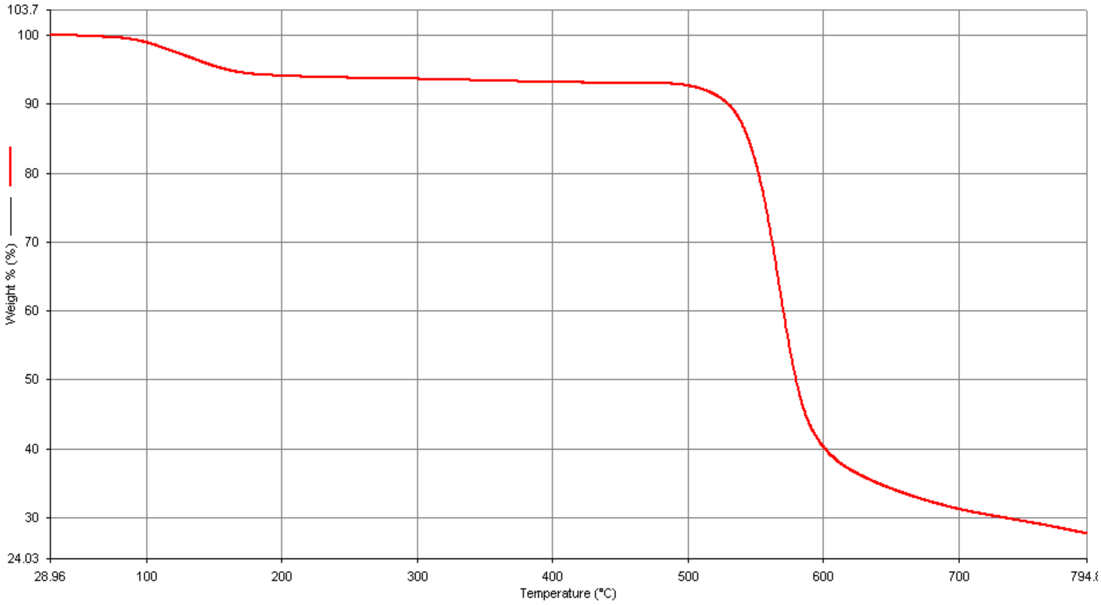


Figure 3.3: Sample B (20wt% Psf, 80 wt% NMP)

3.4.1.2 Discussion on TGA test

Based on the graphs of different membranes, it can be seen that difference in polymer and solvent composition do affect the membrane properties.

Table 3.8 : Data on TGA analysis for both samples

Parameter	**Value**	
Time to achieve T_g (min)	25.5	26.1
Weight loss (%)	18.07	9.04

Sample A recorded higher weight loss (18.07%) as compared to Sample B (9.04 %). For Sample A, time to achieve the loss is much lower which 511.94 °C within 25.5 minutes than Sample B which is at 523.6 °C in 26.1 minutes.

Based on these data, it can be concluded that Sample B is much more stable than Sample A. It is believed that the difference in polymer and solvent composition affects the stability of the membrane.

3.4.2 FESEM Analysis

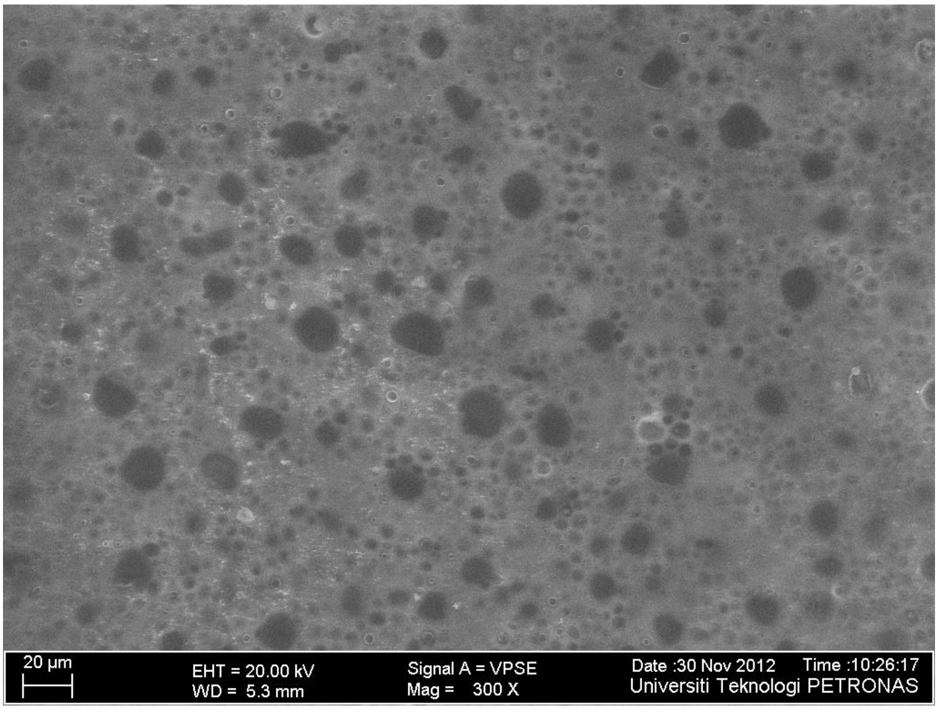


Figure 3.4: Front view of sample A

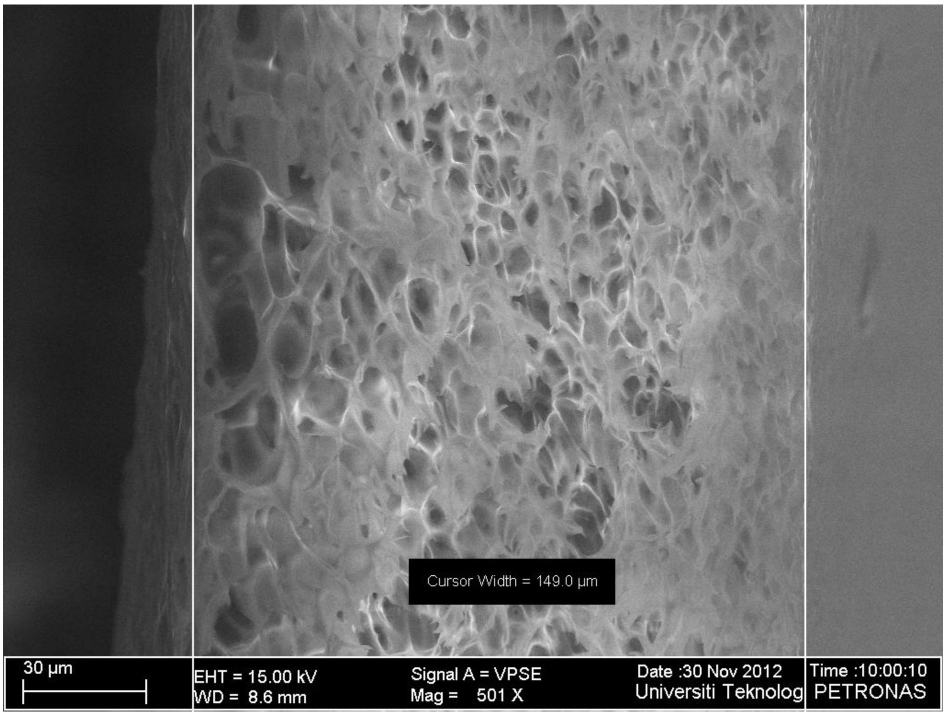


Figure 3.5: Side view of sample A

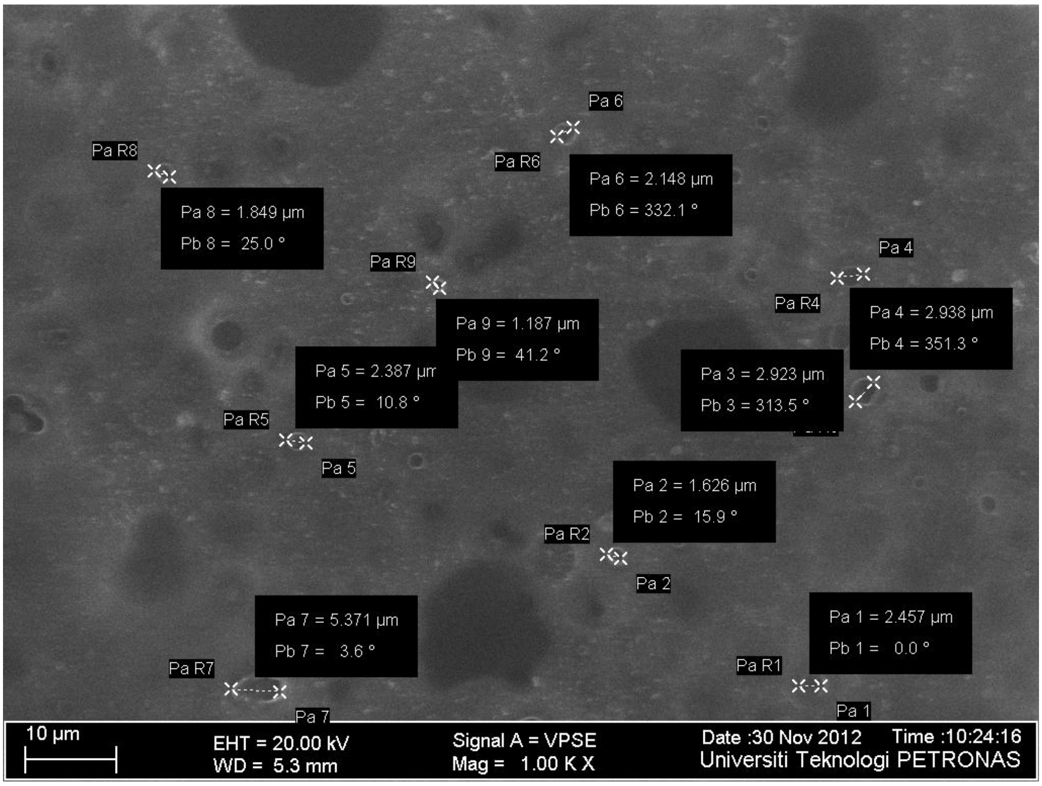


Figure 3.6: Pore size distribution of sample A

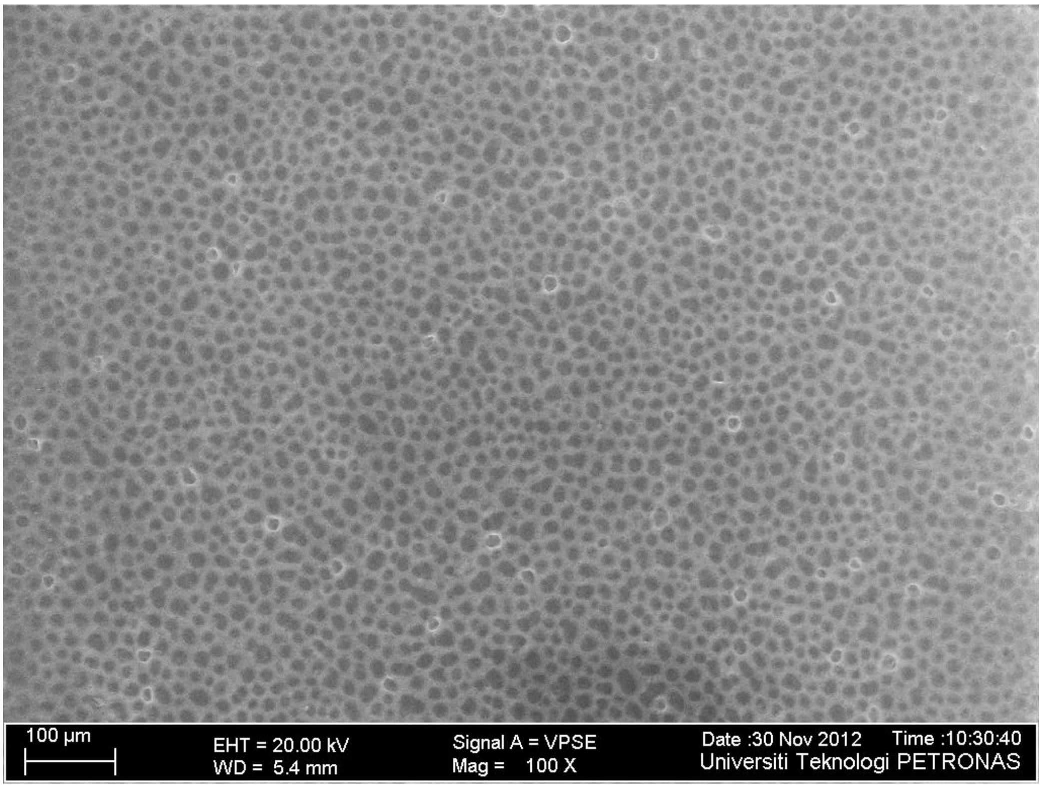


Figure 3.7: Front view of sample B

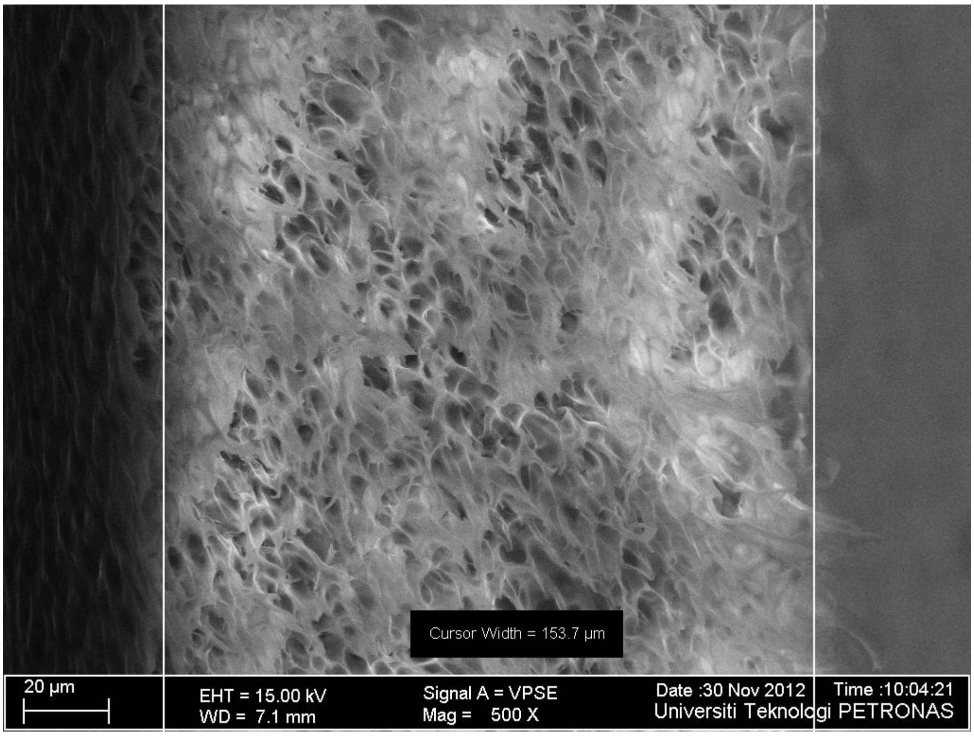


Figure 3.8: Side view of sample B

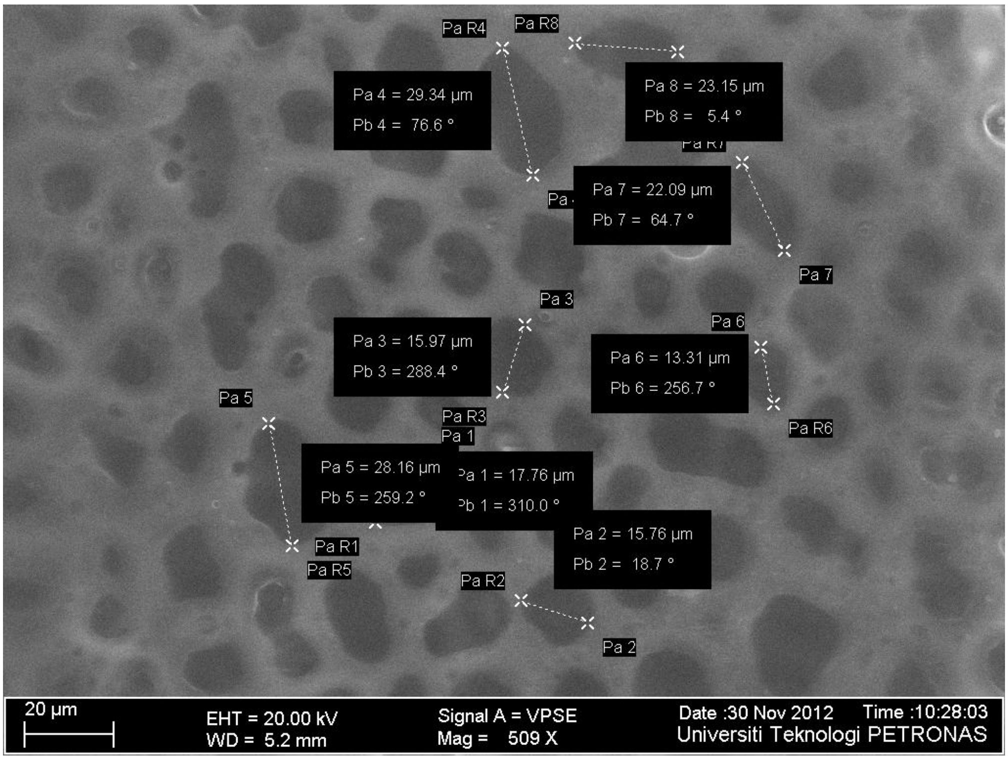


Figure 3.9: Pore size distribution of sample B

3.4.2.1 Discussion on FESEM

From figure 3.6 and 3.9, the pore distribution of sample A ranges from 1.187 μm until 5.371 μm while for sample B, it ranges from 13.31 μm until 29.34 μm. Initially, it can be concluded that with higher concentration of polymer in the casting solution, the smaller the pore range of the membrane.

Asymmetric membranes consist of a thin top layer supported by a porous sub-layer that often contains large void spaces, or macro-voids. These macro-voids may exhibit different morphologies (i.e., finger-like or sponge-like) depending on phase inversion kinetics and thermodynamics. Referring to figure 3.8, from the membrane morphology, it shows that the miscibility of the casting solution and the non-solvent which is deionized waters is low, thus, reflecting the suitability of the non-solvent with the casting solution. Low miscibility will create slow ion exchange between solvent and non-solvent, thus creating sponge-like morphology.

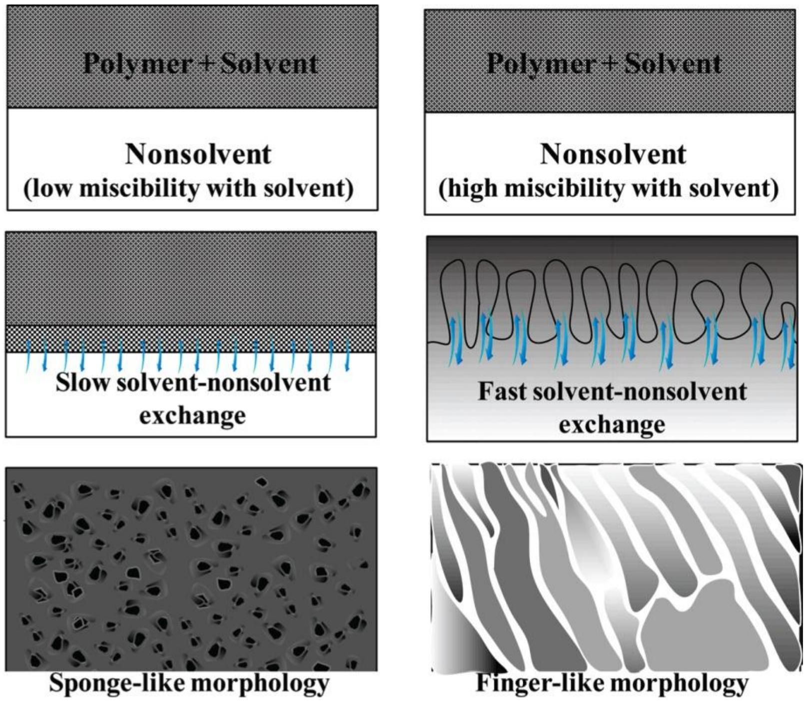


Figure 3.1.1: Morphology analysis based on miscibility of polymer and solvent

(Gregory R. Guillen n.d.)

The presence of macro-voids in membranes has both advantages and disadvantages. Macro-voids could result in compaction or collapse of membranes and therefore limit the application in high pressure processes such as reverse osmosis.

On the other hand, the macro-void structure is suitable for ultrafiltration processes and can be employed as support layers for composite membranes. (Smolders 1992). Macro-voids are generally formed in systems where instantaneous de-mixing takes place, except when the polymer additive concentration and the non-solvent concentration in the polymer solution exceed a certain minimum value (Smolders 1992). Several mechanisms have been proposed to describe the formation of macro-voids. It is suggested that the interfacial hydrodynamic instability driven by a surface tension gradient is responsible for the initiation of macro-voids (Matz 1972) and that precipitation rate determines macro-void structure (Strathmann 1978). Therefore, the polymer solution composition close to the binodal composition favours the formation of spongy structures.

3.5 Conclusion

From the experiments, it is successfully proven that difference in polymer and solvent composition will affect the membrane properties.

Since there is no clear instruction on drying technique of the membrane, it is recommended that the membrane is dried in a closed box with silica gel so that all water moisture will be absorbed into the silica gel as the solvent, NMP is a fast and good moisture absorber and there is possibility that moisture in air is being absorbed into the membrane when it is left for drying. Thus, it causes the morphology of the membrane to change.

It is also recommended more membrane characterizations techniques such as on the surface roughness and charge, permeability and rejection test, and membrane porosity are to be done in the future to provide more data. Also, more membrane with different composition are recommended to be synthesized in the future to have more understanding on the membrane behaviours when the composition changes.