FABRICATION OF POLYSULFONE MEMBRANE; THE EFFECT OF COOLING PROCESS

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ABSTRACT

Three pieces of polysulfone membrane were fabricated by using phase inversion method. In this study, only one parameter was investigated to observe the effect of the parameter on the membrane performance. The parameter that was investigated is the temperature of water bath during the fabrication process of polysulfone membrane. All the membranes were characterized by this technique: modeling of the rejection of sample red colour solution. The interpretation of experiment data was carried out by flux and rejection. In membrane characterization, the important parameter is the optimum temperature in producing the membrane. The result for this project are higher temperature of water bath will produce a more effective polysulfone membrane. However, it must be a limit to prevent the destroyed of polymerization membrane.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Filtration by the use of membranes is becoming increasingly important in the process industries. In this relatively new filtration process, the membrane acts as a semipermeable barrier and filtration occurs by the membrane controlling the rate of movement of various molecules between two liquid phases, two gas phases, or a liquid and a gas phase. The two fluid phases are usually miscible and the membrane barrier prevents actual, ordinary hydro-dynamic flow. (Christie John Geankoplis, 2003)

The technology of membrane filtration has been used for long term such as in electronic industrial, pharmaceutical, chemical industrial, petroleum industrial, mineral water and etc. It is because there are many advantages by using membrane for filtration. Filtration of membrane can be substituted as a good alternative for separation processes like evaporation, distillation and absorption, which need a lot of energy. There are many types of membrane filtration like micro filtration, ultra filtration, reverse osmosis filtration and nano filtration.

In this project, the membranes are produced by a simple phase inversion technique. Polysulfone, which shown as Figure 1.1 is used as polymer and mix with N-Methyl-2- Pyrrolidone solvent to produce membrane for liquid filtration. The sulfur atoms in this oxidation state make the polymer quite polar and thus hydrophilic. As much of the fouling in water comes from hydrophobic organic particles, they are not attracted to the polysulfone. The pH and temperature ranges are wide for using this polymer. (Mathias Ulbricht, 2006)

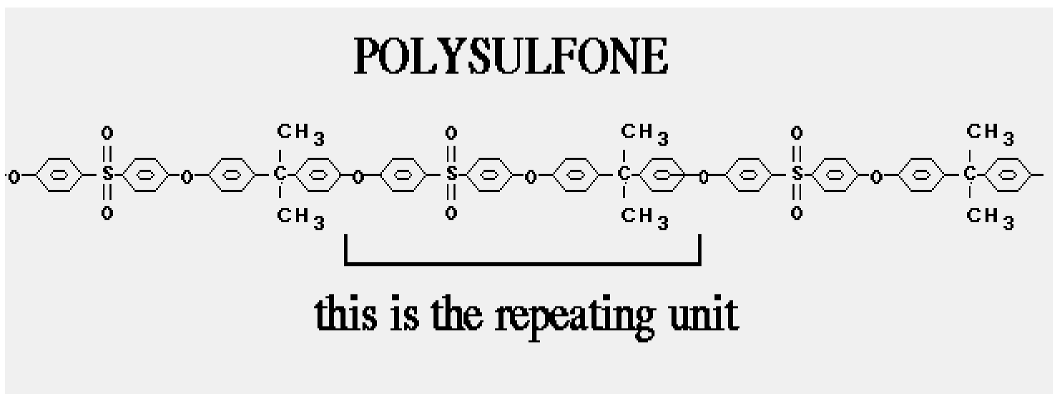

Figure 1.1 The Structure of Polysulfone

Source : E.J. Moon, J.W. Kim and C.K. Kim, 2006 (www.sciencedirect.com)

1.2 Objective of The Study

The aims of this study are to produce the membrane based on polysulfone and to determine the effects of cooling process on membrane's performance.

1.3 Scope of The Study

There are some scopes, which needed to achieve the objective for this study:

a) To develop the membrane with basic of polysulfone by using phase inversion of polymer technique.
b) To study the effects of cooling temperature on membrane performance (fluxes and rejection).
c) To decide the optimum temperature to produce an effective membrane.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Separation Process

Membrane as Figure 2.1 is a permeable or semi-permeable phase, often a thin polymeric solid, which restricts the motion of certain species. This added phase is essentially a barrier between the feed stream for separation and one product stream. This membrane or barrier controls the relative rates of transport of various species through itself and thus, as with all separations, gives one product depleted in certain components and a second product concentrated in these components. (K. Scott and R. Hughes, 1996)

Separation of membrane is the ability of a membrane to control the permeation rate of a chemical species through the membrane. In separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other components which shown as Figure 2.2 (Richard W. Baker, 2004)

In membrane separation process, the particle which is bigger than the other particle in a solution will be block and the small particle can pass through the filtration membrane which called permeate. The big particle, which blocked by the filtration membrane are called result of rejection or retentate.

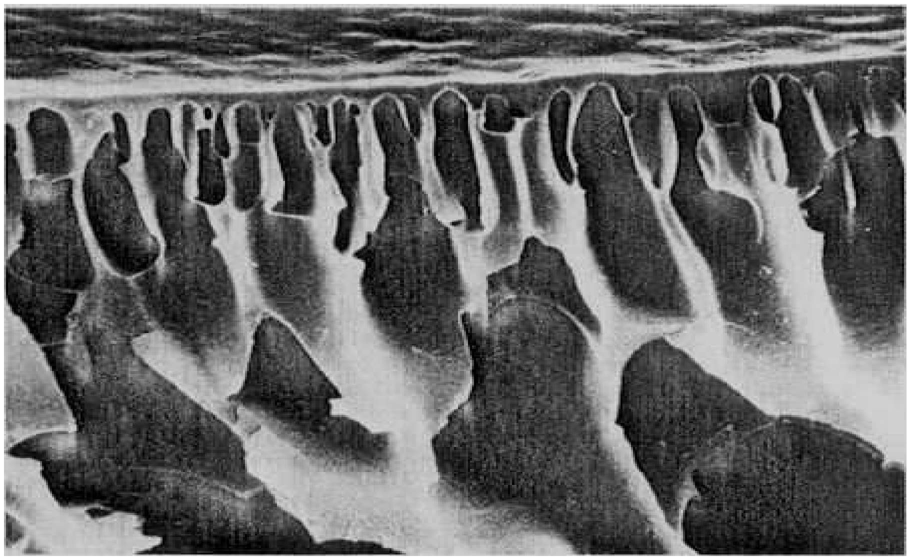

Figure 2.1 Membrane Structure

Source **:** E.J. Moon, J.W. Kim & C.K. Kim, 2006 (www.sciencedirect.com)

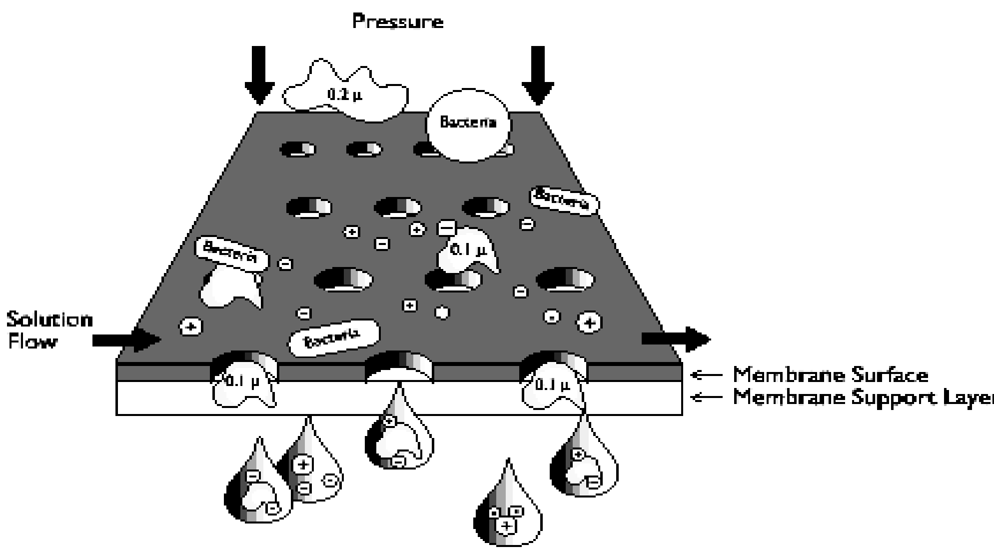

Figure 2.2 Membrane Separation Process

Source **:** E.J. Moon, J.W. Kim & C.K. Kim, 2006 (www.sciencedirect.com)

2.2 Concept of Membrane Separation

Figure 2.3 shows the basic concept of membrane separation. The solution (feed) will flow through the filtration membrane with pressure. During this process, the big particle of solution will be block and the small particle can pass through the membrane which called permeate. The big particle, which blocked by the filtration membrane are called result of rejection or retentate. (Christie John Geankoplis, 2003)

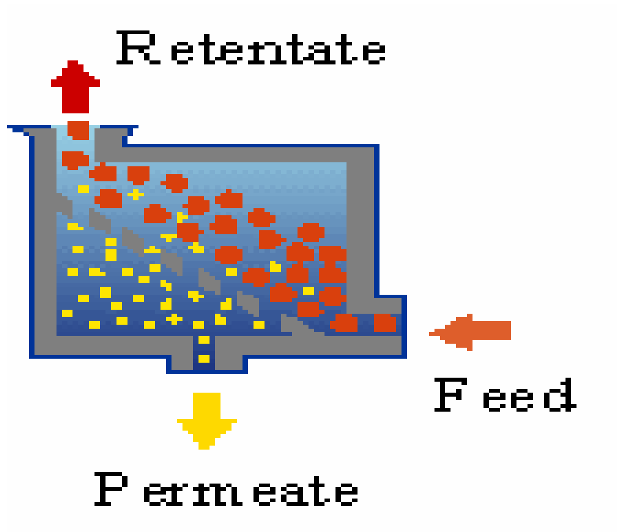

Figure 2.3 Basic Concept of Membrane Separation

Source **:** Lecture note of Membrane Technology subject, 2005

2.3 Types of Filtration Membrane

At this moment, there are many types of filtration membrane. Each of these types has different characteristics and use. Generally, there are 4 main types of filtration membrane. These are micro filtration membrane, ultra filtration membrane, reverse osmosis filtration membrane and nano filtration membrane as Figure 2.4.

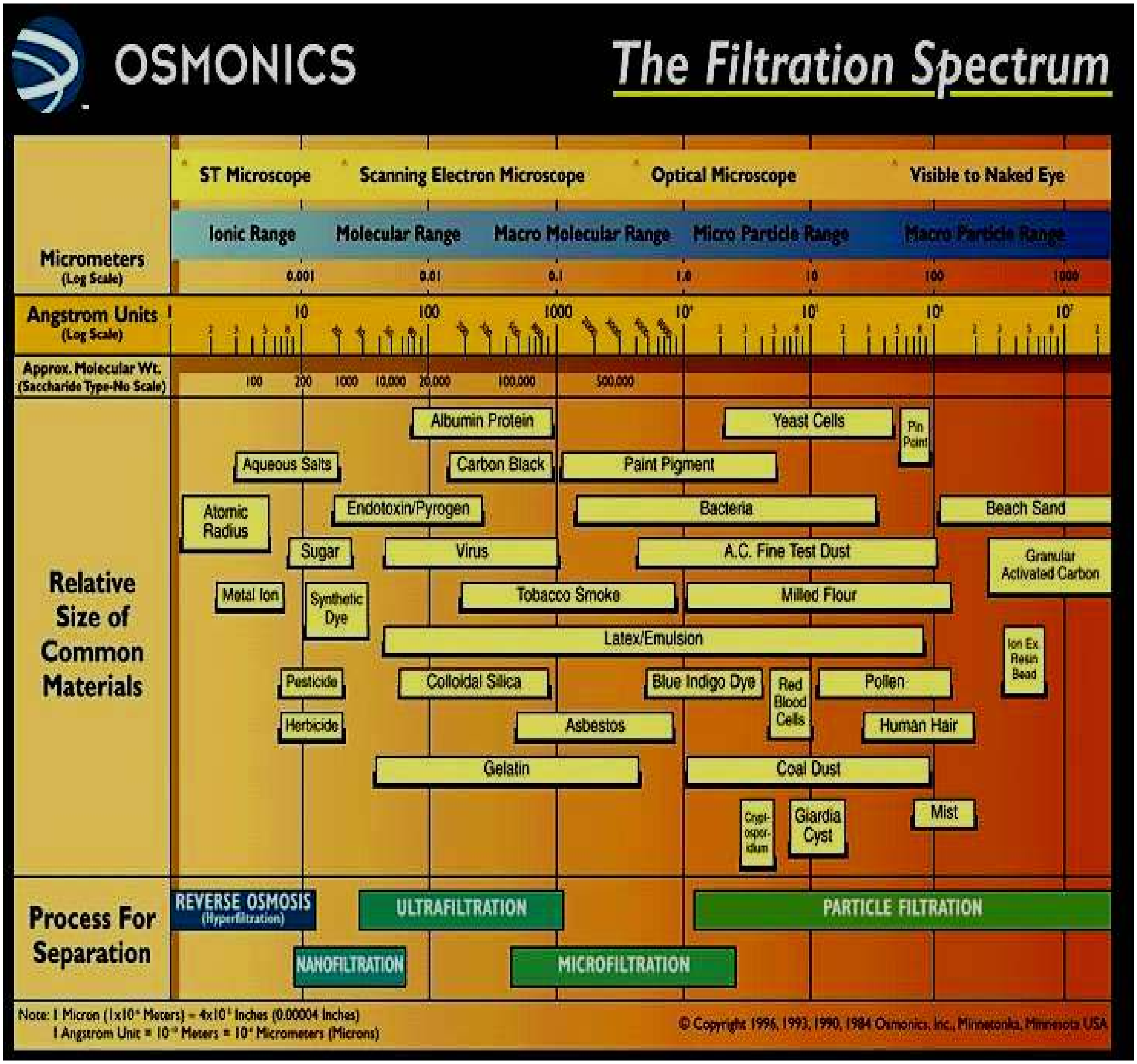

Figure 2.4 Filtration Spectrums for Four Main Basic Types of Filtration Membrane

Source: www.osmonics.com

2.3.1 Micro Filtration Membrane

Micro filtration membrane has the largest pore size among these 4 types of filtration membrane. Micro filtration membranes are considered to refer to membranes that have pore diameters from 0.2 µm (2,000 Å) to 10 µm (100,000 Å) and usually using the pressure from 100 kPa to 500 kPa or 1bar to 5 bar. Micro filtration membranes are used to filter suspended particulates, bacteria or large colloids from solutions.
(K. Scott and R. Hughes, 1996)

2.3.2 Ultra Filtration Membrane

Ultra filtration membranes can be used to filter dissolved macromolecules, such as proteins from solution. In this process, only molecule with smaller size can pass through the layer of membrane and other will retained. The ultra filtration membrane has small pore diameters size, between 0.001 µm (10Å) to 0.2 µm (2000Å). The pressure which used for ultra filtration membrane is between 100kPa to 800kPa (1 bar to 8 bars).
(K. Scott and R. Hughes, 1996)

2.3.3 Reverse Osmosis Filtration Membrane

Reverse osmosis is the process that can separate water from the solution. This process will occur when the water move from high concentration to low concentration by using the pressure. Usually, the pressure that used in reverse osmosis process is from 1MPa to 10MPa. Reverse osmosis filtration membrane has smaller pores size than ultra filtration membrane, between 0.0001 μm – 0.001 μm (1Å - 10Å) that has higher fluxes. Reverse osmosis membranes are used to separate dissolved microsolutes, such as salt from water. The principal application of reverse osmosis is the production of drinking water from brackish groundwater or the sea. (K. Scott and R. Hughes, 1996)

2.3.4 Nano Filtration Membrane

Nano filtration membrane is the latest membrane that is a very thin and it also has small pore size (10 nm to 200 nm). Usually, the pressure that used in nano filtration process is from 0.3 MPa to 3 MPa. This membrane is different than the other type of membranes because it consist charge either positive charge or negative charge. The charges are use for retaining the selected molecule. (K. Scott and R. Hughes, 1996)

2.4 Advantages and Disadvantages of Technology Membrane

2.4.1 Advantages

The technology of membrane separation has been developing to be the top of process separation. It is because there are a lot of advantages by using membrane for separation. The advantages of membrane are:

a) Save energy

The separation of membrane is used for saving energy because it is no change phases happen during the separation process. As we know, the change phase's process needs more and extra energy. So, in separation process using membrane, the energy can be saved and it seems to be more economical to be used by industrial.

b) Easy to operate

The separation process of membrane do not use large or complex machine, which have to move from a part of plant to another part of plant. It only consist some instrument that is very easy to handle and operate. This process can be use continuously.

c) Keep the product quality

The separation process by using membrane can be operating in room temperature. Thus, it no needs to increase or decrease the temperature during separation process. It is suitable for separate the product that will change easily with the changing of temperature. From that, it can keep the product quality. Membranes can also be "tailor-made" so that their properties can be adjusted to a specific separation task or based on costumer's need.

d) Environment friendly

This separation process of membrane is the technology, which not polluted the environment. In this process, the pH of solution or product will not change because it does not use any chemical matter. That's mean, it will not effect to the environment and some process, the separation product can be reused.

e) Save operation cost and place

The separation process of membrane is only using small instrument that is low cost and only need some place.

2.4.2 Disadvantages

a) Membrane fouling

In this separation process, the concentration polarization or membrane fouling maybe will occur. In this situation, the flux and the flow of filtration will decrease. Membrane fouling will give effect to the performance of membrane.

b) Short term used

The technology of membrane filtration cannot be used for long term because the membrane fouling will block the pores of membrane. Thus, it must be clean in short term to avoid clog.

2.5 Definition of Parameters in Filtration System

2.5.1 Fluxes

Volume fluxes can be defined as the volume of filtrate divided by the area of membrane and time. It can be state like the equation below:

$$Jv = P\,(\triangle p - \triangle \pi)\,/\,\ell$$

Where P is a constant of permeation, $\triangle p$ is hydrostatic pressure drop, $\triangle \pi$ is the different of osmosis pressure between flow in phase and the filtrate, and ℓ is the thickness of membrane.

During the polar concentrate at the control range, fluxes will be influence by the concentrate of solute, liquid flow rate and temperature. The fluxes will be linear increasing with log concentrate of solute, and modified by polar controllable. Basically, each membrane will achieve the maximum flow rate at different pressure and interchange flow rate.

2.5.2 Rejection

The performance of membrane also can be calculated by using the formula of rejection. The higher of rejection, it shows the most effective of the membrane. The rejection of membrane can be calculated by the formula as below:

$$\mathbf{R = (C_f - C_p) / C_f}$$
$$\mathbf{= 1 - (C_p / C_f)}$$

Where C_f is the concentration of solution in feed and C_p is the concentration of solution in permeate.

2.5.3 Polar Concentrate

Polar concentrate is a very usual case for all the membrane and it occur when using pressure. The solute will block on the surface of membrane with the concentration Cw. The solute that blocked on the surface of membrane will increase until the filter cake was form. The effect of this situation is the flux will decrease with the increasing of thickness of filter cake.

The polar concentrate allows the small increasing of the fluxes with the increasing of pressure until there is no increasing of fluxes. This situation is called limited fluxes.

2.5.4 Fouling

Fouling occur when the particles of solution are block on or inside the pore of the membrane. For example, when the concentration achieved a point where the solute sediment or thixotropic gel forms, this gel has its own resistance with the membrane. The fouling of membrane can be calculated by the formula as below:

$$\mathbf{Jv = P\,(\triangle \mathit{p} - \triangle\pi)\,/(\,Rm + Rc)}$$

Where Rm is the resistance of membrane to the moving of mass and Rc is the resistance of gel or filter cake. When Rc is higher than Rm, the changes of fluxes would not depends on membrane permeation.

The solutes which are inside the pore of membrane may cause by the factor of pore geometry / tortuosity or interaction of solute. When the fouling happen, the diameter of pore decrease. One of the effects for this mechanism is the fluxes decrease.

2.6 Polysulfone membrane

For this research, we will use polysulfone as the polymer to produce membrane. Polysulfone has many advantages compare to the other polymers. The sulfur atoms in polysulfone's structure make this polymer has high affinity to the water. These atoms also make this polymer quite polar and thus hydrophilic. As much of the fouling in water comes from hydrophobic organic particles, they are not attracted to the polysulfone. (Mathias Ulbricht, 2006)

Polysulfone also has the wide range of temperature and pH. It has good temperature stability allowing operation up to 80^{o}C, and will tolerate a pH from 1.5 to 12 for cleaning. (K. Scott and R. Hughes, 1996)

CHAPTER 3

CHEMICALS, EQUIPMENTS AND METHODOLOGY OF RESEARCH

3.1 Chemicals

3.1.1 N-Methyl-2-Pyrrolidone

N-Methyl-2-Pyrrolidone (NMP) is a powerful solvent with broad solubility for high chemical and thermal stability. NMP was supplied by Fluka Company in Switzerland. It is completely soluble with water at all temperatures and is soluble with most organic solvents. The characteristics of NMP are colorless hygroscopic liquid. The typical pH of NMP is 8.0 to 9.5, the boiling point is 202^0C and the melting point is -24^0C. (http://www.lyondell.com)

3.1.2 Polysulfone Powder

Polysulfone has many advantages compare to the other polymers. Polysulfone was supplied by BP Amoco Company in Singapore. The sulfur atoms in polysulfone's structure make this polymer has high affinity to the water. These atoms also make this polymer polar and thus hydrophilic. As much of the fouling in water comes from hydrophobic organic particles, they are not attracted to the polysulfone. Polysulfone also has the wide range of pH and temperature. (Mathias Ulbricht, 2006)

3.1.3 Polyvidone

Polyvidone (PVP) is used in membrane fabrication process to increase the quantity of pores in membrane. PVP was supplied by Fluka Company in Switzerland.

3.2 Equipments

3.2.1 Water Bath

The water bath (model BS-21) as shown in Figure 3.1 is used to dissolve the solvent into the water. This water bath was supplied by Lab Companion Company in Germany. After fabrication process, the polysulfone membrane will immerse into the water bath.

Figure 3.1 Water Bath model BS-21
Source: www.kochmembrane.com

3.2.2 Pressure Supply

For the pressure supply, nitrogen will be used with the rate pressure from $100kNm^{-2}$ until $500kNm^{-2}$. Pressure is important to make the flow of salt solution and color solution through the membrane faster.

3.2.3 Aluminium Foil

The Aluminium foil is use to cover the beaker, which contain the solution of polysulfone. There are many bubbles forms during mixing this solution and the bubbles take time to come out from the solution. The aluminium foil is use to avoid the solution influenced by environment.

3.2.4 Beaker Amicon

Beaker Amicon (model 8200) as shown in Figure 3.2 is an equipment, which will use for doing the analysis of membrane. The flux of membrane can be check by beaker Amicon where the filtration process of colour solution happens inside this beaker.

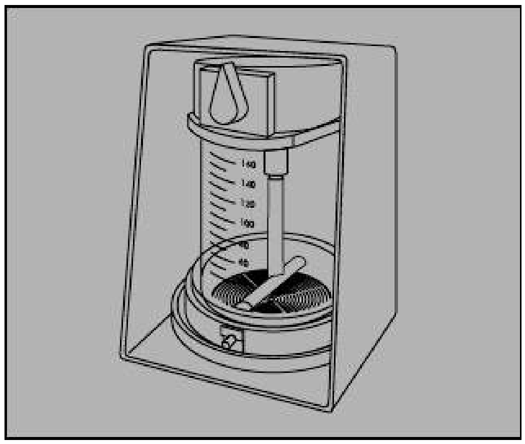

Figure 3.2 Beaker Amicon model 8200
Source: www.kochmembrane.com

3.2.5 Glass rod and a flat glass plate

A glass rod and a flat glass plate are used as the casting knife to fabricate the polysulfone membrane. A cellophane tape was coated constantly at both end of the rod until the thickness of the tape is around 0.05 cm and the membrane was rolled on a flat glass plate using the glass rod. This is to ensure the membrane that fabricated is flat and thin.

3.2.6 Hot Plate with Magnetic Stirrer

The hot plate with magnetic stirrer (model Erla) as shown in Figure 3.3 is use to stir the solution of polysulfone and polyvidone with the solvent (N-Methyl-2-pyrrolidone). In the same time, this equipment will supply the heat to help the solution of polysulfone and polyvidone dissolve into the solvent.

Figure 3.3 Hot Plate with Magnetic Stirrer
Source: www.kochmembrane.com

3.2.7 UV Spectrometer

UV Spectrometer model Hitachi U-1800 is equipment which will be used for doing the analysis of colour solution. The absorption in the colour solution is checking by UV Spectrometer using the wave length of light in colour solution. For this project, the wave length that we will use for doing the analysis of colour solution is 300 nm. Figure 3.4 show the UV Spectrometer.

Figure 3.4 UV Spectrometer model Hitachi U-1800
Source: www.kochmembrane.com

3.3 Fabrication Process of Membrane

The process for fabrication of polysulfone membrane is carried out in chemical laboratory. The process of fabrication as below:

1) A powder of polysulfone (18 wt %) and polyvidone (15 wt %) are dissolve into a solvent N- methyl-2- pyrrolidone (67 wt %).

2) Make sure both of polysulfone and polyvidone are mix well in the different beaker before dissolve into N- methyl-2- pyrrolidone.

3) Infuse the solution carefully into N- methyl-2- pyrrolidone and cover it with aluminium foil and then stir it with hot plat with magnetic stirrer until it mix well as Figure 3.5.

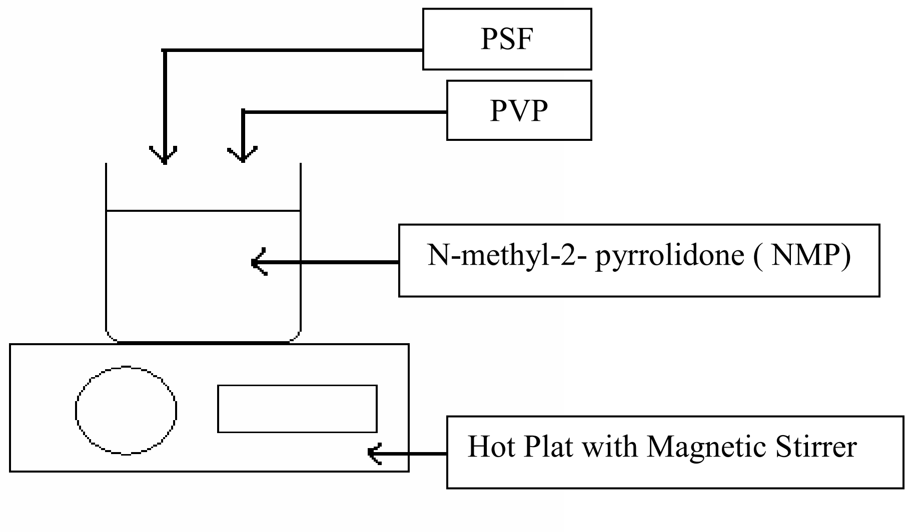

Figure 3.5 Stirring Process of Polysulfone and Polyvidone in NMP

4) A yellow solution like honey will form with a lot of bubble inside.

5) Let it a few hours in ambient condition until no bubble inside the solution as Figure 3.6.

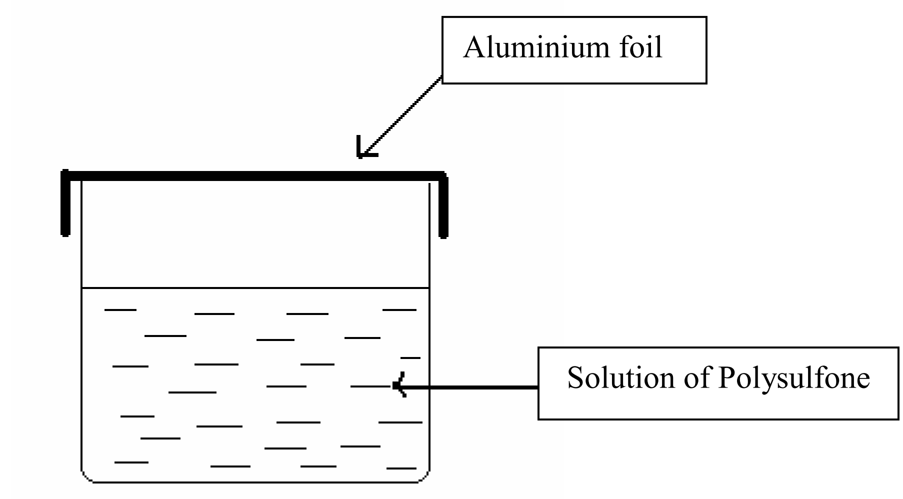

Figure 3.6 Polysulfone Solution Covered with Aluminum Foil

6) Then, the solution is poured onto a flat glass which lining with a piece of paper and flatten it with the glass rod as Figure 3.7 and Figure 3.8.

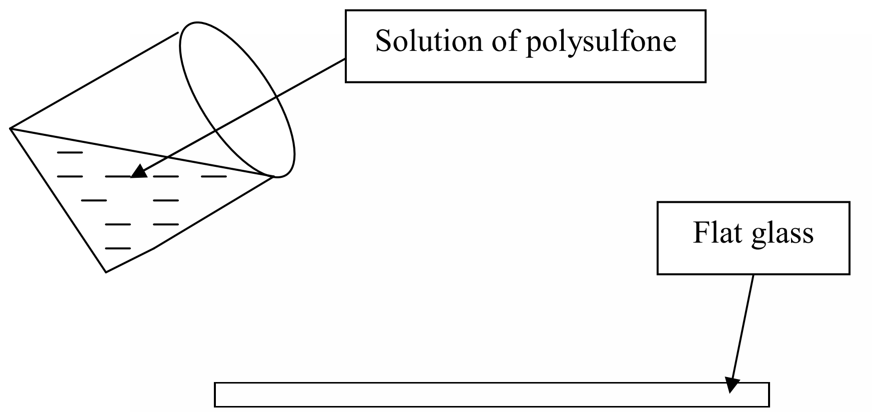

Figure 3.7 Polysulfone Solution Poured onto Flat Glass

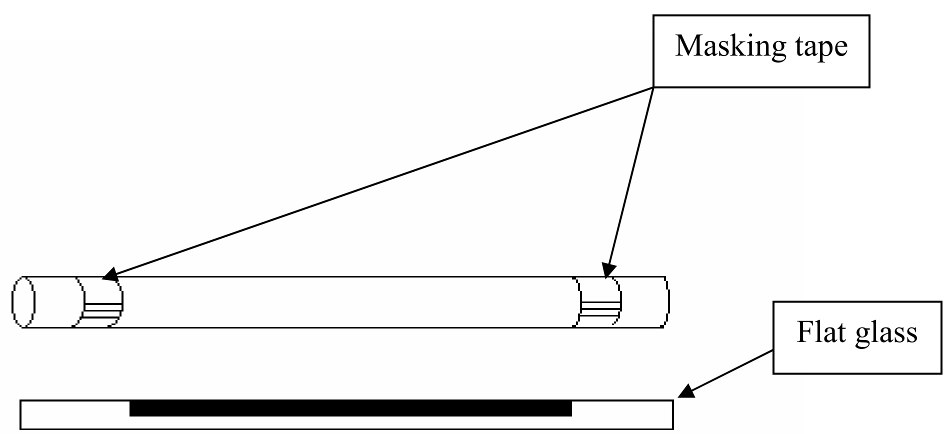

Figure 3.8 The Solution Flatten by Using Glass Rod

7) Then, with fast but careful immerse the flat glass with the liquid film into water bath with the temperature of 20 °C. The liquid film will change from transparent to be polysulfone membrane in white colour because the sedimentation of polysulfone.

8) Left it for a few minutes, the liquid film will automatically take off from flat glass as Figure 3.9.

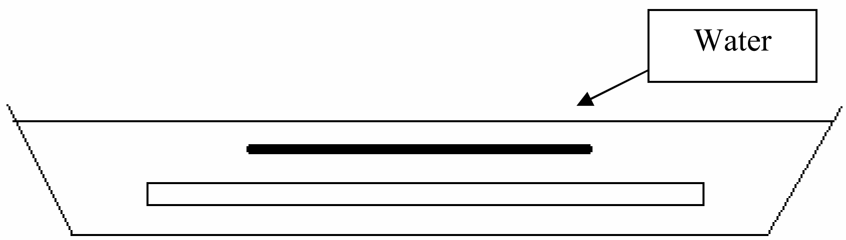

Figure 3.9 The Liquid Film Take Off From Flat Glass

9) Take the membrane and wash carefully with distillation water to take off the plentiful solvent. Then, keep it in a water bath that consist distillation water in ambient temperature.

10) Repeat step no. 6 until step no. 9 with the same solution of polysulfone, but change the temperature in water bath to 15°C and 12°C.

11) These polysulfone membranes have to keep in water at ambient temperature.

12) The polysulfone solution should be kept in refrigerator when do not use.