

**Gas Permeation through Polysulfone-Polyimide (PSF-PI) Miscible Blend  
Membrane**

by

Nur Ain Binti Ahmad Nazar

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

JUNE 2010

Universiti Teknologi PETRONAS  
Bandar Sri Iskandar  
31750 Tronoh  
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

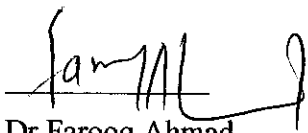
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A project dissertation submitted to the  
Chemical Engineering Programme  
Universiti Teknologi PETRONAS  
in partial fulfillment of the requirement for the  
BACHELOR OF ENGINEERING (HONS)  
(CHEMICAL ENGINEERING)

Approved by,



Dr Farooq Ahmad

Supervisor FYP Jan 2010

UNIVERSITI TEKNOLOGI PETRONAS  
TRONOH, PERAK  
JUNE 2010

## **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



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NUR AIN BINTI AHMAD NAZAR

## ABSTRACT

Gas permeation through polysulfone-polyimide (PSF-PI) miscible blend membranes were studied through the permeability of Carbon Dioxide (CO<sub>2</sub>) and Methane (CH<sub>4</sub>) gas. The asymmetric polymer blend membranes were fabricated with varying weight percentage ratios (100:0, 95:5, 90:10, 85:15, 80:20) of polysulfone and polyimide respectively, by a solution cast method or in other words, by wet phase inversion method. The solvents that will be used for the study are N-methyl Pyrrolidone (NMP) and Dichloromethane (DCM) and the membranes will be subjected to immersion in the Ethanol bath (EtOH). Apart from studying the effects of solvents to the membrane, cloud point determinations were also studied as gave a better view on the point where the dope solution phase separates. Different parameters during fabrication will produce different morphologies of the membranes, which includes the formation of microvoids, porosity, skin layer type and structure of the membrane. These were observed through the SEM Test, Scanning Electron Microscopy, where the photographs of the membrane on molecular level have been obtained. SEM gave a better insight on the membrane structure and homogeneity of the membrane casting solution. The permeability of CO<sub>2</sub> and CH<sub>4</sub> across the membrane will subject to the morphologies of the membranes produced from the research. The effects of varying parameters during the fabrication stage will affect the permeability and selectivity of CO<sub>2</sub> across the membrane. The compatibility of the membranes was also studied in parallel with the cloud point determination mentioned earlier. For polymers, polymer blends may be in homogenous form or heterogeneous form. The homogeneity of the membranes were studied through the FTIR tests (Fourier Transform Infrared Spectroscopy) and UTM (Universal Testing Machine). The PSF-PI combination will show a homogeneous miscible blend, where this compatibility is essential in a new blend polymer material, suitable for the preparation of gas separation membranes. Such membranes will produce combined satisfactory gas permeation properties, reduced cost and advanced resistance (harsh to chemicals, significant temperature conditions, improved tolerance to plasticizing gases).

Experimental results show that by increasing the amount of Polyimide (PI) in the Polysulfone casting solution, the properties of the membranes were improved. The selectivity of CO<sub>2</sub>/CH<sub>4</sub> was observed to be increasing with the addition of PI in the casting solution. From the SEM tests, it was observed that the maximum amount of PI that can be added in the casting solution is 20% by weight of the total polymer weight percentage. At 20% of PI, it is observed that small amounts (minute) PI polymer is scattered and suspended on the surface of the membrane. Beyond 20%, more PI will be suspended at the surface of the membrane thus, this will be considered a non-homogenous mixing.

The effects of solvents were done to study the effects and morphology of the membranes. It was observed that for constant polymer weight percentage, varying the amount of solvents between 50% DCM/ 50% NMP with 80% DCM/20% NMP shows significant difference. For membranes with 80% DCM/20% NMP solvent composition, distinct skin layers were observed compared to the 50% DCM/ 50% NMP. The skin layer is the one responsible for the gas separation system, while the porous part below the skin serves as the support for the membrane. Thick skin layer will improve the gas selectivity of the membranes. From experimental data, it was observed that for membranes with constant polymer weight, with 80% DCM/20% NMP solvent composition shows improved selectivity compared to 50% DCM/ 50% NMP membranes. In terms of mechanical strength, for 80% PSF and 20% PI with 80% DCM/20% NMP, the maximum load for the membrane is observed to reach up to 35.83N. On the other hand, 80% PSF and 20% PI with 50% DCM/ 50% NMP shown a maximum load of 22.18N.

In conclusion, asymmetric PSF/PI membranes produced in this work show promising performance and have high potential to be used for CO<sub>2</sub>/CH<sub>4</sub> separation.

## **ACKNOWLEDGEMENT**

First and foremost, I would like to give my utmost gratitude to ALLAH SWT, the almighty God, for the guidance, wisdom and strength that kept me going in completing this research project.

I want to forward my deepest gratitude and special thanks to my supervisor, Dr Farooq Ahmad for giving me the guidance and support throughout this research project. His patience and constant encouragement has steered me to the right direction in completing this project. I would also want to thank PhD student who is under the supervision of Dr Farooq Ahmad, Sikandar Rafiq for all the guidance and criticism.

I am greatly indebted to the technologists from UTP, Mr. Jailani (Chemical Department), Ms. Hasniza (Chemical Department), Mr. Faizal (Chemical Department), Mr. Irwan (Mechanical Department), Mr. Faisal (Mechanical Department), Mr. Omar (Mechanical Department) and all other technologists who have helped me to conduct the tests for the research project.

I would like to extend my gratitude to my family and friends for their open-mindedness and endless support. Without their support, I may not have completed this research project successfully.

Finally yet importantly, I would like to extend an utmost thank you to those who had assisted directly or indirectly throughout this research project. All the concerns and compassions, throughout the 2 semesters of research period, were highly appreciated.

Nur Ain Binti Ahmad Nazar

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## ABBREVIATIONS

Carbon Dioxide	CO <sub>2</sub>
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>
Diisopropanolamine	DIIPA
Dimethyl Ethanolamine	DMEA
Energy Information Administration	EIA
Ethanol	EtOH
Ferum trichloride	FeCl <sub>3</sub>
Fourier Transform Infrared Spectroscopy	FTIR
Helium	He
Hydrogen	H <sub>2</sub>
Hydrogen Sulfide	H <sub>2</sub> S
Methane	CH <sub>4</sub>
Methyl Ethanolamine	MEA
Nitrogen	N <sub>2</sub>
N-Methyl Pyrrolidone	NMP
Oxygen	O <sub>2</sub>
Pressure Swing Adsorption	PSA
Polycarbonate	PC
Polyethersulfone	PES
Polyimide	PI
Polysulfone	PSF
Scanning Electron Microscopy	SEM
Thermal Swing Adsorption	TSA
Universal Testing Machine	UTM

## NOMENCLATURE

A	Membrane area	(cm <sup>2</sup> )
$\alpha_{i/j}$	Ideal selectivity of component <i>i</i> over component <i>j</i>	(-)
D	Diffusivity Coefficient	(cm <sup>2</sup> /s)
$\delta$	Overall solubility parameter	(J <sup>1/2</sup> /cm <sup>3/2</sup> )
$\delta_{\text{mix}}$	Overall solubility parameter of solvent mixtures	(J <sup>1/2</sup> /cm <sup>3/2</sup> )
$\delta_d$	Solubility parameter for dispersive component	(J <sup>1/2</sup> /cm <sup>3/2</sup> )
$\delta_p$	Solubility parameter for polar component	(J <sup>1/2</sup> /cm <sup>3/2</sup> )
$\delta_h$	Solubility parameter for hydrogen bonding component	(J <sup>1/2</sup> /cm <sup>3/2</sup> )
$\Delta\delta$	Solubility parameter difference	(J <sup>1/2</sup> /cm <sup>3/2</sup> )
( $\Delta G$ ) <sub>m</sub>	Change of Gibbs free energy of mixing	(J/mol)
( $\Delta H$ ) <sub>m</sub>	Change of enthalpy of mixing	(J/mol)
( $\Delta S$ ) <sub>m</sub>	Change of entropy of mixing	(J/mol.K)
$\Delta E$	Energy change upon isothermal vaporization	(J/mole)
$\varepsilon$	Porosity	(%)
$E_h$	Molar attraction constant for hydrogen bonding	(J/mol)
F	Molar attraction constant	(J <sup>1/2</sup> /cm <sup>1/2</sup> .mol)
$F_d$	Molar attraction constant for dispersive component	(J <sup>1/2</sup> .cm <sup>3/2</sup> /mol)
$F_p$	Molar attraction constant for polar component	(J <sup>1/2</sup> .cm <sup>3/2</sup> /mol)
$J_i$	Flux of component <i>I</i>	(g/cm <sup>2</sup> .s)
<i>l</i>	Membrane thickness	(cm)
p	Pressure	(bar)
P	Permeability	(cm <sup>3</sup> (STP).cm/cm <sup>2</sup> .s.cmHg)
P/l	Permeance	(cm <sup>3</sup> (STP)/cm <sup>2</sup> .s.cmHg)
$\rho$	Density	(g/cm <sup>3</sup> )
Q	Volumetric flow rate	(cm <sup>3</sup> /s)
Q <sub>stp</sub>	Volumetric flow rate at standard temperature and pressure	(cm <sup>3</sup> (STP)/s)
S	Henry's law solubility coefficient	(cm <sup>3</sup> (STP)/cm <sup>3</sup> .atm)
t	Time	(s)

T	Temperature	(K)
V	Molar volume	(cm <sup>3</sup> /mol)
$\phi$	Volume fraction	(-)

# CHAPTER 1

## INRODUCTION

### 1.1. Problem Statement

Natural gas is a vital source for energy supply industry, whereby it is the safest, cleanest and most useful energy among all. Wide range of applications of natural gas such as feedstock for chemical plant or as fuel in power generation plant to being the gas which is used in a human daily activities, have made the demands for natural gas increase from year to year.

Malaysia, being one of the natural gas producers in the world, contains 75 trillion cubic feet of proven natural gas reserves, according to *Energy Information Administration (EIA)*. The consumption and production of natural gas are summarized in the following figure.

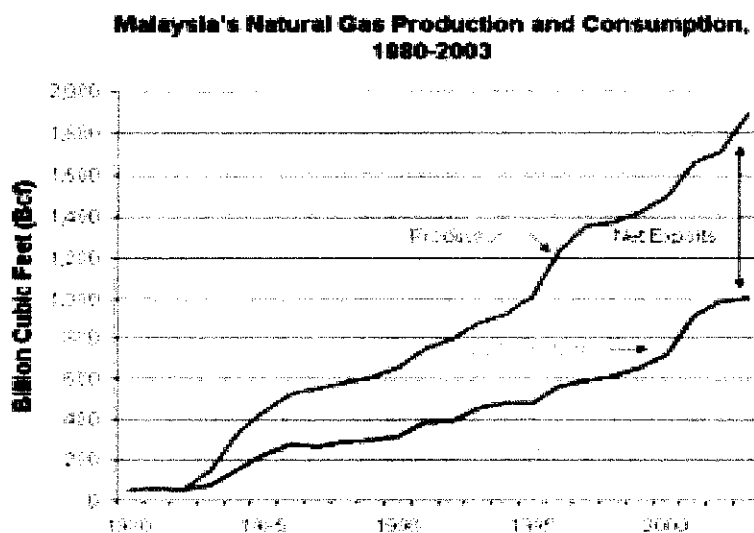


Figure 1: Malaysia's Natural Gas Production and Consumption 1980-2003 (courtesy of Energy Information Administration , January 2007)



Thus, there is a need for the natural gas industry to increase in production of natural gas to cater the need of the growing technological world. The compositions of natural gas differ from one source to the other. Natural gas consist , mainly Methane ( $\text{CH}_4$ ), being the major component in the natural gas, constituting of 75-90%, significant amount of Ethane, Propane, Butane and other higher hydrocarbons, including impurities such as Carbon Dioxide,  $\text{CO}_2$ , Hydrogen Sulfide,  $\text{H}_2\text{S}$ , heavy hydrocarbons such as mercaptans and water vapor,  $\text{H}_2\text{O}$ . All of the impurities need to be separated (Natural Gas Purification Process) in order for the natural gas to meet the specifications for the pipes or customers. In addition, the impurities needed to be removed so as to increase the gross heating values of natural gas.  $\text{CO}_2$ , specifically, needs to be in the range of 1-3 mole % of concentration. The gross heating values for natural gas typically has to be approximately 950 Btu/scf (min) while the total sulfur content must be below than 1.5 grain/100scf. In our study,  $\text{CO}_2$  and Methane ( $\text{CH}_4$ ), will the main concern of the permeability aspects.

$\text{CO}_2$ , in the presence of water, can be corrosive, thus, it is a need to remove it from the system as much as possible. There are various ways available in the industry of removing  $\text{CO}_2$  from natural gas. Some of them are Amine absorption, Adsorption process and the newly developed Membrane Technology. However, some of these technologies have limitations in the purification process of natural gas.

Absorption using amine absorbents has proven its way in separating carbon dioxide from the natural gas stream. Some of the absorbents are Methyl Ethanolamine (MEA), Dimethyl Ethanolamine, (MDEA) and Diisopropanolamine (DIPA). The removal of carbon dioxide using amines is carried out at elevated pressures and lower temperature. Although amine absorption separates carbon dioxide efficiently, they also offer some limitations. Tertiary amine absorbents can form foam in the system, thus reduces the efficiency of the absorption process. In addition, amine absorbents can be easily

contaminated through the presence of heat stable salts, degradation of amine absorbents, injection chemicals, other hydrocarbons and presence of particulate. The contaminants formed can be corrosive and cannot be regenerated back.

For the adsorption process on the other hand, utilizing Pressure Swing Adsorption (PSA) and Thermal Swing Adsorption (TSA) have also been used in the industry for the purification process of natural gas. Carbon dioxide is absorbed onto the absorbent until it is fully saturated. After saturation, the bed will then be regenerated by releasing the absorbed carbon dioxide. Again, although adsorption process provides better efficiency on the separation of carbon dioxide, they also offer some disadvantages. TSA is operated at a low temperature, after saturation, sufficient energy must be supplied due to the fact that the regeneration process of TSA takes place at an elevated temperature. This can lead to heat loss during the regeneration process and thus would increase the cost for energy supply. In addition, the regeneration process for TSA is very slow. PSA on the other hand, the cycle for regeneration is very short and desirable, but the bed has to be operated at an elevated pressure for the adsorption process to occur. This would increase the operating costs of the purification process.

Membrane technology has been given crucial attention for the past decade because it offers additional advantage compared to the conventional methods of CO<sub>2</sub> separation. Membranes are environmental friendly, have low energy consumption, space efficient and are lower in capital costs. Although it has some promising advantages, membrane also offers some disadvantages in low stability for long term usage, and is highly sensible to the presence of impurities other than CO<sub>2</sub> and H<sub>2</sub>S. In addition, single stage separation is not efficient enough, as the purification process needs several stages at least. But, overall, membrane technology has been viewed to have the potential in the future natural gas purification. Thus, this serves the purpose on doing research

on the membrane technology so as to improve the efficiency of the membranes that have already been applied in the industry.

Polymeric membranes have attracted major industries in using it as separation media, as polymeric membranes provide significant separation for industrial processes. Though many of the researches have developed good performance membrane, the research in achieving membranes with specific permeability characteristics has been given crucial attention. Membrane technologies have been adopted to perform separation in the industries over the past decades. Gas separations via membranes are one of the most exciting and newly develop processes for the separations, which have evolved in many years. In addition, through several breakthroughs in the advancement of the membrane technology, membranes applications have come to compete with more established technologies. Membranes are often used as a separating media, which has become one of the most important recent developments in process engineering and environmental protection. It has been forecast that the future promises to be equally exciting as new membrane materials, processes and innovations make their way to the market place. According to Mahanim (2005), "The development of new applications using synthetic membrane requires polymers with outstanding properties. Polymer materials not only have to resist acids, bases, oxidants or reductants, high pressures and high temperatures, but also have appropriate chemical properties so as to lead to high flux and high selectivity membranes for the foreseen applications". In the industry, lack of membranes with high flux and high selectivity has caused the technology to be operated at a minimum. During fabrication, crucial attention is needed to be given on the membrane fabrication and formation as it will affect the morphology of the membrane. Therefore, in order to produce membranes with desired characteristics, quality and performance, the parameters affecting the transport and morphology of the membrane are crucial to be studied and understood. However, these are not accessible through literature alone. In literature, there is no study done on the effects of varying the amount PSF and PI

with regards to NMP and DCM as the solvent and EtOH as the non solvent. Thus it is a need to study the basic of membrane formation and relate its performance through industrial and engineering perspective. This project focuses mainly on the studies of Gas Permeation through Polysulfone-Polyimide (PSF-PI) Miscible Blend Membrane.

## **1.2. Background of Study**

Polymeric membranes are commonly used in our daily life routines. The strength, reproducibility and suitability that these polymers offer have made it well known in the science and technology industry. The membrane technology is an advanced method in the separation of gases or filtration, as well as in the protective coating of a particular material. Polysulfone has been a traditional polymer material used in the fabrication of reverse osmosis or ultrafiltration asymmetric membranes for many years. Polysulfone has satisfactory gas permeabilities and acceptable permselectivities, which it can be used with highly sorbing plasticizing agents. With those properties, and relatively low cost, polysulfone polymers are often used as standard membrane materials. In the development of polymeric materials, the need for temperature and chemical resistant polymers led to the birth or the development of advanced engineering polymers such as various types of polyimides. Polyimides show an improved correlation between permeability and selectivity, excellent mechanical properties, high temperature resistance and improved chemical resistance in the gas separation process membranes.

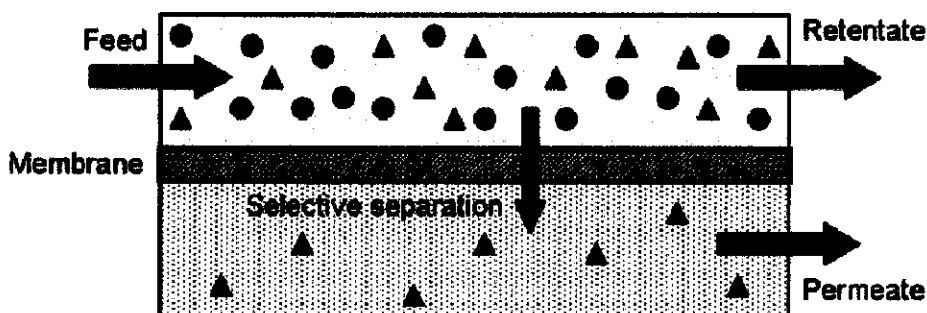


Figure 2: Schematic diagram of membrane gas separation

In order to produce a membrane with a combination of the two polymers, the solubility ‘compatibility’ of the two polymers must be analyzed first, to ensure that the membrane solution that would be produced will be a homogeneous one. Most polymers do not mix or blend together due to the fact that there is entropy resistance between them. The term ‘like-dissolve-like’ is used to study the miscibility of the two polymers. The homogeneity of the polymers would be seen as having one transition temperature, in which they did not show the two transition temperatures upon mixing. In addition, the product combination of the two would produce an excellent characteristics compared to the individual ones. From literature, it has been seen that polysulfone and polyimide really mix well, forming a one phase solution. Upon mixing, it does not phase separate.

*“Preparation, testing and examination of gas separation polymer membranes prepared from mixtures of the polysulfone Udel P-1700 and the aromatic polyimide Matrimid 5218. Polysulfone and polyimide proved to be completely miscible polymers as confirmed from optical microscopy, glass transition temperatures and spectroscopy analyses of the prepared mixtures. The complete miscibility permits the preparation of symmetric and asymmetric blend membranes in any proportion (1-99% wt) of polysulfone and polyimide. Permeability measurements for various gases of industrial importance (such as*

*carbon dioxide and monoxide, hydrogen, oxygen, nitrogen etc.) through polysulfone-polyimide blend membranes showed significant permeability improvements, compared to pure polyimides, with a minor change in their selectivity. Blend membranes were considerably more resistant to the plasticization phenomenon compared with those of pure polyimides. Therefore, the use of polysulfone-polyimide polymer blends for the preparation of gas separation membranes offers a new, economic, high performance technical solution for application in the separation of industrial gases, with the typical compositions of gaseous mixtures encountered in the recovery of hydrogen from refinery gases, the separation of hydrogen from ammonia synthesis purge gases, the separation of gaseous products in coal, lignite and other solid fuel gasification processes, the separation of carbon dioxide from the exhaust gases of power generating stations using solid, liquid, gas or biomass as fuels, air separation for the production of nitrogen and/or oxygen enriched streams etc.”*

**(source:** New polymer membranes prepared from polysulfone and polyimide blends for the separation of industrial gas mixtures, freepatentsonline)

The permeability of the membranes is directly related with the free volume present in the polymer matrix. For ideal gases, the permeability is related to the gas permeation rate through the membrane ( $Q$ ), the surface area of the membrane ( $A$ ), the thickness of the membrane ( $l$ ) and the driving force for separation, the pressure difference across the membrane ( $\Delta p$ ).

According to Scholes (1997), polymeric membranes are generally non-porous, and therefore gas permeation through them is described by the solution-diffusion mechanism. This is based on the solubility of specific gases within the membrane and their diffusion through the dense membrane matrix. Hence, separation is not just diffusion dependent but also reliant on the physical-chemical interaction between the various gas species and the polymer, which determines the amount of gas that can accumulate in the membrane polymeric matrix.

### **1.3. Objectives**

- To fabricate the Polysulfone-Polyimide (PSF-PI) membrane at various weight percentage using Wet Phase Inversion Process.
- To investigate the effects of varying weight percent of solvents in the casting solution subjected to ethanol (non-solvent).
- To study the cloud point (coagulation value) for each of the membranes.
- To evaluate the performance of the asymmetric Polysulfone-Polyimide (PSF-PI) miscible blend membranes in terms of CO<sub>2</sub> permeability.
- To obtain the morphology and performance data for the phase inversion miscible blend membranes.

### **1.4. Scope of Study**

The scope of this project is divided into the following sections:

#### **1.4.1 Cloud Point (Coagulation Value) Determination**

The cloud point (coagulation value) will be determined and studied for each of the casting solution. The dope solution, consists of a blend of polysulfone-polyimide (PSf-PI), mixed with varying weight percent of solvents, N-Methyl Pyrrolidone (NMP) and Dichloromethane (DCM) will be titrated using the non-solvent for the system, which is ethanol (EtOH) until turbidity or cloudy point has been achieved. The cloud point (coagulation value) will indicate the tolerance on the homogeneous dope solution to the addition of the non-solvent (coagulant). The cloud point will be used later to produce the binodul curve for the blend membrane system.

#### **1.4.2 Fabrication of Polysulfone-Polyimide (PSF-PI) Miscible Blend Membrane**

Polysulfone (PSF) and Polyimide (PI) will be used as the membrane forming material during the fabrication. N-Methyl Pyrrolidone (NMP) and Dichloromethane were selected as the main solvent for the system, while Ethanol (EtOH) will be the coagulant. Fabrication of the membrane would be carried out using the wet phase inversion process, whereby the parameters of weight percentage of polymers in the membrane and solvents will be varied throughout the experiments.

#### **1.4.3 Characterization of Polysulfone-Polyimide (PSF-PI) Miscible Blend Membrane**

Characterization of the miscible blend membranes will be carried using Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Universal Testing Machine (UTM). SEM will be used to observe the morphology of the membranes while FTIR would give the dynamics of the membranes. In addition, the miscible blend membranes will be subjected to UTM, in order to determine the tensile properties of the membranes.

#### **1.4.4 Evaluation of the Polysulfone-Polyimide (PSF-PI) Miscible Blend Membrane**

The performance of the asymmetric Polysulfone-Polyimide (PSF-PI) miscible blend membranes will be evaluated through the CO<sub>2</sub> permeability by using Bubble-Flow meter Permeation Cell.



Thus from the above project background, problem statement, objectives and scopes, it can be summarized that this project would be an excellent base for the application of the technical knowledge and ability of the student. This project governs the separation process, transport phenomena, chemical engineering thermodynamics and including polymer process engineering. FYP were done continuously throughout the first and second semester, thus give ample of time for the completion of the project. But due to time constraints of electrical supply to the laboratory blocks, the experiment would be proceed with only one non solvent that is Ethanol.

## **CHAPTER 2**

### **LITERATURE REVIEW**

Membrane is defined as selective barrier between two phases that has the ability to transport one component that the other (Mulder, 1996). A membrane separation system separates an influent stream into two effluent streams known as the permeate and the concentrate .The permeate is the portion of the fluid that has passed through the semipermeable membrane, whereas the concentrate stream contains the constituents that have been rejected by the membrane. (Sastre, et al., 2009)

According to Mark (1990)

Membranes are used on large scale to produce potable water from the sea by reverse osmosis, to clean industrial effluents and recover valuable constituents by electrodialysis, to fractionate macromolecular solutions in the food and drug industry by ultrafiltration, to remove urea and other toxins from the blood stream by dialysis in an artificial kidney, and to release drugs such as scopolamin, nitroglycerine, etc. at a predetermined rate in medical treatment.

Membrane morphologies can be divided into symmetric and asymmetric membrane (Mulder, 1996). Symmetric membrane refers to the membranes that have essentially same structure and transport properties throughout its thickness (Koros, et al., 1996). On the other hand, asymmetric membrane is a membrane constituted of two or more structural planes of non-identical morphologies (Koros, et al., 1996)

Iqbal (2007) says that basically, membrane morphologies can be classified as shown in Figure 3 below.

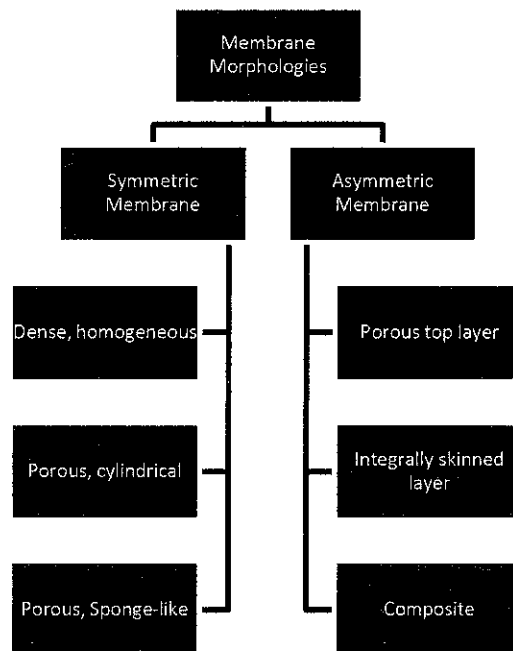


Figure 3: Classification of the typical membrane morphologies

Iqbal (2007) points out that morphology of membranes play a major role in determining the performance and application of membrane. High total flux and selectivity is highly desired. Symmetric membrane has advantages in term of selectivity but it is slow in total flux of product. In order to enhance total flux with sufficient selectivity, asymmetric membrane is preferred. Therefore, asymmetric membrane has been used commercially at various applications in the industry.

Phase separation is a process in which an initially homogeneous casting solution becomes thermodynamically unstable due to external effects (Yip and McHugh, 2006). Keith (1998) points out that the Phase Inversion methods in the fabrication of polymer membranes are divided as per listed in the table below (p.208):

Table 1: Phase Inversion Membrane Preparation

Precipitation Method	Principle
Solvent Evaporation	Evaporation on inert support or porous substrate in an inert atmosphere. Produces dense membranes (homogenous).
Vapor Phase	Casting of a film into a vapor phase of solvent and nonsolvent. Membrane formation is due to penetration of nonsolvent into cast film, producing a porous membrane with no top layer.
Controlled Evaporation	Polymer is dissolved in a solvent/nonsolvent mixture. Evaporation of solvent during evaporation shifts the composition to a higher nonsolvent and polymer content. This leads to polymer precipitation and the formation of a skin on the membrane.
Thermal Precipitation	A polymer and solvent solution is cooled to enable phase separation. Evaporation of solvent can allow the formation of a skinned membrane. Frequently used to prepare microfiltration membranes.
Immersion	A solution of polymers plus solvent is cast (on a support) and immersed in a coagulation bath. Precipitation occurs by the exchange of solvent and non-solvent in the coagulation bath.

According to Keith (1998), Phase Inversion process is a process whereby a polymer solution inverts into a swollen three-dimensional macromolecular complex or gel.

Porous membranes are produced from a two or three component dope mixture containing polymer, solvent and nonsolvent. Keith (1998) stated that the membrane performance characteristics (flux, selectivity) of phase inversion membranes depend on many parameters. Some of them are as per listed blow.

- Polymer Concentration
- Evaporation time before immersion
- Humidity
- Temperature
- Composition of casting solution
- Coagulation bath composition and condition

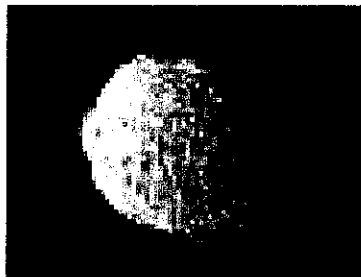


Figure 4: Polyimide Resin

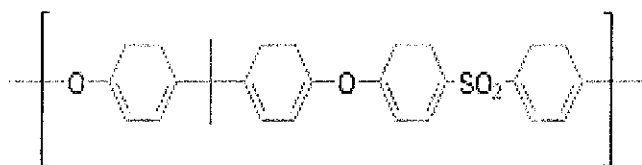


Figure 5: Polysulfone chemical formula

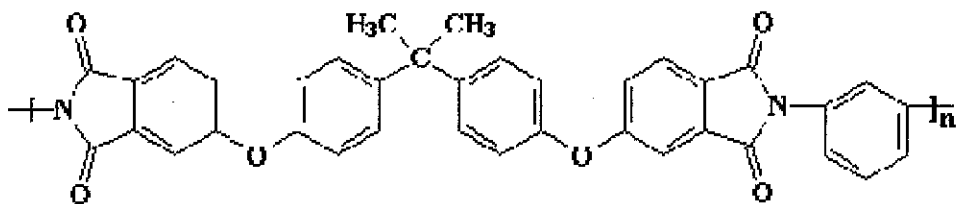


Figure 6: Polyimide chemical formula

According to Acharya et al, (2007), permeability is the rate at which permeate traverse through the membranes and based on the solution diffusion model. The permeability is often expressed in barrier, in which 1 barrier =  $10^{-10}$  cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cm-Hg. The permeability of the membrane is the product of diffusivity and solubility coefficients. The permeability can be related through the Fick's law.

Several studies have been done in order to study the morphology of the polymeric/ synthetic membranes. Researchers Acharya et. al. (2007) studied the Hydrogen separation in doped and blend polymer membranes. Polymer blend membranes of PSF and PC (polycarbonate) in different concentration ratios (9:1, 3:1 and 1:1) were prepared by a solution cast method. Ferum trichloride (FeCl<sub>3</sub>) doped polycarbonate membranes in different concentration ratios (10, 20, and 30) were also prepared using the same technique. For the membranes, the gas permeability of H<sub>2</sub> and CO<sub>2</sub> were observed. From their research, they found out that permeability of the membranes was increased with an increase in etching time. The rapid variation in permeability was found after a critical etching time. For the blend membranes specifically, it was observed that as the concentration of PC in PSF increases, the permeability of both of the studied gases increases. The permselectivity of hydrogen over carbon dioxide was calculated to be 2.52 for pure PSF and it reduces as the concentration of PC in PSF increases.

The PC and PSF are glassy polymers having a common ring structure (bisphenol-A) in their repeating unit. The PSF has additional ring structure and -SO<sub>2</sub> group in its repeating unit which leads to the relatively higher strength. The blend of these materials forms some new bonds. The PC in PSF alters the free volume properties of PSF that provides for relatively fast permeation. Due to the common ring structure it is expected that they form a miscible blend.

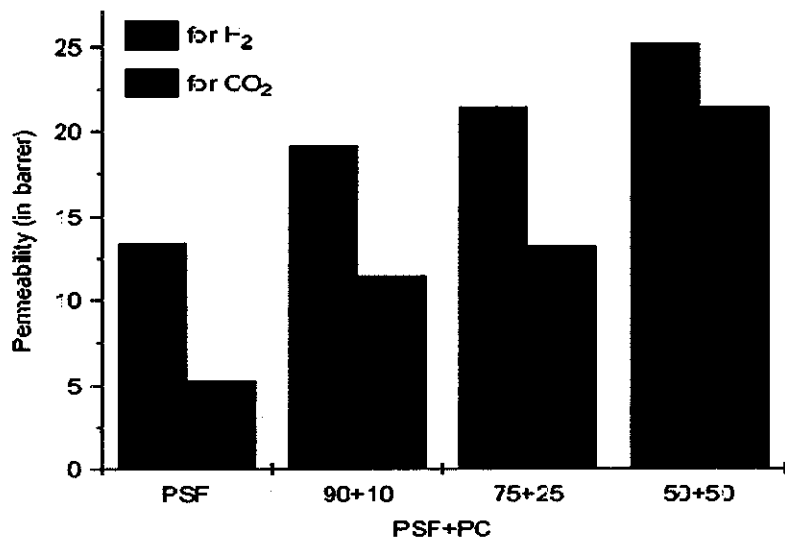


Figure 7: Bar graph of permeability versus composition of polymer blend.

S. no.	Sample (PSF + PC) (in barrer)	$P(H_2)$ (in barrer)	$P(CO_2)$ (in barrer)	$P(H_2)/P(CO_2)$
1	100	13.45	5.33	2.52
2	90% + 10%	19.15	11.44	1.67
3	75% + 25%	21.45	13.20	1.62
4	50% + 50%	25.11	21.45	1.17

Figure 8: Permeability data for polymer blends

From the bar chart above, it can be observed that for equal amount of PC and PSF, the permeability is larger compared to the other samples, whereas the permselectivity is found to be minimal. This phenomenon can be explained through the concept of free volume. The free volume content between the polymeric chains increases as the PC concentration increases. At higher concentrations of PC, the membrane will allow both of the gases to pass.

In another study done by Kapantaidakis et al, (1995), the gas permeation through PSF-PI miscible blend membranes was studied. Similar to the project, the researches used the solution cast method, where the solvent that they used is Methylene Chloride. They also study the gas permeation effect on each individual polymeric membrane, with PSF using chloroform as the solvent whereas for PI, Methylene Chloride was used. The non-solvent for this case was water.

They did research on the permeation rates of Helium (He), Hydrogen (H<sub>2</sub>), Carbon Dioxide (CO<sub>2</sub>), Nitrogen (N<sub>2</sub>), and Oxygen (O<sub>2</sub>) on a series of miscible PSF-PI membranes. For the gases which do not interact with the polymer matrix, (He, N<sub>2</sub> and O<sub>2</sub>), gas permeabilities in the miscible blends vary monotonically between those of the pure polymers. In the case of CO<sub>2</sub>, which greatly interacts with PI, they found out that blend permeabilities decrease somewhat compared to the pure PSF and PI. Differential scanning calorimetry measurements of pure and PSF/PI blend membranes show one glass transition temperature, supporting the miscibility of PSF and PI blend. The micrograph of the blend PSF-PI is as shown in the figure below and the FTIR test for PI, PSF and PSF-PI is as shown in the next figure.



Figure 9: Optical micrograph of a PSF/PI blend (1:1 composition) at  $\times 400$  magnification.



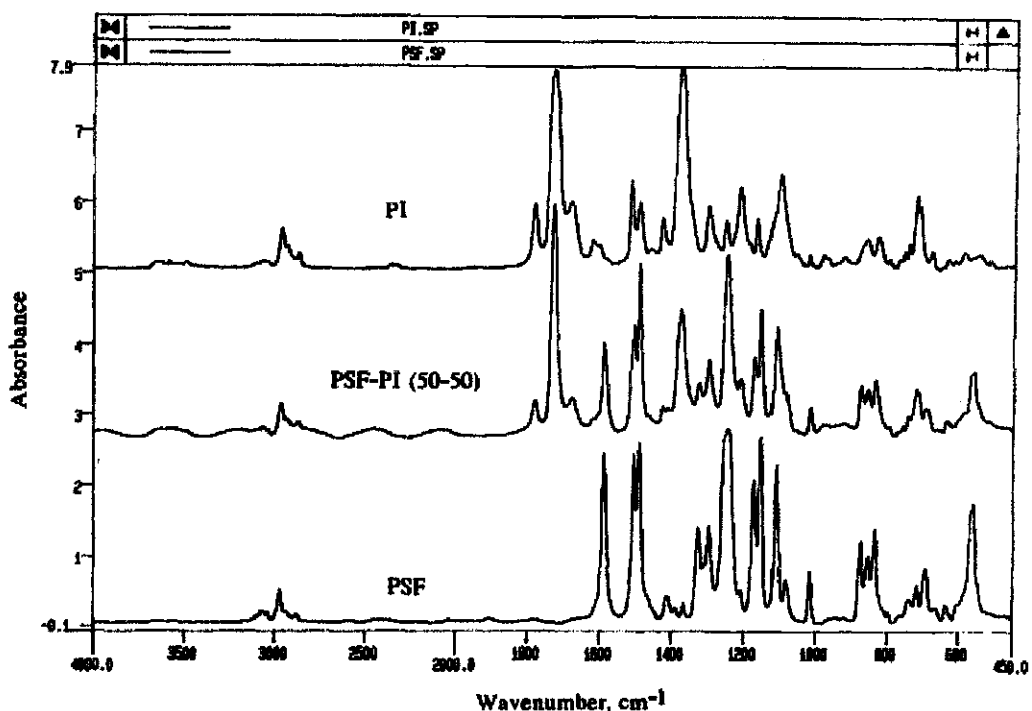


Figure 10: FTIR Spectra for PI, PSF and PSF-PI Membrane

From the results obtained using FTIR characterization, the sulfonate groups of PSF give characteristic peaks at  $1152\text{ cm}^{-1}$ . Antisymmetric C-O stretching frequencies occur at  $1250\text{ cm}^{-1}$  and  $1014\text{ cm}^{-1}$ , while strong absorptions in the  $1600\text{--}1475\text{ cm}^{-1}$  region are associated with the benzene ring stretching mode. The carbonyl groups of PI give a characteristic peak at  $1740\text{ cm}^{-1}$  (stretching vibration), while the C-N primary and secondary vibrations give peaks at  $1250\text{--}1350\text{ cm}^{-1}$ . Other than that, properties wise, they also did a research on the glass transition temperature of varying weight percent of PSF-PI in the casting solution. The results are as shown in the table below.

PI/PSF (% w/w)	T <sub>g</sub> (°C)
0/100	185
20/80	203
50/50	242
80/20	296
100/0	330

Table 2: Glass transition temperature of PI, PSF and PI-PSF blend

The results for the permeability of all the gases are provided in the Appendix 6. From the results obtained, it was said that the miscible blend membranes exhibit improved thermal stability, chemical resistance, and comparable permselectivity factors, due to the presence of PI in the polymeric blend. Compared to PI, the blend membranes are less sensitive to plasticizing gases and less expensive, with minimal loss in permeability or selectivity. In addition, as can be seen in table 2 above, PI has a high glass transition temperature up to 330 °C. Thus, increasing the amount of PI in the PSF casting solution would increase and improve the transition temperature of the membrane.

In another study done by Ismail et al (2008), the permeability of both O<sub>2</sub> and N<sub>2</sub> increased with the increasing zeolite loading compared to the Polyethersulfone and Polyimide polymeric membranes, as they studied the characterization of polyethersulfone (PES)/Matramid 5218 miscible blend mixed matrix membranes for O<sub>2</sub> and N<sub>2</sub> gas separation incorporated with zeolite particles. From their observation through DSC, the polymer solution (blend) shows only one glass temperature, which signifies the homogeneity and miscibility of the polymer blend and zeolite particles. It has been concluded from their research that the addition of zeolite particles into the matrix of PES/PI polymer blend has significant effect on the membrane structures and properties.

A study has been done by Han, M.J, and Bhattacharya, D., (1994) with regards to the changes in morphology and transport characteristics of polysulfone membranes prepared by different demixing conditions. They did an experiment of

producing a Polysulfone membrane, utilizing Dimethylformamide as the solvent and water as the nonsolvent. The results for the experiments are as below.

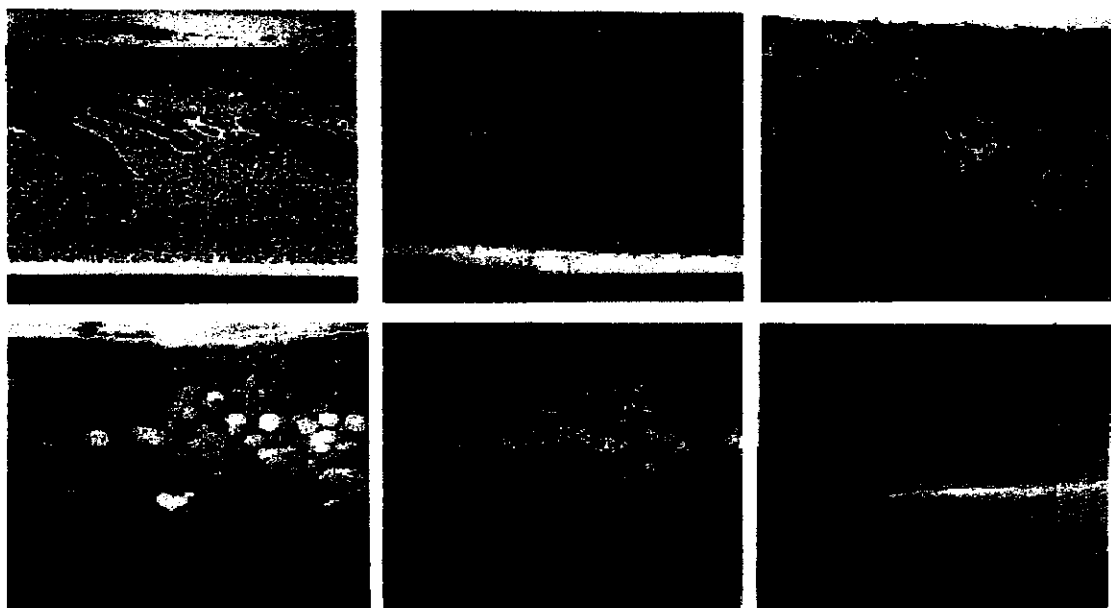


Figure 11: Cross sections (top) and cross sections of skin region (bottom) of PS membranes: coagulated by direct immersion into a water bath after casting (a), by immersion into a water bath after 3-min evaporation (b), and by complete evaporation (c).

The figure (SEM photographs) above dictates that for every changes made in the demixing condition, the morphology of the membranes will be different. From figure 2 (a), it has been observed that, it has graded pore structures from skin to sublayer. The skin region of the membrane consists of nodule structures, which are formed by polymer aggregates and the membrane has finger-like voids in the sublayer. Different morphologies were observed for the membranes which were produced by immersion into water bath after 3-min evaporation and complete evaporation respectively. For the membrane produced in figure 2 (b) and (c), the membrane have cell like structures in the whole cross section. However, it has been observed that the membrane skin produced in part (b) is totally different from part (c). The membrane from part b shows nodular structures in each phase which surrounds the spherical voids in the skin region of the membrane. On the other hand,

the membrane in part (c) shows no sign of nodular structures, and the top skin of the membrane is very dense and homogenous polymer phase exists.

Another research was done by Kang, Y.S, Kim, H.J, and Jo, W.H, regarding the mechanism of asymmetric membrane formation via phase inversion process. The experiment was done in casting a Polysulfone membrane, using 1-Methyl-2-pyrrolidinone as the solvent and ethanol as the nonsolvent, with the application of different ratios of Formic Acid additives. The sample compositions of the samples are as per described below.

Code	PSf <sup>a</sup> (g)	NMP <sup>b</sup> (g)	FA <sup>c</sup> (g)
N	20	80	0
F4	20	76	4
F8	20	72	8
F12	20	68	12

Figure 12: The sample compositions of the membrane casting solution.

The casting solutions were prepared and were immersed in the Ethanol coagulation bath. The results of the SEM photographs are as per shown below.

Figure 13: Membrane prepared Code (N)

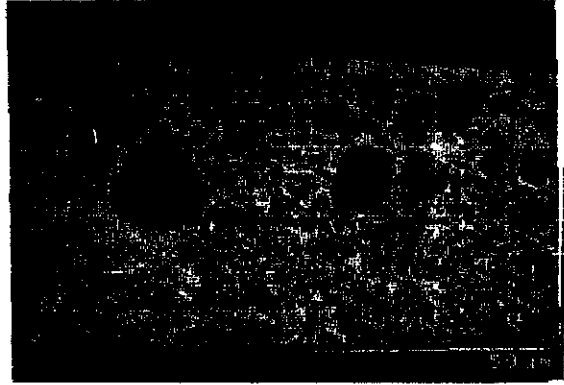


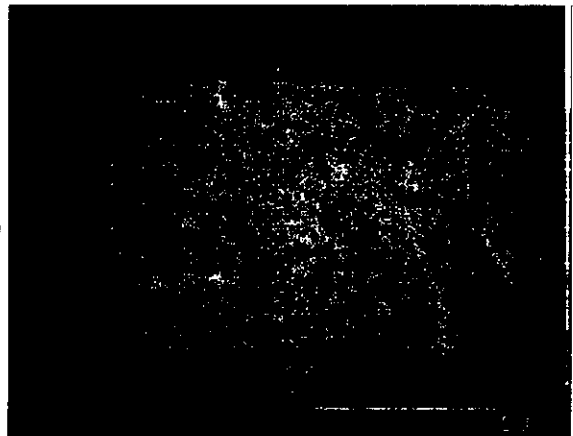
Figure 14: Membrane prepared Code (F4)



Figure 15: Membrane prepared Code (F8)



Figure 16: Membrane prepared Code (F12)



From the results shown above, it can be observed that for different amount of additives and solvents used, the structure of the membrane will be different. The size of the pores decreases as the amount of Formic Acid increases.

Another study has been done by Baik et.al (2001), with regards to the morphology of membranes formed from polysulfone/polyethersulfone/N-methyl-2-pyrilodone/water system by immersion precipitation. The research governs the variation in the coagulation bath, dope solution composition and blend ratio of the polymers. According to their findings, as the solvent contents in the coagulation bath increased, in the single polymer system, the number of macrovoids decreased and the structure or the morphology changed from finger-like structure to cellular like structure. In addition, in a given coagulation bath condition, the precipitation of the blend membrane is much faster compared to the single polymer cast solution. They observed that a horizontally layered structure and horizontal protuberances inside the microvoids of the blend membrane.

In the experiment that they did, Baik et. Al (2001) uses the blend ratio of 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100 for PSf and PES respectively. For the weight ratios of water and NMP in the coagulation bath, the ratio that they used were 100/0, 80/20, 60/40, 40/60 and 20/80 respectively. The results of cloud point measurement are as shown next.

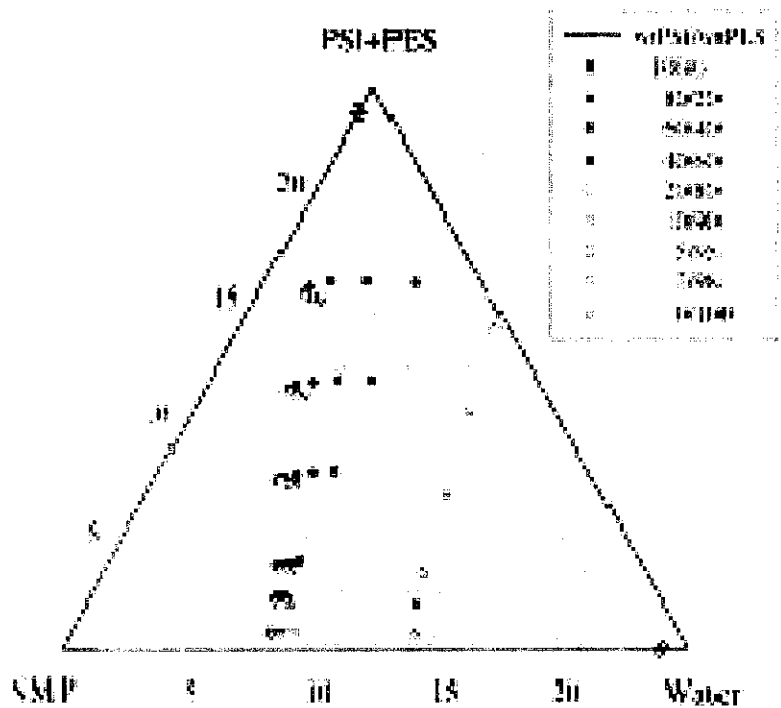


Figure 17: The experimental cloud point measurement conducted at 20°C with various weight ratios of PSf to PES.

From the cloud point experiments, they found out that the cloud point for the blend polymers does not fall in the region of pure polymers. As the weight ratio of PSf to PES decreases, the cloud point curve will approach the solvent polymer axis. The experimental phase diagram also conveys that phase separation (unstable condition) occurs with the addition of smaller amount of coagulant (water) when the polymer solution contains the polymer blends compared to the single ones. Thus it can be said that the miscible region in the solution decreases compared to the pure polymer solutions. The membranes that were produced are as shown in the figures below:

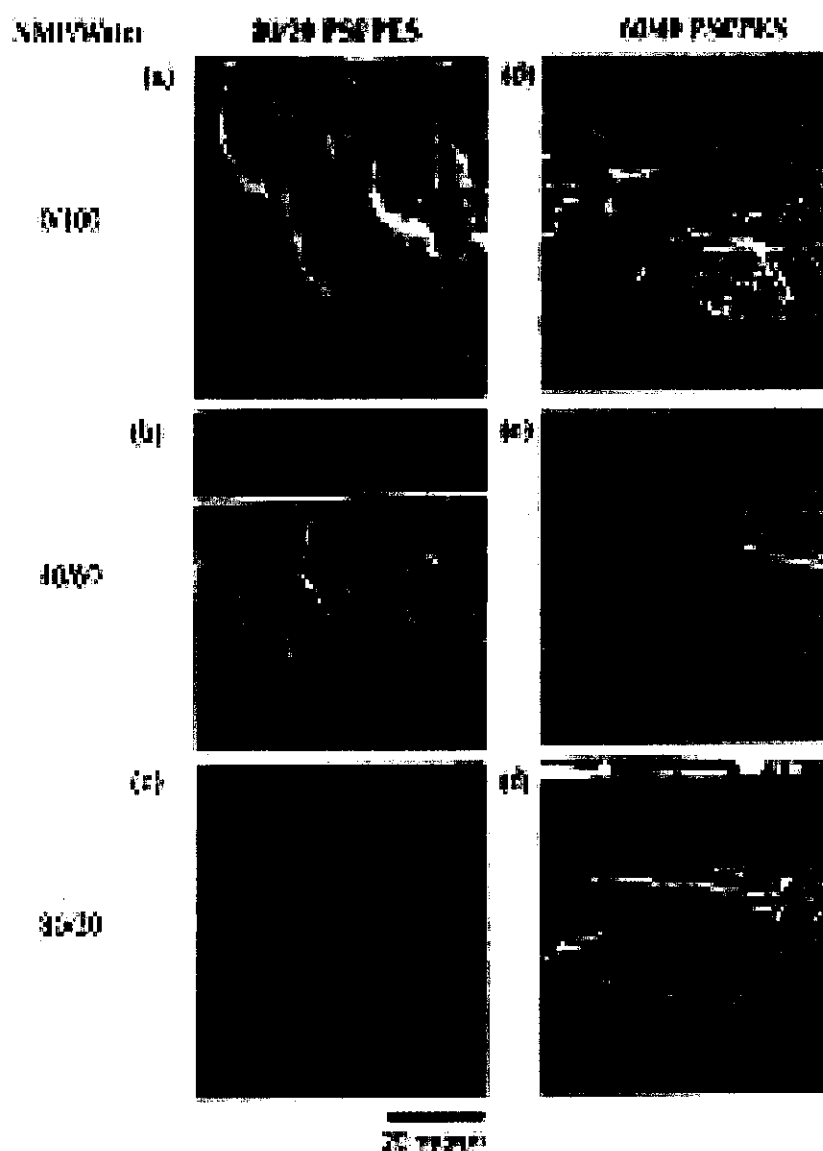


Figure 18: SEM photographs of PSf/PES polymer blend membranes for various ratios of PSf/PI and coagulation bath ratios of NMP/water.



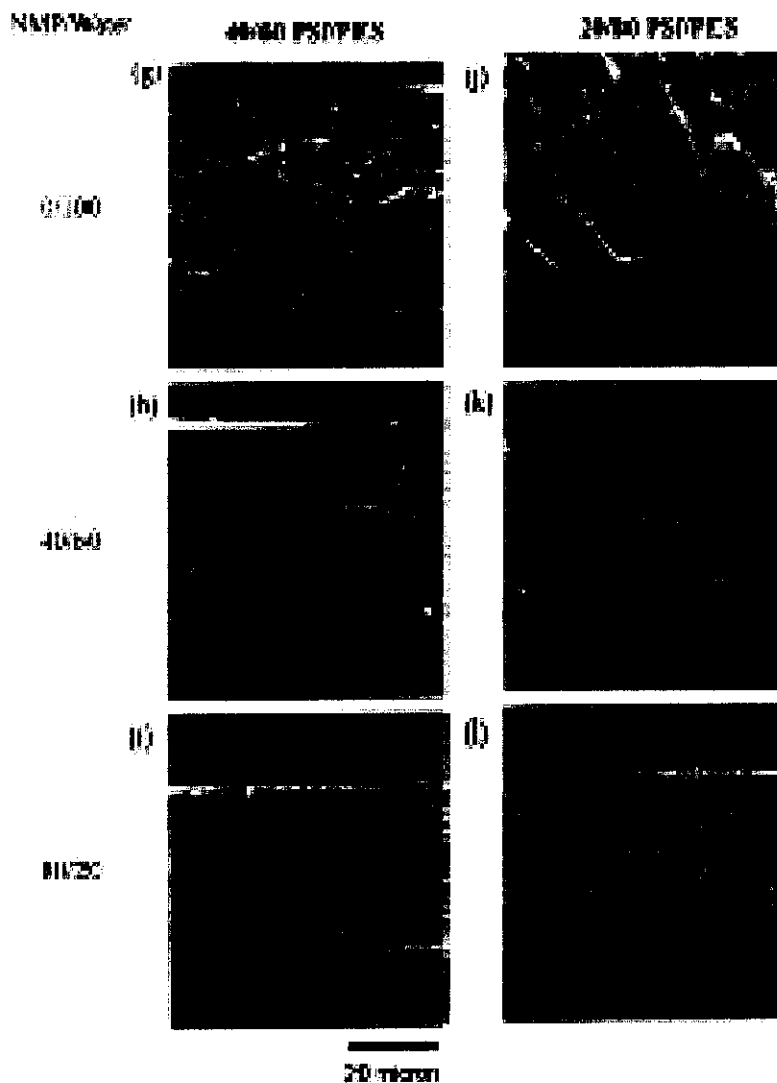


Figure 19: SEM photographs of PSf/PES polymer blend membranes for various ratios of PSf/PI and coagulation bath ratios of NMP/water.

From the experiments, they concluded that with the increase amount of solvent (NMP) in the coagulation bath for a single polymer system, the number of macrovoids decreased and the morphology are cellular like. The sponge-like structure increases in cell size with the increase of solvents in the coagulation bath. For the blend membranes, it has been observed that there are multilayer of

membrane formed. Although multilayer of PSf/Pi membranes were formed, in each layer, the membrane is still homogeneous.

The multilayered phase can be explained through the polymer-rich and polymer-lean concept. The multilayer phase was formed during the exchange of solvents and non solvents. When the first layer (the surface top of the casting solution) gets into contact with the coagulation bath, it is separated into a PSF-rich and PES-rich phase (polymer-polymer separation) at the beginning of the precipitation. After that, the PSF-rich phase is separated into a polymer-rich phase and polymer lean phase (polymer-liquid separation). Although that is the case, the PES-rich phase is still in homogeneity because the system needs more non-solvent (coagulant) to induce the precipitation. For the second layer, the same condition occur at this phase, before the PSE-rich phase in the first layer is separated. The third, fourth and other layers experience the same phenomenon.

From literature, it can be observed that, the morphology of the membrane depends strongly on the compositions of the polymer cast solution, demixing conditions and types of solvents and non-solvents used. The morphology of the membrane is an important point to cater during the fabrication of the membrane as it will determine the flux and selectivity of the membrane produced. In order to study further on this issue and to enhance understanding on the membrane morphology, this project will cater the study of miscible blend membranes (assymmetric) with various preparation parameters, and the performance of the membranes will be evaluated through the CO<sub>2</sub> permeability test.

## **CHAPTER 3**

### **METHODOLOGY**

For this project study, the phase inversion method, by means of immersion, will be used in fabricating the polymeric membrane. The polymer used in the research is the Polysulfone (PSf) and Polyimide (PI), with N-Methyl Pyrrolidone (NMP) and Dichloromethane (DCM) as the solvents. The non-solvent for the immersion method is ethanol solution. The experiments will be divided into two parts which are the Cloud Point measurement and the Membrane Fabrication experiment.

#### **3.1 Cloud Point Measurement**

According to *Kesting et. al. (1990)*, coagulation value is the amount of coagulant in grams required to make 100g of polymer dope solution containing 2g of polymer to become cloudy. Coagulation value determination is to be carried out by means of titration of the dope solution with the coagulant which is EtOH. The solvents for the experiment, NMP and DCM, will be added together and stirred for 10 minutes in order to ensure complete mixing of the solvents. Then, the solvents will be added to the powdered polymer and is stirred for another 1 hour. The dope solution will be titrated slowly with the non solvent under agitation until the initially clear solution becomes cloudy visually. The quantity in grams of the ethanol required for the dope solution to become cloudy and turbid is the coagulation value of the sample. The compositions and fractions of the polymer and solvents are as shown in the table below.

Table 3: Ratio of Solvents 50/50

Ratio DCM/NMP	PSf (g)	PI (g)	DCM (ml)	NMP(ml)
50/50	2	0	36.953	47.554
	1.90	0.10	36.953	47.554
	1.80	0.20	36.953	47.554
	1.70	0.30	36.953	47.554
	1.60	0.40	36.953	47.554

Table 4: Ratio of Solvents 80/20

Ratio DCM/NMP	PSf (g)	PI (g)	DCM (ml)	NMP(ml)
80/20	2	0	59.125	19.02
	1.90	0.10	59.125	19.02
	1.80	0.20	59.125	19.02
	1.70	0.30	59.125	19.02
	1.60	0.40	59.125	19.02

Table 5: Ratio of Solvents 20/80

Ratio DCM/NMP	PSf (g)	PI (g)	DCM (ml)	NMP(ml)
20/80	2	0	14.78	76.07
	1.90	0.10	14.78	76.07
	1.80	0.20	14.78	76.07
	1.70	0.30	14.78	76.07
	1.60	0.40	14.78	76.07

The titration configuration for the experiments is as shown in the figures below. The initially clear solution in figure 20 will become cloudy at the end of the titration as shown in figure 21.

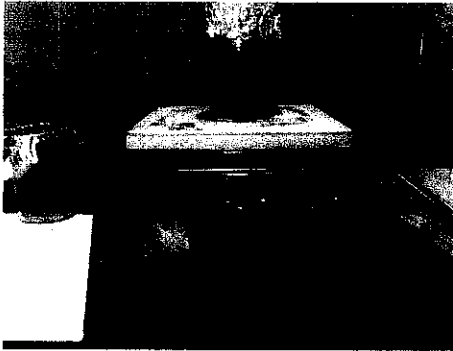


Figure 20: Initially clear homogeneous solution

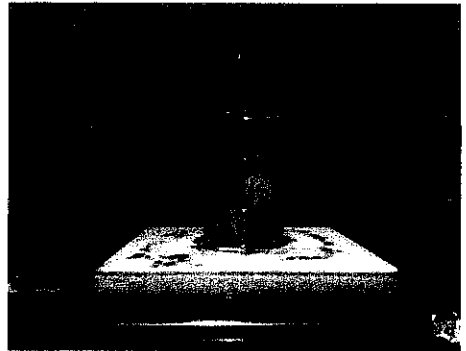


Figure 21: The turbid solution at the end of titration

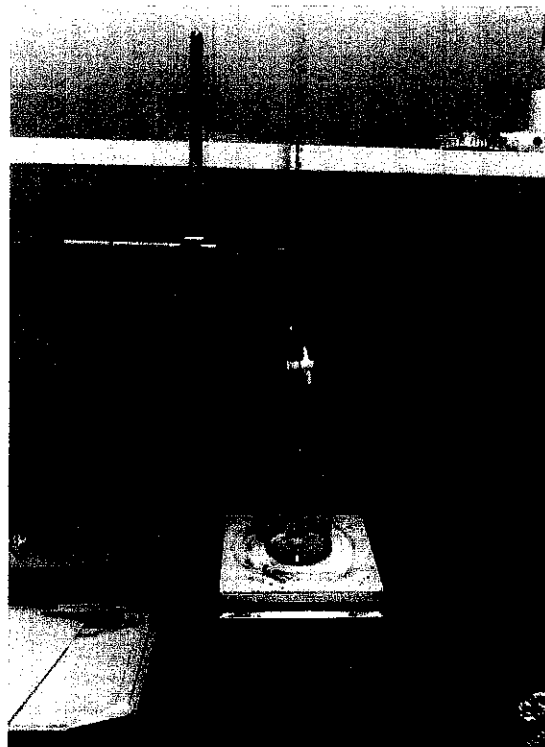


Figure 22: Titration configuration for coagulation value determination

### 3.2 Membrane Casting Preparation

For each of the membrane, it has been decided that the weight percentage of polymer of the solution will be in the range of 15% - 20% of the total dope solution. Thus, the total weight percentage of solvents in the solution would be 80% - 85%. For this experiment, the total weight percentage of the polymer in the solution has been chosen to be 15%, while the solvents will be the remaining 85%. These values will be used constantly throughout the whole experiments conducted. The dope solutions were prepared according to the calculated fractions shown below.

Table 6: Ratio of Solvents 50/50

Ratio DCM/NMP	PSf (g)	PI (g)	DCM (ml)	NMP(ml)
50/50	3.7546	-	8.01	10.31
	3.5625	0.1875	8.01	10.31
	3.3750	0.3750	8.01	10.31
	3.1875	0.5625	8.01	10.31
	3.0000	0.7500	8.01	10.31

Table 7: Ratio of Solvents 80/20

Ratio DCM/NMP	PSf (g)	PI (g)	DCM (ml)	NMP(ml)
80/20	3.7546	-	12.82	4.12
	3.5625	0.1875	12.82	4.12
	3.3750	0.3750	12.82	4.12
	3.1875	0.5625	12.82	4.12
	3.0000	0.7500	12.82	4.12

Table 8: Ratio of Solvents 20/80

Ratio DCM/NMP	PSf (g)	PI (g)	DCM (ml)	NMP(ml)
20/80	3.7546	-	3.12	16.5
	3.5625	0.1875	3.12	16.5
	3.3750	0.3750	3.12	16.5
	3.1875	0.5625	3.12	16.5
	3.0000	0.7500	3.12	16.5

Detailed calculations can be referred to Appendix 17. The dope solution will be produced accordingly. The solvents for each case, NMP and DCM will be added together and will be subjected to stirring for 5 minutes to ensure homogeneous solution. PI will be added to the solvents and the agitation will progress at a temperature of 35°C and speed of 2-3 RPM. PSF will be added slowly to the dope solution and it is subjected to 21-22 hours of stirring. This is to ensure all the polymers will dissolve and produce a homogeneous solution. The homogeneous casting solution will be subjected to ultrasonic degasser to remove any bubbles from the agitation. The casting solution will then be cast on a casting glass and the thickness of the membrane will be adjusted using the casting knife, which will be set up to desirable thickness. The casting solution of the glass plate will be immersed in a coagulant bath at room temperature until the membrane detached completely from the glass plate. The coagulant will induce the precipitation of the membrane film. The membrane will be left to dry in room temperature for 3 days to ensure that the membrane is completely dried. Another alternative is to dry the membrane in the oven for 12 hours at 35°C to 100°C to make sure the membrane is dried evenly.

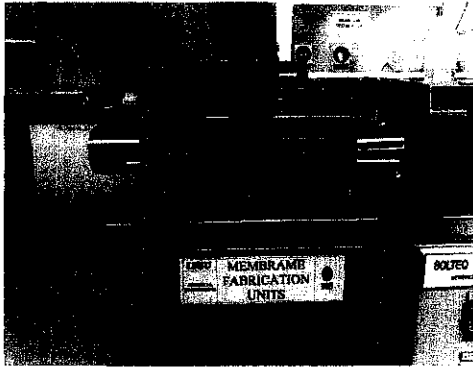


Figure 23: Membrane Casting Unit  
(Side View)



Figure 24: Membrane Casting Unit  
(Top View)



Figure 25: Ultrasonic Degasser

### 3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) enables the observation of the membrane cross sections and surfaces. The effectiveness of the blend can also be determined by observation on the photographs. The air dried membrane samples were fractured under cryogenic conditions using liquid nitrogen and dried at 21°C atmosphere. The fractured specimens were coated with gold-palladium alloy (60:40) before the SEM photographs were taken. Photographs will be obtained from the Hitachi 800 Field Electron Microscopy.



### 3.3 FTIR Test

According to the *Thermo Nicolet Corporation (2001)*, FTIR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, infrared radiation will be passed through the sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present.

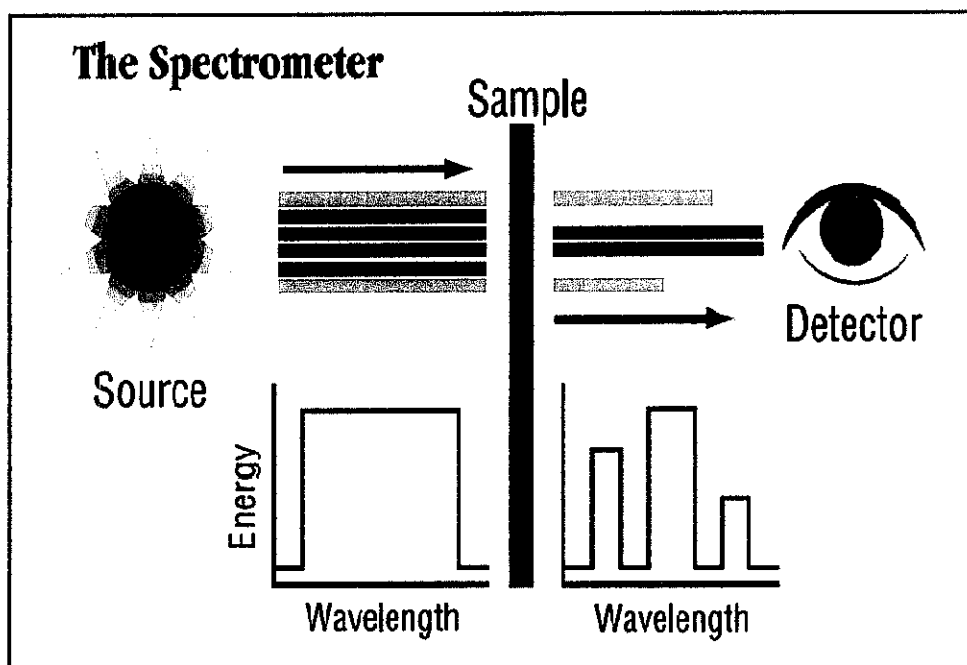


Figure 26: Simple diagram to represent FTIR process.

For the experiments, each of the membranes prepared will be subjected to the FTIR test to observe the dynamics of the membranes prepared.

### **3.4 Permeability Test**

As proposed by Iqbal (2007) gas permeation test were measured using pure CO<sub>2</sub> at the laboratory. Feed side pressure will be applied from 2 bar to 10 bar. The set up consists of a feed gas tank, a pressure gauge of inlet gas, a dead end membrane cell and a bubble soap flow meter. This type of module allows the feed gas to flow into the membrane perpendicularly to the position of the placed membrane.

The gas permeation test unit will be evacuated to less than 0.1 bar by vacuum pump for 1 hour to remove residual gas remained in the system, before the experiments begins. The feed gas will be supplied by the gas tank which is equipped with a pressure regulator. The feed gas pressure will be set up within the range of test pressure and the permeate stream will be assumed at atmospheric pressure.

The gas bubbles will escape through the soap solution. The time taken for the bubble to travel from the starting point to the last determined point will be used taken in order to determine the selectivity if the membrane.

### **3.5 Universal Testing Machine Test**

The Universal Testing Machine (UTM) 5 kN, is a measuring device which is used to observe the tensile properties of the material when force is applied. The tensile strength measure the ability of membrane to store energy when force is applied and retain its original form or position elastically after the force is removed. The maximum load, yield and point at break were studied for all 10 the 10 membranes.

### 3.6 Schematic of Project Methodology

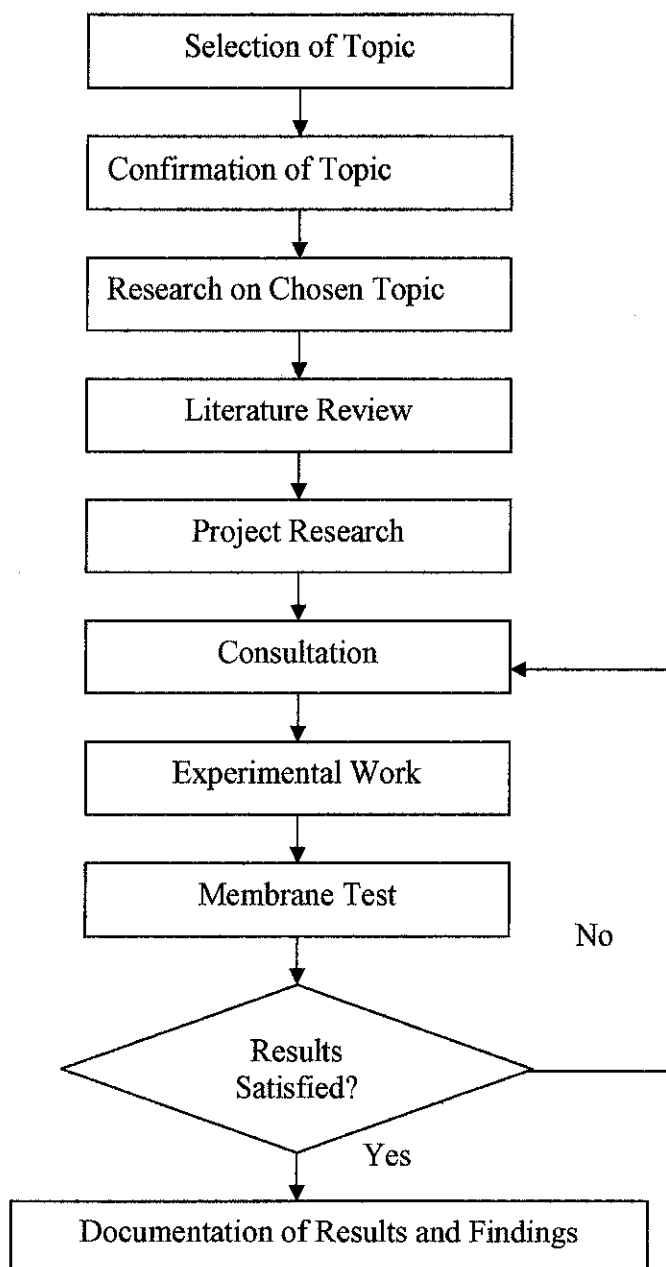


Figure 27: Schematic of Project Methodology to completion

## CHAPTER 4

### RESULT AND DISCUSSION

Asymmetric PSF-PI blend membrane formations and morphologies at various preparation parameters (varying weight of polymer and varying amount of solvent content) will be presented in this section. Skin layer region, formation of macrovoid in the substructure and overall porosity of the membranes will also be discussed.

#### 4.1 Solubility Parameter Determination

According to Matsura (1994), solubility parameter is a parameter used to express the nature and magnitude of the interaction force working between the molecules. In the membrane application, solubility parameter gives the measure to the interaction force working between the molecules that constitute the membrane material, and also the interaction force between the latter molecule and the permeant molecule. In addition, Iqbal (1996) added that solubility parameter measures the affinity between two components or more, where a small solubility parameter difference between the two molecules means the polymer and solvent are miscible (strong affinity between each other). In other words, it can be said that the affinity between two components will increase if the difference between their solubility parameters  $\delta_1$  and  $\delta_2$  are smaller.

Iqbal (1996) also conveys that solubility parameters will be used in determining the heat of mixing, through the application of the equation below:

$$\frac{\Delta H_m}{V} = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \dots\dots\dots(1)$$

where  $\Delta H_m$  is the total heat of mixing,  $V$  is the total molar volume of the mixture, while  $\delta_i$  and  $\phi_i$  refers to the volume fraction and solubility parameters

of component  $i$ , respectively. Equation (1) above is known as the Hildebrand's regular solution theory.

Among others, this equation, proposed by Hildebrand is by far the most popular used. The magnitude of the total heat of mixing  $\Delta H_m$  primarily determines the extent of the free energy change  $\Delta G$  (or otherwise known as the Gibbs free energy of mixing), whether it gives a minus or plus value.  $\Delta G$  can be defined as below:

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots(2)$$

where  $T$  is the absolute temperature and  $\Delta S$  is the entropy of mixing. As can be seen from equation (2),  $\Delta G$  is dependent on the values of the right hand side of the equation. Thermodynamically, dissolution of polymeric materials is accompanied by a free energy change. Gibbs free energy of mixing or free energy change represents the stability of the mixture. As it is known, during the formation of the membrane by means of phase inversion method, it involves a change in its thermodynamics properties, stable polymer solution into an unstable polymer solution. Instability can be caused by changes in pressure, temperature and composition of the casting solution. In other words, homogeneous stable casting solution must meet the following condition at constant  $T$  and  $P$ ;

$$(\Delta G_m) < 0 \dots\dots\dots(3)$$

while instability in the casting solution occurs if

$$(\Delta G_m) > 0 \dots\dots\dots(4)$$

Dissolution of polymeric materials involves large change in the entropy, which means that  $\Delta S_m$  is always positive because the volume fraction are less than unity, thus it is proven that  $\Delta G$  depends greatly on the total heat of mixing.

#### 4.2 Prediction of Solubility Parameter

According to Matsuura (1994), equation (1) above can be rewritten in the form of;

$$\frac{\Delta H_m}{V\phi_1\phi_2} = \left[ \left( \frac{\Delta E_1}{V_2} \right)^{1/2} - \left( \frac{\Delta E_2}{V_2} \right)^{1/2} \right]^2 \dots\dots\dots(5)$$

where  $\Delta E$  is the heat of vaporization for the  $i$ th species, or it is also known as the cohesive energy (CE).  $\Delta E$  is the degree of attraction between molecules in a liquid, and is a measure of strength of secondary bond. Secondary bond will be formed or brake during the process of dissolving, melting, vaporizing, diffusion and deformation.  $\Delta E/V$  is equal to the density of heat of vaporization, often be called internal pressure or cohesive energy density (CED). The solubility parameter and CED can be related in the formula below:

$$\delta_i = \sqrt{CED} = \sqrt{\frac{\Delta E_i^V}{V_i}} \dots\dots\dots(6)$$

From equation (5), it can be seen that the total heat of mixing  $\Delta H_m$  is always positive and the value reduces with as cohesive energy densities of the  $i$ th species becomes smaller. Thus, as  $\Delta H_m$  increases,  $\Delta G$  decreases with smaller difference between the cohesive energy densities. This favors the dissolution of polymer, 1, in the respective solvent, 2.

The values of  $\sqrt{\Delta E/V}$  for both polymer repeat unit and solvent can be obtained from available literature. It can be said that a polymer will be soluble in a solvent where their solubility parameters are close to each other.

In other cases, equation (6) can be used to predict the solubility parameter for vapors that obeys the ideal gas law, (i.e. nonpolar fluids) and of a pure solvent. It is not possible to calculate solubility parameter of a solid polymer since vaporization does not takes place. Thus, the solubility parameter of a polymer can be determined using the proposed method, which is the Group Contribution Method.

#### 4.2.1 Group Contribution Method

Calculation of solubility parameter,  $\delta$ , by means of group contribution method requires the molar attraction constant,  $F_i$ , for each chemical group in the polymer repeating unit. According to Iqbal et.al (1996) The group contribution method of calculating solubility parameter is given as follow;

$$\delta_i = \frac{\rho \sum_{i=1} F_i}{M_r} \dots\dots\dots(7)$$

where  $M_r$  and  $\rho$  refer to the molecular weight and density of polymer respectively. Several scientists such as Small, Hoy and Van Krevelen has proposed numerous group contribution method. If the data for one chemical is not available in that particular method, it can be obtain using another method, i.e. if the molar attraction constant is not available in the Small's method, then it can be obtained by using the Van Krevelen and Hoy's method.

Many works have been done and numerous formulations have been proposed to predict the affinity between polymer and solvents, but the predictions will be less accurate if hydrogen bonding exists in the molecular structure of the polymer or solvent. According to Hertz (1989) Hansen, a chemical scientist has proposed the usage of three-dimensional solubility parameter, which is explained as below.

Polar (aqueous and nonaqueous electrolytes) fluids had three major intermolecular forces to consider:

- Dispersion (London) forces "D"-common in all cohesive energy
- Hydrogen bonding "H", now referred to as H-bonding
- Dipole moment "P", a measure of the polar (electrostatic) aspect of a molecule.

The overall solubility parameter can be calculated using the formula below:

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \dots\dots\dots(8)$$

where  $\delta_d$  ,  $\delta_p$  ,  $\delta_h$  are the dispersive, polar and hydrogen bonding solubility parameters respectively. The total cohesive energy is approximated by the sum of energy densities required to overcome atomic dispersion London Forces ( $\delta_d^2$ ), forces between permanent dipoles of adjacent molecules (polar interaction), ( $\delta_p^2$ ), and to break hydrogen bonds (exchange of electrons, proton donor/acceptor) between molecules, ( $\delta_h^2$ ).



According to Matsura (1994) from  $\sqrt{\Delta E/V}$ , it can be shown that it can be used to obtain an equation as shown in equation (7).

$$\Delta E/V = \Delta E_d/V + \Delta E_p/V + \Delta E_h/V \dots\dots\dots(9)$$

The heat of vaporization can be divided into three components, with each component representing a molecular interaction force of different kinds, where  $\Delta E_d$  is the London Dispersion Force,  $\Delta E_p$  is the dipole force and  $\Delta E_h$  is the hydrogen bonding force component. In terms of solubility parameter, it can be rewritten in the form,

$$\delta_{sp}^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \dots\dots\dots(10)$$

where ;

$$\delta_d = (E_d/V)^{1/2} \dots\dots\dots(11)$$

$$\delta_p = (E_p/V)^{1/2} \dots\dots\dots(12)$$

$$\delta_h = (E_h/V)^{1/2} \dots\dots\dots(13)$$

In equation (8), the magnitude of  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  are limited to certain solvents only, thus, Van-Krevelen and Hoftyzer have developed formulations in order to obtain those solubility parameters values.

Those solubility parameters can be calculated by means of applying additivity rules to the structural components of the repeat unit of the macromolecule and to those solvent molecules by using the following equations;

$$\delta_{sp} = \sqrt{\sum E_{coh} / V} \dots\dots\dots(14)$$

$$\delta_d = \sum F_{di} / V \dots\dots\dots(15)$$

$$\delta_p = \sqrt{\sum F_{pi}^2 / V} \dots\dots\dots(16)$$

$$\delta_h = \sqrt{\sum E_{hi} / V} \dots\dots\dots(17)$$

Van Kralaven-Hoftzyer proposed that the total solubility parameter,  $\delta_{sp}$  can be known by using equation (14). The numerical values assigned to each structural component of the organic compounds can be obtained readily from literature.

On the other hand, according to Barton, the total solubility parameter should be calculated by using this formula below:

$$\delta^2 = \left(\sum \delta_d^i \phi^i\right)^2 + \left(\sum \delta_p^i \phi^i\right)^2 + \left(\sum \delta_h^i \phi^i\right)^2 \dots\dots\dots(18)$$

The interaction among all components will be analyzed by calculating the solubility parameter differences. According to Hansen,

there are three solubility parameters that contribute to the total solubility parameter.

Thus, the differences between solubility parameter can not be taken as just  $\delta_1 - \delta_2$ . Thus, the total solubility parameter can be calculated as follows:

$$\Delta\delta_{ij} = \sqrt{(\delta_{i,d} - \delta_{j,d})^2 + (\delta_{i,p} - \delta_{j,p})^2 + (\delta_{i,h} - \delta_{j,h})^2} \dots\dots\dots(19)$$

where i is the solute and j is the solvent. The parameter follows the rule that the smaller  $\Delta\delta_{ij}$  is, the greater the affinity between solute and liquid, also known as like dissolves like.

**4.2.2 Polymer**

The solubility parameter for Polysulfone and Polyimide were calculated accordingly. The calculations for both of the solubility parameter can be referred from Appendix 7, Appendix 8 and Appendix 9. The values for solubility parameter of pure PSF and PI are  $10.5589 \text{ (Mpa)}^{1/2}$  and  $8872.4962 \text{ (Mpa)}^{1/2}$  respectively. The experiment will proceed in a way that the weight percentage of the polymer blends will vary from one another. The weight ratio of Polysulfone to Polyimide is in the order of (100:0, 95:5, 90:10; 85:15, 80:20). It has been decided that the polymer composition in the dope solution contributes to 15% of the total solution.

The summary of all the calculations are represented below.

Table 9: Weight Percent of Polymers

Case	Solubility Parameter(Mpa) <sup>1/2</sup>
95% PSf, 5% PI	533.7612
90% PSf, 10% PI	1047.653
85%PSf, 15% PI	1551.876
80%PSf, 20%PI	2046.696

#### 4.2.3 Solvents

The solubility parameters for all the solvents were calculated accordingly. The calculations for the solubility parameter determination can be referred to Appendix 10, Appendix 11 and Appendix 12 respectively. The values of pure NMP and DCM has been calculated to be 10.5050(Mpa)<sup>1/2</sup> and 10.8561(Mpa)<sup>1/2</sup>. For the solvents, the experiment will be proceeding in the manner of different ratios of DCM to NMP, i.e. 20/80, 50/50, 80/20 respectively. The summary of the whole calculations are tabulated below:

Table 10: Ratio of Solvents 20/80

Case(DCM/NMP)	Solubility Parameter(Mpa) <sup>1/2</sup>
20/80	10.51614
50/50	10.57606246
80/20	10.70961

### 4.3 Cloud Point Determination

Cloud point value will be obtained by dissolving 2g of polymer into 98g of solvents. The amount of non-solvent to be added for the solution to become cloudy is the cloud point. The experiments for cloud point determination for each case are as shown as below:

Table 11: Cloud Point Determination

Ratio(DCM/NMP)	PSf(g)	PI(g)	DCM (ml)	NMP (ml)	Cloud Point(ml)
20/80	2	0	14.78	76.07	35.9
	1.90	0.10	14.78	76.07	36.1
	1.80	0.20	14.78	76.07	36.6
	1.70	0.30	14.78	76.07	36.7
	1.60	0.40	14.78	76.07	36.9
50/50	2	0	36.953	47.554	13.6
	1.90	0.10	36.953	47.554	13.7
	1.80	0.20	36.953	47.554	14.0
	1.70	0.30	36.953	47.554	14.2
	1.60	0.40	36.953	47.554	14.5
80/20	2	0	59.125	19.02	11.0
	1.90	0.10	59.125	19.02	11.2
	1.80	0.20	59.125	19.02	11.3
	1.70	0.30	59.125	19.02	11.6
	1.60	0.40	59.125	19.02	11.9

As can be seen from the table above, it can be observed that the cloud point for the respective ratio of solvents does not vary highly with each other. It is observed that for 20/80 ratio, the cloud point is higher compared to 50/50 and 80/20. This shows that, as we increase the amount of Dichloromethane (DCM) in the casting solution, the cloud point would decrease. The faster the solution becomes turbid, the faster is the

precipitation rate (membrane casting). High value of cloud point indicates that the membrane would phase separates very slowly when immersed in the Ethanol bath.

The solubility parameter of solvent mixtures must also be taken into account in expressing the interaction between the solvent and polymer. From the solubility parameter calculated in the previous section, it can be observed that coagulation value decreases with smaller solubility parameter differences between polymer and solvents. Let us take 95% PSF and 5% PI, dissolved in 20/80, 50/50, and 80/20 of DCM to NMP respectively. The solubility parameter differences are as tabulated as below:

Table 12: Solubility Parameter Difference

Fraction	$\delta$ 95% PSF- 5% PI	$\delta$ DCM/NMP	$\delta$ Difference
(20/80)	533.7612	10.5161	523.2451
(50/50)	533.7612	10.5761	523.1851
(80/20)	533.7612	10.7096	523.0516

Smaller solubility parameter differences would lower the coagulation value. The graph of the solubility parameter difference is as shown below.

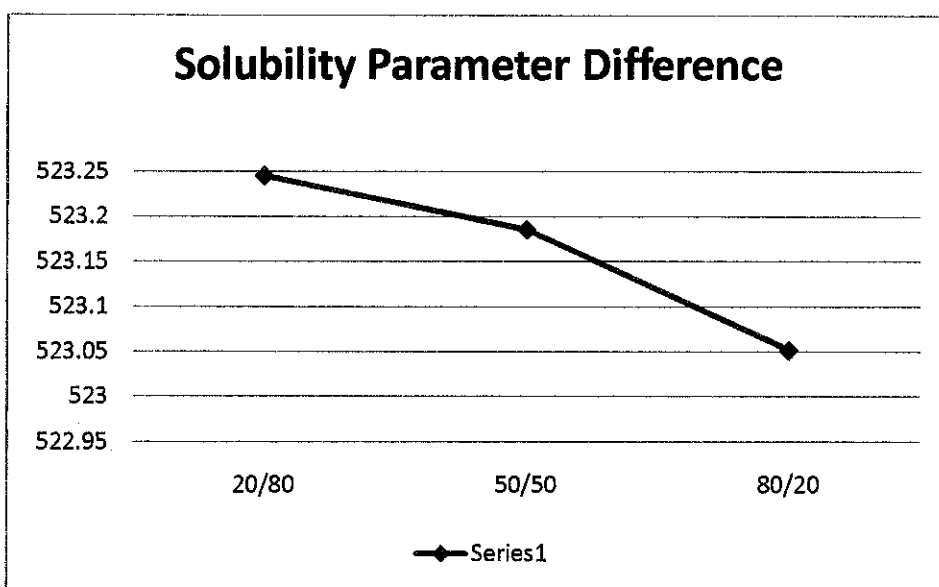


Figure 28: Solubility Parameter Difference for 20/80, 50/50, 80/20 DCM to NMP respectively

Casting solution that can be easily separated is referred to as having lower coagulation value and thus this kind of casting solution will undergo instantaneous demixing to become unstable instantly. On the other hand, a more stable homogeneous casting solution that has higher coagulation value will experience a delayed demixing mechanism for the induction of the asymmetric membrane structure formation.

In the membrane casting experiment, only two of the classes were taken into consideration for the studies, which is 50/50 and 80/20 of DCM to NMP. It has been observed in the previous section that casting solution of 80/20 DCM to NMP classes has smaller coagulation value compared to the 50/50 DCM to NMP. Therefore, once it is immersed in the coagulation bath, it should demixed instantaneously. Thus, a more porous substructure should be obtained for the membranes of 80/20 solvent composition.

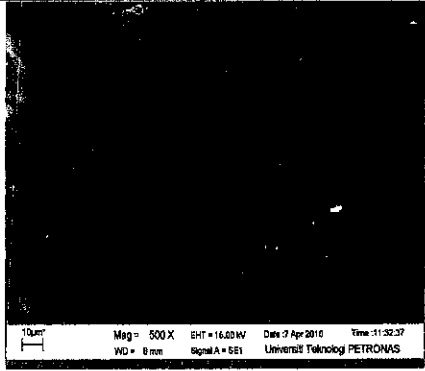
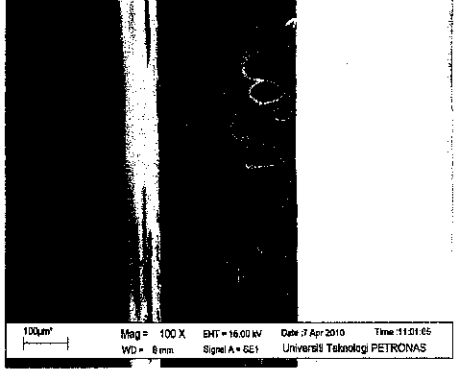
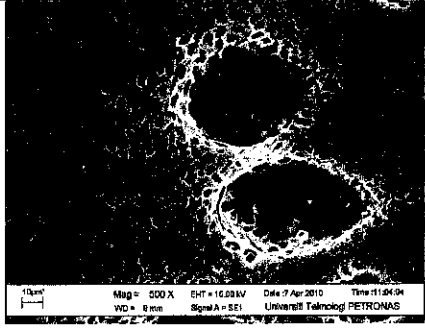
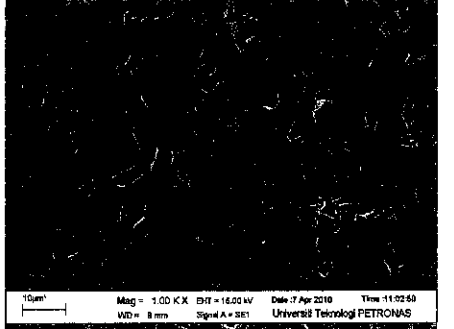
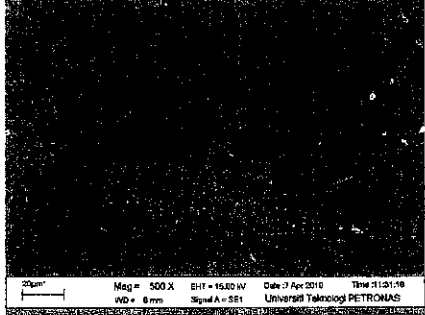
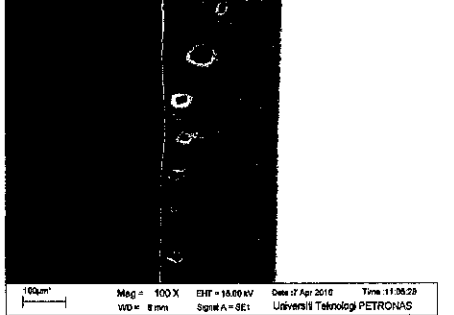
However, contradictive results were obtained. Membranes of 80/20 DCM to NMP solvents composition shows delayed demixing, in which a distinct skin layer was formed compared to the 50/50 DCM to NMP solvents composition. This phenomenon suggest that the effect of different rate of vaporization of the solvents out of the casting solution before immersion into the coagulation bath is more dominant compared to solvent-polymer and solvent coagulant interaction in controlling the mechanism of asymmetric PSF-PI membrane formation. This can be concluded to be the effects of amount of DCM in the casting solution, as DCM has low boiling point (40 °C).

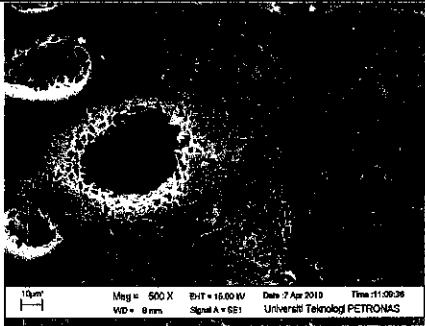
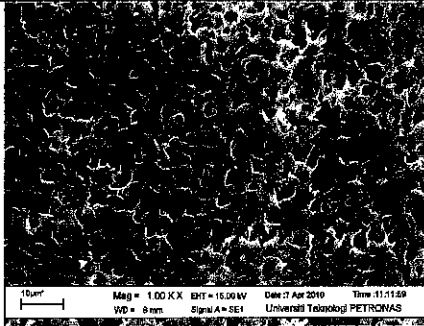
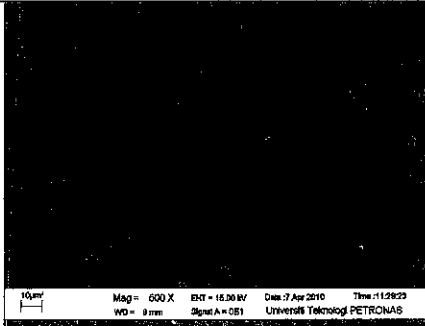
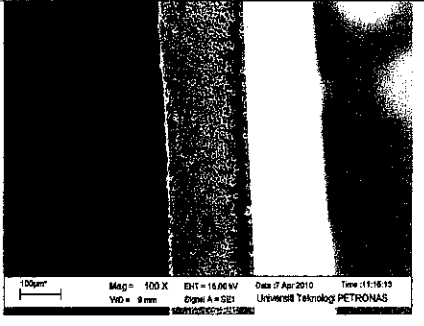
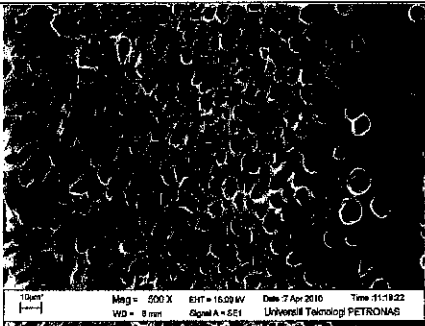
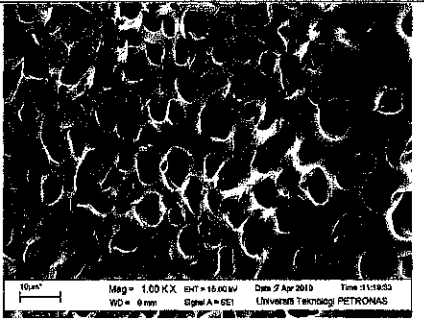
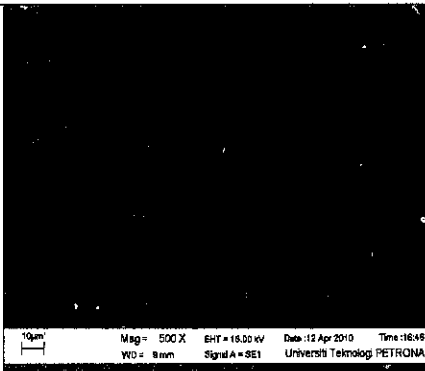
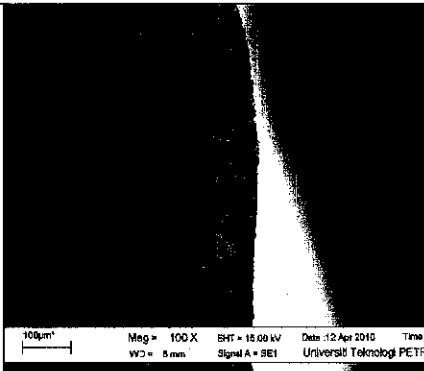


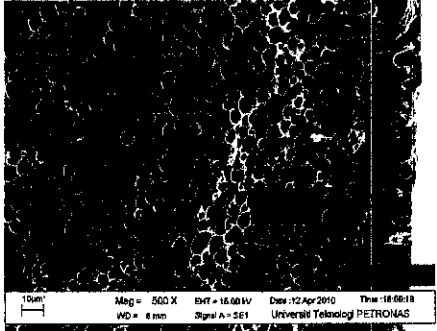
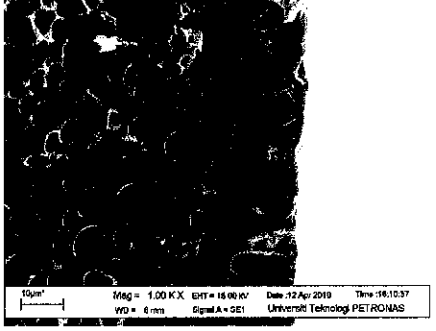
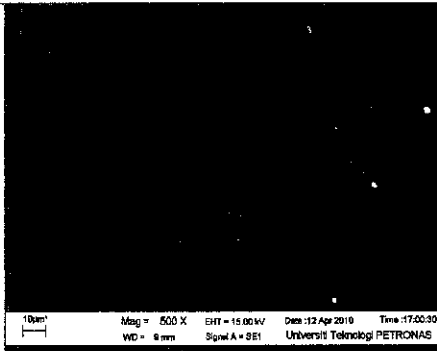
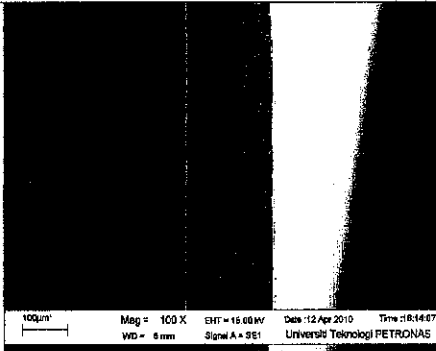
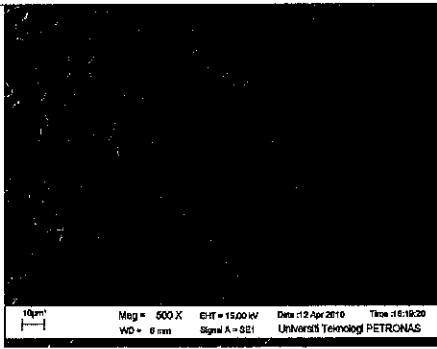
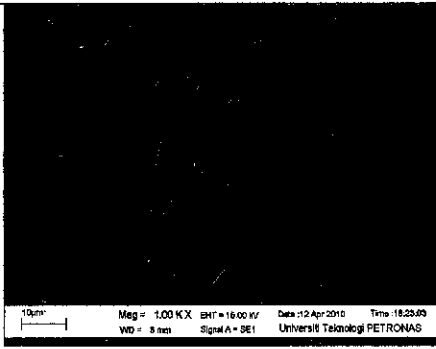
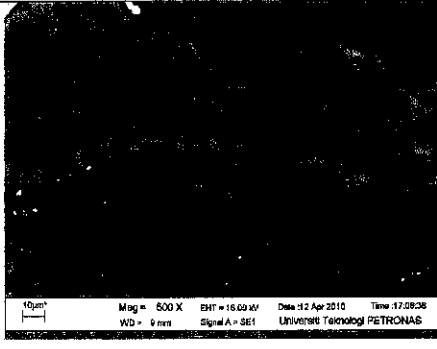
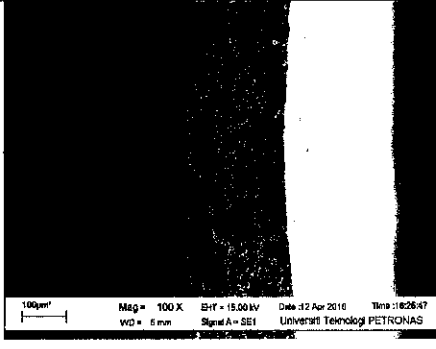
#### 4.4 SEM Test

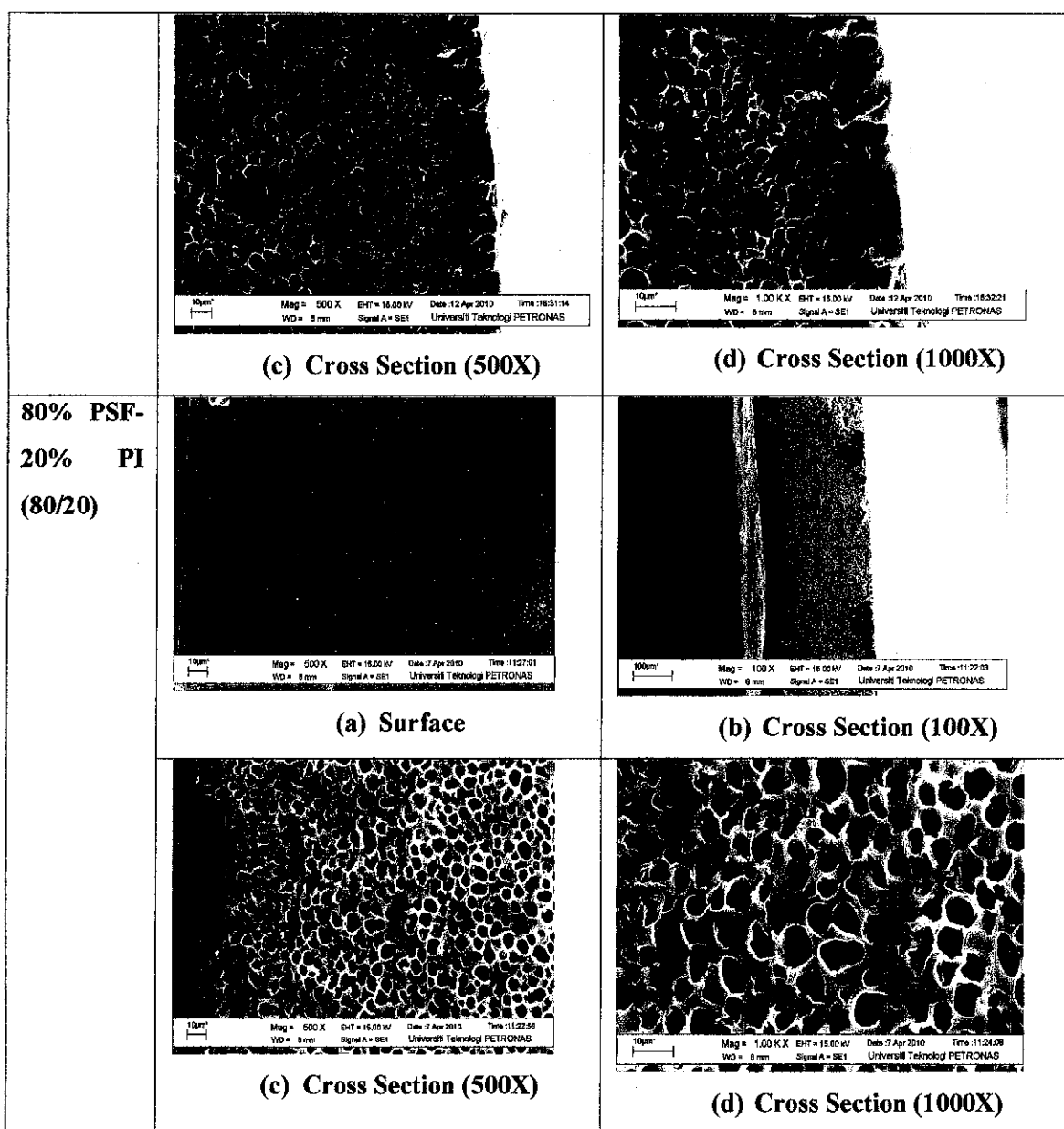
The SEM photographs for each sample are as shown on the table below;

Table 13: SEM Images

Membrane	SEM Images	
<b>100% PSF (50/50)</b>	 <p data-bbox="520 1039 758 1077"><b>(a) Surface (500X)</b></p>	 <p data-bbox="988 1039 1299 1077"><b>(b) Cross Section (100X)</b></p>
	 <p data-bbox="483 1433 795 1471"><b>(c) Cross Section (500X)</b></p>	 <p data-bbox="980 1433 1292 1471"><b>(d) Cross Section (1000X)</b></p>
<b>80% PSF – 20% PI (50/50)</b>	 <p data-bbox="520 1823 758 1861"><b>(a) Surface (500X)</b></p>	 <p data-bbox="973 1823 1270 1861"><b>(b) Cross Section (100X)</b></p>

	 <p><b>(c) Cross Section (500X)</b></p>	 <p><b>(d) Cross Section (1000X)</b></p>
<b>100% PSF (80/20)</b>	 <p><b>(a) Surface</b></p>	 <p><b>(b) Cross Section (100X)</b></p>
	 <p><b>(c) Cross Section (500X)</b></p>	 <p><b>(d) Cross Section (1000X)</b></p>
<b>95% PSF- 5% PI (80/20)</b>	 <p><b>(a) Surface</b></p>	 <p><b>(b) Cross Section (100X)</b></p>

	 <p>(c) Cross Section (500X)</p>	 <p>(d) Cross Section (1000X)</p>
<p><b>90% PSF – 10% PI (80/20)</b></p>	 <p>(a) Surface</p>	 <p>(b) Cross Section (100X)</p>
	 <p>(c) Cross Section (500X)</p>	 <p>(d) Cross Section (1000X)</p>
<p><b>85% PSF- 15% PI (80/20)</b></p>	 <p>(a) Surface (500x)</p>	 <p>(b) Cross Section (100x)</p>



As can be seen from the SEM photographs, distinct skin layer can be observed for solvents ratio of 80% DCM / 20% NMP compared to the 50% DCM / 50% NMP. This is due to the evaporation that occurred on the top surface of the membrane after the casting process. DCM has low boiling point, thus DCM will be evaporated out very quickly in membranes that contains 80% of DCM compared to the 50% DCM case. The dense skin layer is responsible in the separation of gases, while the porous part of the

membrane serves as mechanical support of the membrane. In addition, it has been observed that for the case of 80% DCM / 20% NMP, as the weight percent of PI increases, the pore diameter reduces.

The surface photographs can give the indication of the efficiency of the blends. It has been observed that all the casting solution forms well blending of the polymers. Well blending of the polymers increases the efficiency of the separation of the gas. In figure 80% PSF- 20% PI (80/20) (a), minute or small amounts of PI were observed to be suspended on the surface of the membrane. This shows that some of the PI does not dissolve in the casting solution. Although that is the case, the amount of PI suspended on the surface is very minute and little. Thus, it can be considered as homogeneous blending. Beyond 20% amount of PI in the casting solution, it is predicted that more PI will be suspended on the surface, thus, the casting solution would be homogeneous anymore. It can be concluded that the highest amount of PI in the casting solution for this research is not more 20%.

100% PSF (50/50) (d) and 80% PSF – 20% PI (50/50) (d) show undesirable results due to the fact that the pores of the membrane were sheared by the razor blade. Thus, the pores are not well visible in the SEM photographs. In order to obtain desirable photographs (pores are visible), liquid nitrogen must be used to fracture the membrane. Otherwise, the pores will be slightly closed due to the shearing of the membrane with the razor blade. The porosity calculation can be viewed in Appendix 14.

The formation of skin layer affects the formation mechanism of asymmetric PSF-PI membrane structure. Skin layer will act as a barrier for solvent-coagulant exchange during the phase inversion process. A thicker skin layer would cause the phase inversion process to be slowed down leading to lower precipitation rate. Lower precipitation rate resulted in less porous substructure of asymmetric PSF-PI blend membranes with reduced number and size of macrovoid. As can be seen from the SEM photographs, 80/20 ratio of DCM to NMP solvent composition for 80% PSF- 20% PI shows distinct skin layer and very low number macrovoids present in the substructure compared to 50/50 ratio of DCM to NMP for the same amount of polymer weight percentage. Thus, it can be concluded that, increasing the amount of low boiling point solvents in the casting solution would enhance the thick skin formation. This factor would be the dominant effect that affects the membrane morphology compared to the interaction between the polymer-solvent and solvent-coagulation.

#### 4.5 FTIR Test

FTIR tests were conducted using the Pelkin Elmer device. The membrane casted cannot be subjected to FTIR tests since light could not pass through the opaque colored membrane. Thus, the FTIR tests were done by means of using the casting solution for each membrane. The results of the FTIR tests can be viewed in Appendix 13. Sample 100% PSF (80% DCM / 20% NMP) could not be tested as the Pelkin Elmer device was not working properly.

The FTIR tests would give the indications of the bonds of the casting solution. It would give the compositions bonds strength with the respective wavelengths. The bonds for the casting solution can be referred to the Infrared Spectroscopy Correlation Table in Appendix 15.

From the results obtained, it can be seen that peak  $1718\text{ cm}^{-1}$  is not present in the 50/50 ratio of solvents for all of the polymer weight percentage classes. For 80/20 ratio of DCM to NMP solvents, peak  $1718\text{ cm}^{-1}$  becomes narrower and larger as the amount of PI in the solution increases. Peak  $1718\text{ cm}^{-1}$  shows the bonds of a PI in the system. Thus, it can be concluded that PI is well blended in the 50/50 DCM to NMP ratio of solvents while on the other hand, minute amounts of PI were undissolved in the 80/20 ratio of solvents in the system.

#### 4.6 UTM Test

Tests have been conducted using the Universal Testing Machine to measure the strength of the membranes. The results are as shown in Appendix 16. Summary of the comparison is made for some of the membranes, as shown in the table below.

Table 14: Membrane Strength Comparison

Membrane		Maximum Load (N)	Yield (N)
Polymer Weight %	Solvent %		
100% PSF	50% NMP, 50% DCM	35.19	15.62
100% PSF	20% NMP, 80% DCM	71.04	67.63
80% PSF, 20% PI	50% NMP, 50% DCM	22.18	6.54
80% PSF, 20% PI	20% NMP, 80% DCM	35.83	35.78

It has been observed that the membrane with the ratio of solvent 80% DCM / 20% NMP has higher tensile strength compared to ratio of solvent of 50% DCM/ 50% NMP. Although there is a reduce of tensile strength for 80% PSF- 20% PI (80% DCM/ 20% NMP) compared to 100% PSF (50% DCM/ 50% NMP), it is expected that the latter membrane would give a better efficiency of CO<sub>2</sub> permeation compared to the 100% PSF(50% DCM/ 50% NMP). In addition, although PSF alone shows high possible maximum load and yield, but PSF has high tendency towards plasticization. Plasticization is an undesired effect due to the fact that plasticization will swell the membrane, thus would increase undesired permeability across the membrane. Thus, selectivity would be affected. The purpose of adding PI to the system is to reduce the effect of plasticization of PSF and to increase the selectivity of CO<sub>2</sub> across the membrane as PI has high tendency towards CO<sub>2</sub> gas.



From the table above, it is observed that 100% PSF containing 80/20 DCM to NMP ratio of solvents has highest possible maximum load and yield compared to 100% PSF that contains 50/50 DCM to NMP ratio of solvents. This is due to the fact that 100% PSF which contains 80/20 DCM to NMP ratio of solvents has thicker dense skin layer. The same conclusion can be made for 80% PSF, 20% PI which contains 80/20 DCM to NMP ratio of solvents.

#### 4.7 Permeability Test

The results for permeability test can be viewed in Appendix 18. The permeability test was carried out using a bubble flow meter which uses soap solution to determine the time taken for the gas bubble to travel from the starting point to the end point. The gas studied for the permeation cell is CO<sub>2</sub> and CH<sub>4</sub>. The selectivity of the membranes can be viewed in Appendix 18.

Some of the membranes fail when the permeability test was conducted. This may occur due to errors that may occur during the fabrication process. Then membranes will crack upon the introduction of pressures even as low as 2 bar. Thus, for future works, the surrounding environment has to be taken into consideration when conducting the membrane casting preparation. The environment needs to be free of water as possible as the polymer has high tendency towards water. In addition, after the coagulation bath, it is recommended to wash the membranes produced with warm water to wash all the excess solvents in the membrane. Indirectly, this would increase the mechanical strength of the membrane (observed during experiment). For this study purpose, the membrane was dried without the introduction of water onto the surface of the membrane. The membrane is dried at room temperature for 3 days to ensure complete drying. In addition, this failure may also occur due to the presence of many bubbles in the membrane. The bubbles and casting line on the membrane serves as a weak point to the membrane. It is observed that the membranes cracked at the casting line on the surface of the membrane.

The thick skin layer affects the permeability of the gases through the membrane. In addition the increase in amount of PI affects the selectivity of CO<sub>2</sub> across the membrane. The overall permeability efficiency were not

able to be determined in this research due to the fact that many of the membranes fail during permeability test. But, comparing to the available results, it shows that the results obtained is similar to theory proposed in the literature. Increase in PI would decrease the effect of plasticization and directly increases the separation of CO<sub>2</sub>. The selectivity of CO<sub>2</sub> to CH<sub>4</sub> is seen to be improved.

## **CHAPTER 5**

### **CONCLUSION**

In conclusion, from the literature review, it can be said that the membrane will have different morphologies from different preparation parameters. Different morphologies would give different permeability of CO<sub>2</sub> across it. In order to get the best membrane which contributes to the highest performance of the permeability, the morphology study of the membrane is very crucial. The studies of weight percentage of polymers, solvents, non solvents, evaporation time and coagulation composition would affect the permeability of the membranes.

Blending of PSF and PI will yield membranes which can be applied to high pressure operations or to gas mixtures with high CO<sub>2</sub> content, as proposed by literature. In addition, the polyimide portion of PSF/PI blend membrane would offer additional thermal stability and chemical resistance compared with those of pure polysulfone gas separation membranes.

Increasing the amount of low boiling point solvents in the casting solution affects the total thickness of skin layer and the macrovoids produced. 80/20 DCM to NMP ratio was observed to give better performance of the PSF-PI blend membranes compared to the 50/50 DCM to NMP ratio. Thus, the objective is satisfied. In addition, for this study, it is seen that the membranes are dominant in the vaporization of solvents in the formation of the substructure of the membranes compared to the interaction between polymer-solvent and solvent-coagulation.

The objectives of this project have been achieved. It is proven that increasing PI weight percent in the PSF total casting solution would increase the efficiency and would enhance the properties of the membranes.

## CHAPTER 6

### RECOMMENDATIONS

From the research, literature review and background study, the importance of polymeric membranes would significantly contribute to the advancement of separation process and media. In order to improve this project several recommendations are made, as listed below.

- In order to improve the miscible blend membranes, ways of increasing the strength of the membranes can be done and studied further as PSF/PI miscible blend membrane has been seen to have potential in producing economic yet improved characteristics.
- From literature review, it is stated that CO<sub>2</sub> can cause membrane plasticization at elevated pressures for PI membranes. The critical pressure of plasticization for CO<sub>2</sub> increases appreciably by using moderate PSF amount in the blending as compared to pure polyimide, while permeabilities remain constant. In order to prevent plasticization, more studies can be done on other combination pairs of polymers as what has been done in this project (PSF-PI).
- This project governs the testing of CO<sub>2</sub> permeability across the miscible blend membrane. For future development, studies can also be done to test on the permeability of other gases i.e. He, CO, N<sub>2</sub>, O<sub>2</sub> and other gases in concern.
- Use a more accurate calibrated Permeation cell as the equipment used for this project does not give accurate results due short to air flowrate indicator.

## **CHAPTER 7**

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## CHAPTER 8

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Appendix 1: Suggested Milestone for the Second Semester of 2-Semester Final Year Project

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continue	█													
2	Submission of Progress Report 1				●										
3	Project Work Continue			█											
4	Submission of Progress Report 2								●						
5	Seminar (compulsory)								█	█					
5	Project work continue								█	█					
6	Poster Exhibition									●					
7	Submission of Dissertation (soft bound)												●		
8	Oral Presentation													●	
9	Submission of Project Dissertation (Hard Bound)														●

Mid-Semester Break

● Suggested milestone  
 █ Process

Appendix 2: Milestone for FYP (Final Year Second Semester)

No.	Event/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Research and Lab Work														
2	Submission of Progress Report 1														
3	Research and Lab Work														
4	Submission of Progress Report 2														
5	Seminar (compulsory)														
5	Lab Work														
6	Poster Exhibition														
7	Submission of Dissertation (soft bound)														
8	Oral Presentation														
9	Submission of Project Dissertation (Hard Bound)														
Mid Semester Break															

### Appendix 3: Physical Properties of Polyimides

Tensile Strength	Mpa	215
Young's Modulus	Gpa	2.5
Tensile Elongation	%	85
Glass Transition Temperature	°C	285
Thermal Decomposition Temperature	°C	525
Coefficient of Thermal Expansion	ppm/ °C	55
Coating Stress (100 silicon)	MPa	33
Dielectric Constant 1MHz; 0%/50% RH		3.2/3.3
Dissipation Factor 1 MHz; 0%/50% RH		0.003/0.008
Dielectric Strength	V/μm	345
Moisture Absorption @ 50% RH	%	1.08
Density	g/cc	1.39
Refractive Index @ 633nm		1.69

(Source: Polyimides Properties, Polyimide Bridge Design Rule, 2002)

#### Appendix 4: Physical Properties of Polysulfone

Density	g/cc	1.13 - 1.66
Melt Flow	g/10 min	5.50 - 115
Hardness, Rockwell M		69.0 - 118
Hardness, Rockwell R		120 - 128
Tensile Strength, Yield	MPa	48.0 - 160
Elongation at Break	%	0.500 - 120
Elongation at Yield	%	1.30 - 7.50
Modulus of Elasticity	GPa	1.59 - 24.1
Compressive Yield Strength	MPa	13.0 - 176
Tensile Impact Strength	kJ/m <sup>2</sup>	110 - 420
Impact Test	J	2.00 - 14.0
Electrical Resistivity	ohm-cm	10.0 - 1.00e+17
Thermal Conductivity	W/m-K	0.218 - 0.600
Refractive Index		1.63 - 1.66
Processing Temperature	°C	260 - 410
Glass Temperature	°C	185 - 266

(Source: Overview of Materials of Polysulfone, MatWeb, Material Property Data)

## Appendix 5: Material Safety Data Sheet (MSDS) Polysulfone

# Material Safety Data Sheet

### Section 1

**Contact Name & Address:** American Polymer Standards Corporation,  
8680 Tyler Blvd., Mentor, OH 44060  
**Product Name:** Polysulfone  
**CAS #:** 25135-51-7  
**Emergency Telephone No.:** (440) 255-2211  
**Synonyms:** PSF; Polysulfone resin  
**Formula:** (C<sub>27</sub>H<sub>22</sub>O<sub>4</sub>S)<sub>n</sub>  
**HMIS RATING:** Health: 0 Fire: 0 Reactivity: 0 Personal Protection: B

### Section 2 (Physical Data)

**Physical Appearance:** Pellets  
**Boiling Point:** Not Available  
**Critical Temperature:** Not Available  
**Vapor Pressure:** Not Available  
**Volatility:** Not Available  
**Odor:** Odorless  
**Melting Point:** Not Available  
**Specific Gravity:** Not Available  
**Vapor Density:** Not Available  
**Solubility:** Insoluble in Water

### Section 3 (Fire & Explosion Hazards Data)

**Flammability of Product:** May be combustible at high temperatures.  
**Flash Points:** Not Available  
**Products of Combustion:** None Known  
**Fire & Explosion Hazards in Presence of Various Substances:** None Known  
**Fire Fighting Media and Instructions:** Use DRY Chemical Powder, Use water spray, fog or foam. Do Not Use Water Jet! Firefighters must wear SCBA & Full Protective Clothing.  
**Special Remarks on Fire & Explosion Hazards:** None Known  
**Auto-Ignition Temp.:** Not Available  
**Flammable Limits:** Not Available

### Section 4 (First Aid Measures)

**Eye Contact:** Check for & remove contact lenses. Immediately flush eyes with running water for a least 15 min., keeping eyelids open. Seek medical attention.  
**Skin Contact:** After contact with skin, wash immediately with plenty of water. Seek medical attention is irritation develops.  
**Inhalation:** Allow the victim to rest in a well ventilated area. If not breathing give artificial respiration. If breathing is difficult give oxygen. Seek immediate medical attention.  
**Ingestion:** If swallowed wash out mouth with water provided person is conscious. Seek immediate medical attention.

### Section 5 (Toxicology Information)

**Route of Exposure:** **Skin:** May cause skin irritation, May be harmful if absorbed through the skin. **Eyes:** May cause eye irritation. May cause allergic skin reaction. **Inhalation:** May be irritating to mucous membranes and upper respiratory tract. May be harmful if inhaled. **Ingestion:** May be harmful if swallowed.  
**Toxicity Data:** To the best of our knowledge the chemical, physical & toxicological properties have not been thoroughly investigated.  
**Toxic to Animals:** Not Available  
**Chronic Effects on Humans:** Not Available  
**Other Toxic Effects on Humans:** Not Available

### **Section 6 (Stability & Reactivity Data)**

**Stability:** Product is Stable at typical use temperatures      **Instability Temp.:** Not Available  
**Conditions of Instability:** None Known      **Polymerization:** Will not Occur  
**Hazardous Decomposition of products formed under fire conditions:** Carbon oxides  
**Incompatibility with various substances:** None Known

### **Section 7 (Accidental Release Measures)**

**Spill:** Use appropriate tools to clean spill. Store spilled material in a suitable container for disposal.  
**Disposal:** Consult and follow local and regional authority requirements

### **Section 8 (Special Protection Information)**

**Personal Protection:** Splash goggles, Lab coat, Gloves and Dust respirator. Be sure to use an approved/certified respirator or equivalent.  
**Exposure Limits:** Not Available (AVOID BRATHING DUST)  
**Other Protective Equipment:** Rubber Boots, Safety Shower and Eye Bath after clean up.  
**Other Precautions:** Use protective clothing, gloves, safety goggles and mask. Wash thoroughly after handling.

### **Section 9 (Storage & Handling)**

**Handling:** Use good housekeeping procedures. Normal measures for preventive fire protection.  
**Storage:** Keep container dry and tightly closed. Keep in a cool place that is well-ventilated.

### **Section 10 (Transport & Regulatory Information)**

#### **DOT**

**Proper Shipping Name:** None  
**Non-Hazardous for Transport:** This substance is considered non-hazardous for transport.  
**Non-Hazardous for Air Transport:** This substance is considered non-hazardous for air transport

#### **USA Regulatory Information**

**SARA Listed:** No

**TSCA Inventory Listed:** On the TSCA Inventory or exempt for TSCA Inventory requirements

#### **Canada Regulatory Information**

**WHMIS Classification:** This product has been classified in accordance with the hazards criteria of the CPR, and the MSDS contains all the information required by the CPR.

**DSL:** No

**NDSL:** No

**DISCLAIMER:** For R&D use only. Not for use in Food, Drugs or Cosmetics. The information contained in this MSDS is the most accurate and complete information available to us. APSC expresses or implies no warranty to the information provided and assumes no liability. The material covered in this MSDS is only provided in 1 gram quantities and is not expected to pose any health or environmental risks based on these quantities.

**Last Updated: 7/07/2008**

(Source: <http://www.ampolymer.com/MSDS/PSF.pdf>)



**Appendix 6: Results for the Permeability of He, H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> (Kapantaidakis et al (1996))**

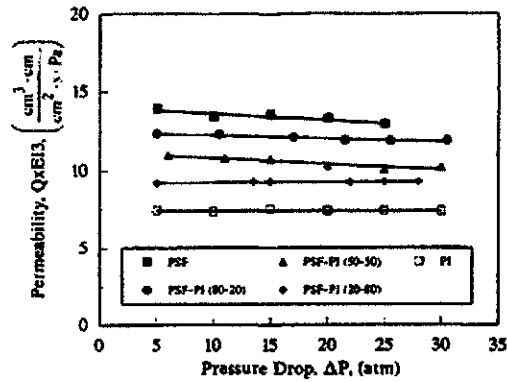


Figure I: Permeability of He for various PSF/PI blends at 40°C.

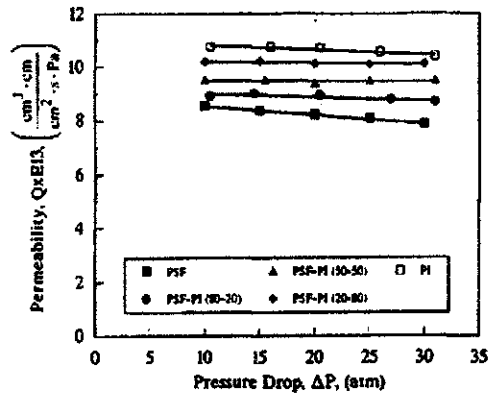


Figure II: Permeability of H<sub>2</sub> for various PSF/PI blends at 40°C.

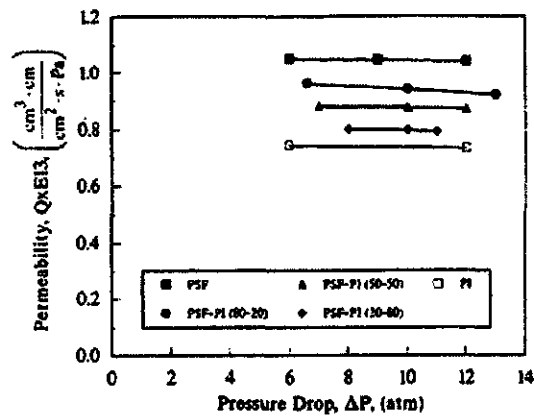


Figure III: Permeability of O<sub>2</sub> for various PSF/PI blends at 40°C.

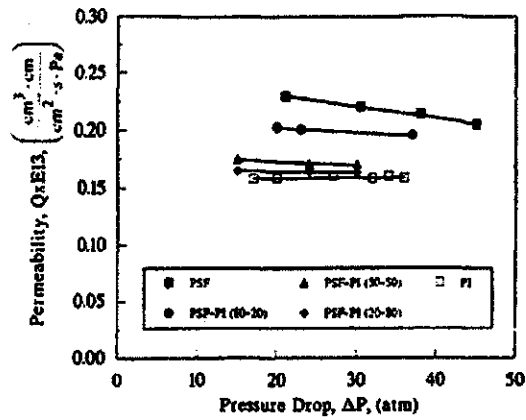


Figure IV: Permeability of N<sub>2</sub> for various PSF/PI blends at 40°C.

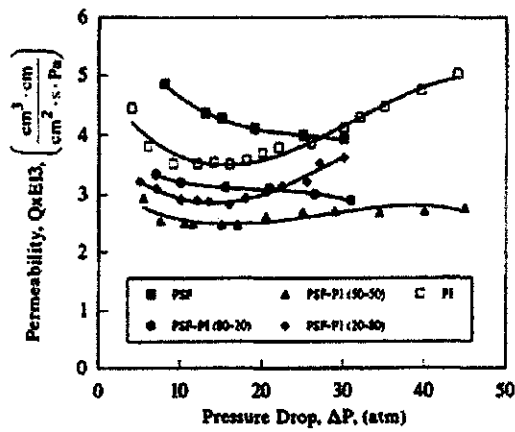
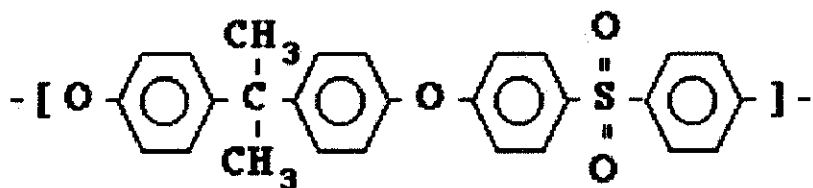




Figure V: Permeability of CO<sub>2</sub> for various PSF/PI blends at 40°C.

### Appendix 7: Calculations for Polysulfone (PSf) Solubility Parameter



Structural Group	Fdi cal 1/2 cm <sup>3</sup> /2/mol	Fpi cal 1/2 cm <sup>3</sup> /2/mol	Ehi cal/mol	No.
CH <sub>3</sub>	205	0	0	2
C	-34	0	0	1
O	49	196	717	2
SO <sub>2</sub>	289	0	3224	1
	699	54	0	4

Structural Group	Fdi	Fpi <sup>2</sup>	Ehi
CH <sub>3</sub>	410	0	0
C	-34	0	0
O	98	76832	1434
SO <sub>2</sub>	289	0	3224
	2796	11664	0
Total	3559	88496	4658

Molecular Weight (g/mol) = 442.52

Density (g/cm<sup>3</sup>) = 1.23

Molar Volume, V (cm<sup>3</sup>/mol) = MW/density  
= 359.7723577

Solubility Parameter (Group Contribution Method)

$$\delta_d = \sum F_a / V$$

$$\delta_d = 9.892366447$$

$$\delta_p = \sqrt{\sum F_{pi}^2} / V$$

$$\delta_p = 0.826863894$$

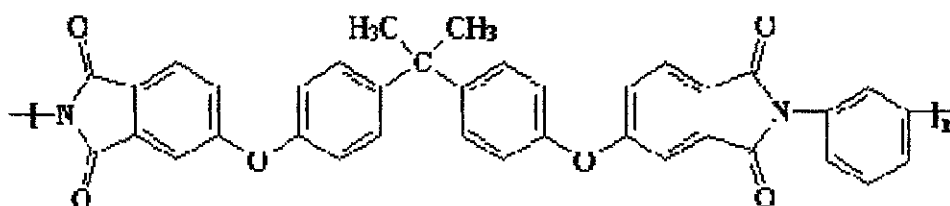
$$\delta_h = \sqrt{\sum E_{hi}} / V$$

$$\delta_h = 3.59820453$$

$$\delta^2 = \left(\sum \delta_d^i \phi^i\right)^2 + \left(\sum \delta_p^i \phi^i\right)^2 + \left(\sum \delta_h^i \phi^i\right)^2$$

Overall Solubility Parameter,  $\delta = 10.5589(\text{Mpa})^{1/2}$

## Appendix 8: Calculations for Polyimide (PI) Solubility Parameter



Structural Group	Fdi cal 1/2 cm <sup>3</sup> /2/mol	Fpi cal 1/2 cm <sup>3</sup> /2/mol	Ehi cal/mol	No.
C=O	142	376	478	4
=C	34	0	0	12
CH=	98	0	0	18
N	78	103	740	2
O	49	196	717	2
C	-34	0	0	1
CH <sub>3</sub>	205	0	0	2

Structural Group	Fdi	Fpi <sub>2</sub>	Ehi cal/mol
C=O	568	565504	1912
=C	408	0	0
CH=	1764	0	0
N	156	21218	1480
O	98	76832	1434
C	-34	0	0
CH <sub>3</sub>	410	0	0
Total	3370	663554	4826

Molecular Weight (g/mol) = 528

Density (kg/m<sup>3</sup>) = 1390

Molar Volume, V (cm<sup>3</sup>/mol) = MW/density

$$= 0.379856115$$

Solubility Parameter (Group Contribution Method)

$$\delta_d = \sum F_{di} / V$$

$$\delta_d = 8871.780303$$

$$\delta_p = \sqrt{\sum F_{pi}^2 / V}$$

$$\delta p = 0.0918179$$

$$\delta_h = \sqrt{\sum E_{hi} / V}$$

$$\delta h = 112.7156183$$

$$\delta^2 = \left(\sum \delta_d^i \phi^i\right)^2 + \left(\sum \delta_p^i \phi^i\right)^2 + \left(\sum \delta_h^i \phi^i\right)^2$$

Overall Solubility Parameter,  $\delta = 8872.4963 \text{ (Mpa)}^{1/2}$

### Appendix 9: Sample Calculation for 95% PSf, 5% PI Solubility Parameter

Dope Solution Total Weight,g	25
Polymer Weight, g	3.75
PSf Weight	3.5625
PI Weight	0.1875

Polymer	V (cm <sup>3</sup> )	Volume Fraction, $\Phi$
PSf	2.896341	0.940887
PI	0.181968	0.059113
Total	3.07831	-

For PSf,

$\delta_d$	9.892366
$\delta_p$	0.826864
$\delta_h$	3.598205

For PI,

$\delta_d$	8871.78
$\delta_p$	0.091818
$\delta_h$	11.27156

For mixture of PSf and PI according to the fraction,

$$\delta_d = (\delta_d^{\text{PSf}} \times \Phi^{\text{PSf}}) + (\delta_d^{\text{PI}} \times \Phi^{\text{PI}})$$

$$\delta_p = (\delta_p^{\text{PSf}} \times \Phi^{\text{PSf}}) + (\delta_p^{\text{PI}} \times \Phi^{\text{PI}})$$

$$\delta_h = (\delta_h^{\text{PSf}} \times \Phi^{\text{PSf}}) + (\delta_h^{\text{PI}} \times \Phi^{\text{PI}})$$

Thus,

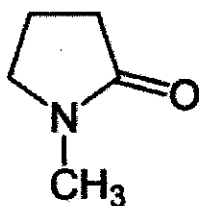
$\delta_d(\text{mix})$	533.7453
$\delta_p(\text{mix})$	0.783413
$\delta_h(\text{mix})$	4.0518

$$\delta_{\text{mix}} = (\delta_d^2 + \delta_p^2 + \delta_h^2)$$

The overall solubility parameter for the mixture is  $\delta_{\text{mix}} = 533.7612(\text{Mpa})^{1/2}$



## Appendix 10: Calculation for NMP Solubility Parameter



Structural Group	F <sub>di</sub> cal 1/2 cm <sup>3</sup> /2/mol	F <sub>pi</sub> cal 1/2 cm <sup>3</sup> /2/mol	E <sub>hi</sub> cal/mol	No.
CH <sub>2</sub>	132	0	0	3
C=O	142	376	478	1
N	10	391	1194	1
CH <sub>3</sub>	205	0	0	1

Structural Group	F <sub>di</sub>	F <sub>pi</sub> <sup>2</sup>	E <sub>hi</sub>
CH <sub>2</sub>	396	0	0
C=O	142	141376	478
N	10	152881	1194
CH <sub>3</sub>	205	0	0
Total	753	294257	1672

Molecular Weight (g/mol) = 99.13

Density (g/cm<sup>3</sup>) = 1.03

Molar Volume, V (cm<sup>3</sup>/mol) = MW/density

$$= 96.24271845$$

Solubility Parameter (Group Contribution Method)

$$\delta_d = \sum F_{di} / V$$

$$\delta_d = 7.823968526$$

$$\delta_p = \sqrt{\sum F_{pi}^2} / V$$

$$\delta_p = 5.636318416$$

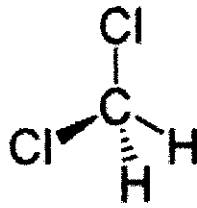
$$\delta_h = \sqrt{\sum E_{hi}} / V$$

$$\delta_h = 4.168062243$$

$$\delta^2 = \left(\sum \delta_d^i \phi^i\right)^2 + \left(\sum \delta_p^i \phi^i\right)^2 + \left(\sum \delta_h^i \phi^i\right)^2$$

Overall Solubility Parameter,  $\delta = 10.50501364 \text{ (Mpa)}^{1/2}$

### Appendix 11: Sample Calculation for DCM Solubility Parameter



Structural Group	Fdi cal 1/2 cm <sup>3</sup> /2/mol	Fpi cal 1/2 cm <sup>3</sup> /2/mol	Ehi cal/mol	No.
CH <sub>2</sub>	132	0	0	1
Cl	220	269	96	2

Structural Group	Fdi	Fpi <sub>2</sub>	Ehi
CH <sub>2</sub>	132	0	0
Cl	440	144722	192
Total	572	144722	192

Molecular Weight (g/mol) = 84.93

Density (g/cm<sup>3</sup>) = 1.325

Molar Volume, V (cm<sup>3</sup>/mol) = MW/density  
= 64.09811321

Solubility Parameter (Group Contribution Method)

$$\delta_d = \sum F_{di} / V$$

$$\delta_d = 8.923819616$$

$$\delta_p = \sqrt{\sum F_{pi}^2} / V$$

$$\delta_p = 5.935017885$$

$$\delta_h = \sqrt{\sum E_{hi}} / V$$

$$\delta_h = 1.730724699$$

$$\delta^2 = (\sum \delta_d^i \phi^i)^2 + (\sum \delta_p^i \phi^i)^2 + (\sum \delta_h^i \phi^i)^2$$

Overall Solubility Parameter,  $\delta = 10.8561 \text{ (Mpa)}^{1/2}$

**Appendix 12: Sample Calculation for 50% DCM, 50% NMP Solubility Parameter**

Dope Solution Total Weight,g	25
Solvents Weight, g	21.25
PSf Weight	10.625
PI Weight	10.625

Solvent	V (cm3)	Volume Fraction, $\Phi$
DCM	8.012820513	0.437277203
NMP	10.3115295	0.562722797
Total	18.32435	-

For DCM,

$\delta_d$	8.923819616
$\delta_p$	5.935017885
$\delta_h$	1.730724699

For NMP,

$\delta_d$	7.823968526
$\delta_p$	5.636318416
$\delta_h$	4.168062243

For mixture of NMP and DCM according to the fraction,

$$\delta_d = (\delta_d^{NMP} \times \Phi^{NMP}) + (\delta_d^{DCM} \times \Phi^{DCM})$$

$$\delta_p = (\delta_p^{NMP} \times \Phi^{NMP}) + (\delta_p^{DCM} \times \Phi^{DCM})$$

$$\delta_h = (\delta_h^{NMP} \times \Phi^{NMP}) + (\delta_h^{DCM} \times \Phi^{DCM})$$

Thus for mixtures,

$\delta_d(\text{mix})$	8.304908334
$\delta_p(\text{mix})$	5.766932884
$\delta_h(\text{mix})$	3.1022701

$$\delta_{\text{mix}} = (\delta_d^2 + \delta_p^2 + \delta_h^2)$$

The overall solubility parameter for the mixture is  $\delta_{\text{mix}} = 10.5761 \text{ (Mpa)}^{1/2}$

### Appendix 13: FTIR Results

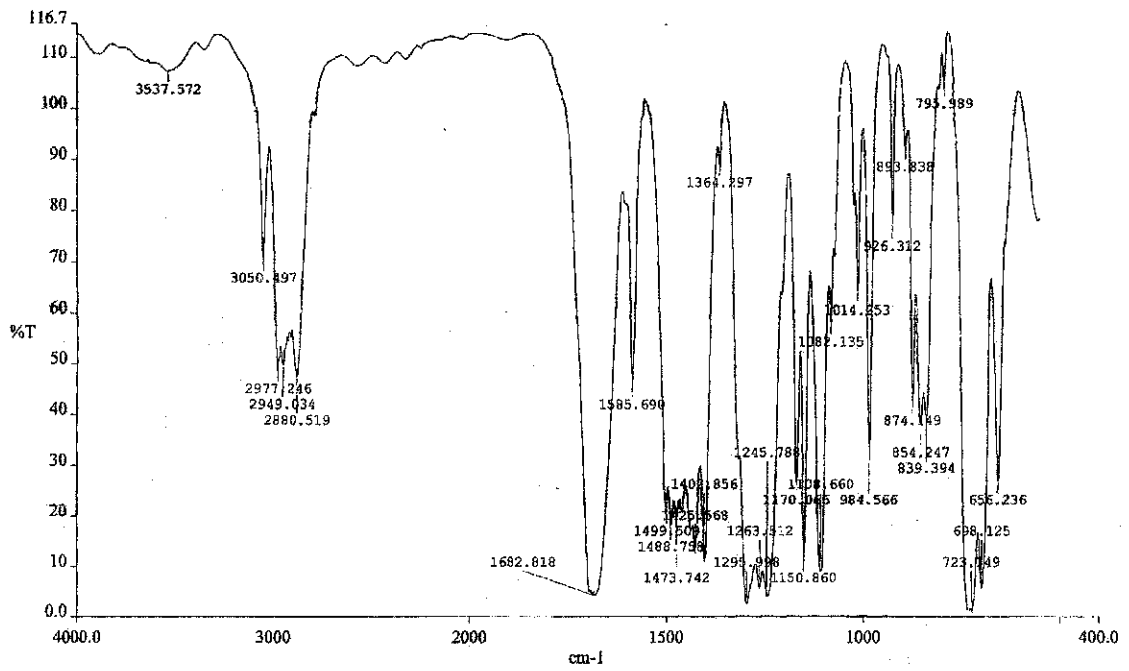


Figure 1: 100% PSF (50% DCM / 50% NMP)

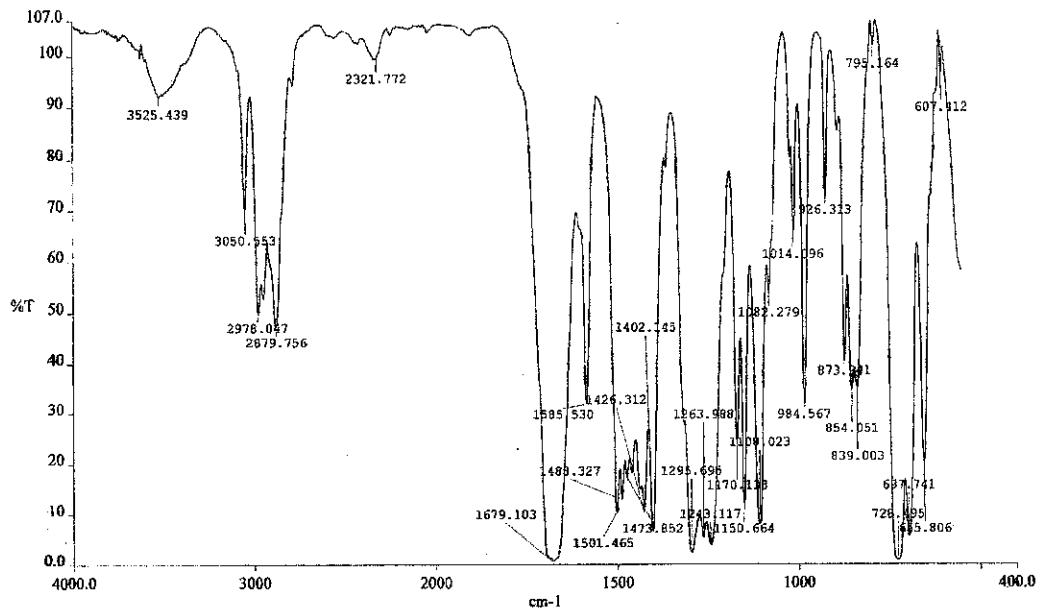


Figure 2: 95% PSF - 5% PI (50% DCM / 50% NMP)

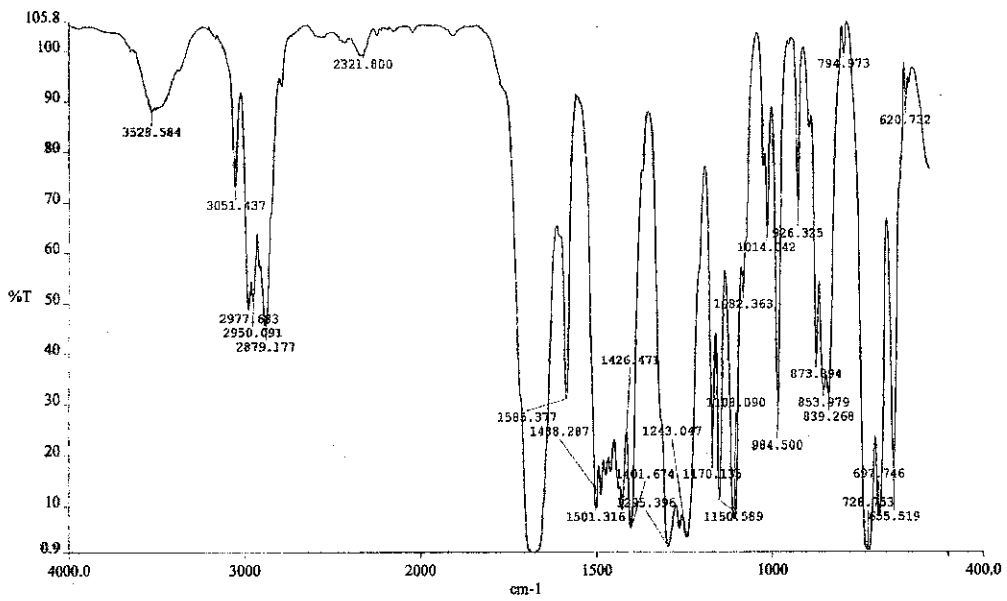


Figure 3: 90% PSF – 10% PI (50% DCM / 50% NMP)

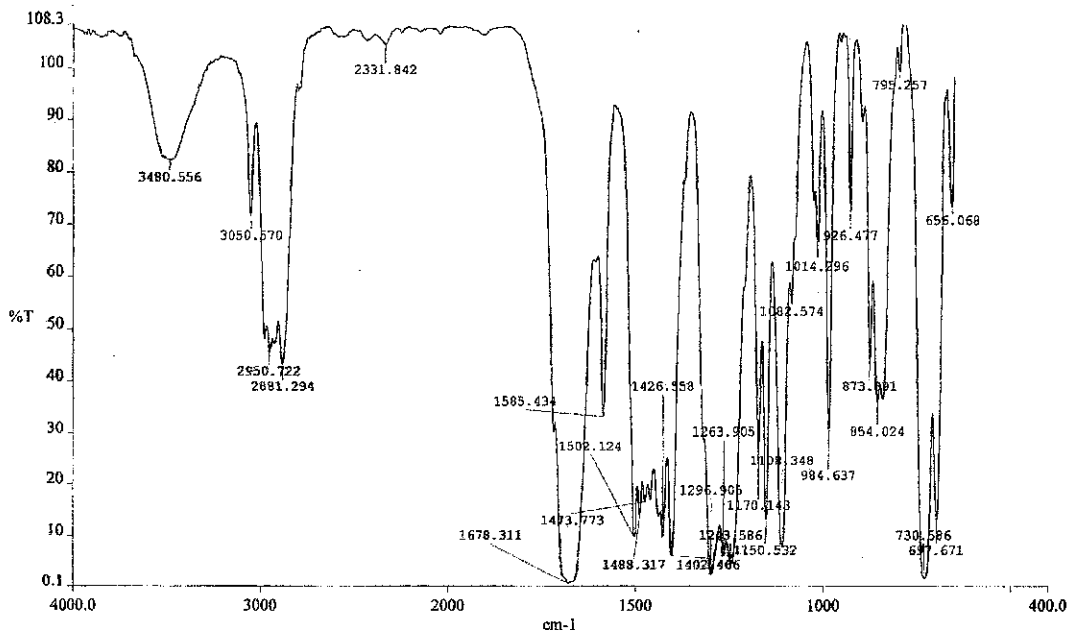


Figure 4: 85% PSF – 15% PI (50% DCM / 50% NMP)



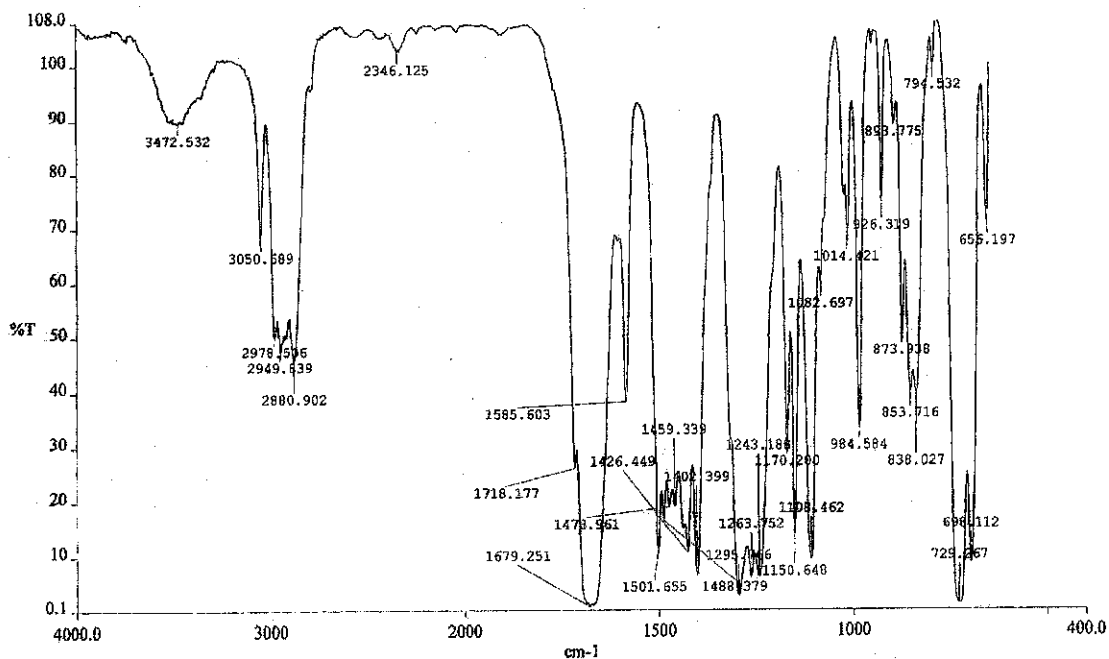


Figure 5: 80% PSF – 20% PI (50% DCM / 50% NMP)

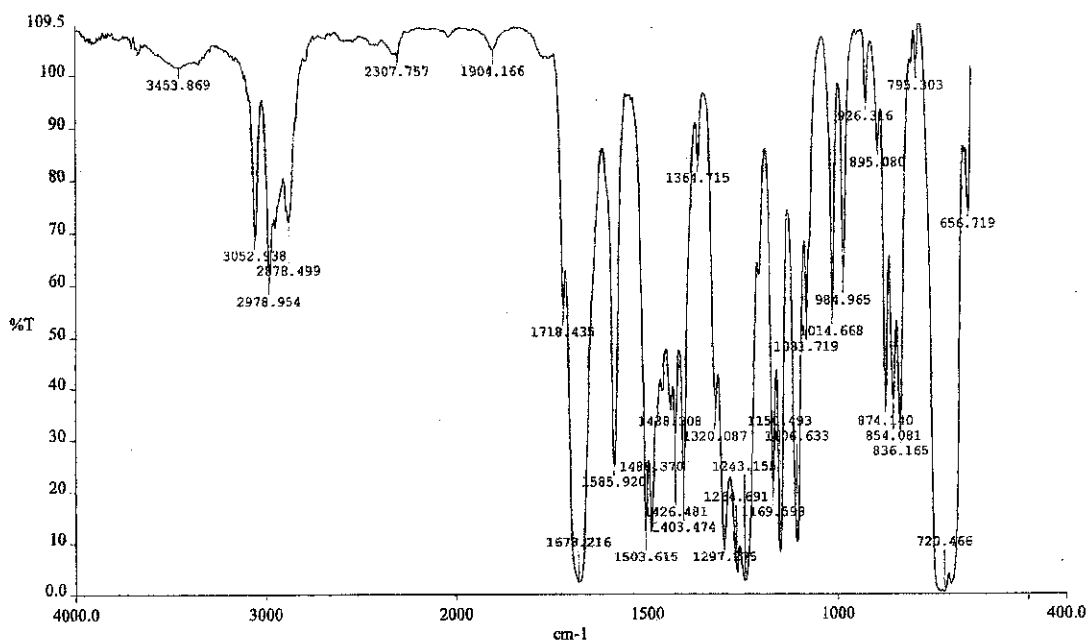


Figure 6: 95% PSF – 5% PI (80% DCM / 20% NMP)

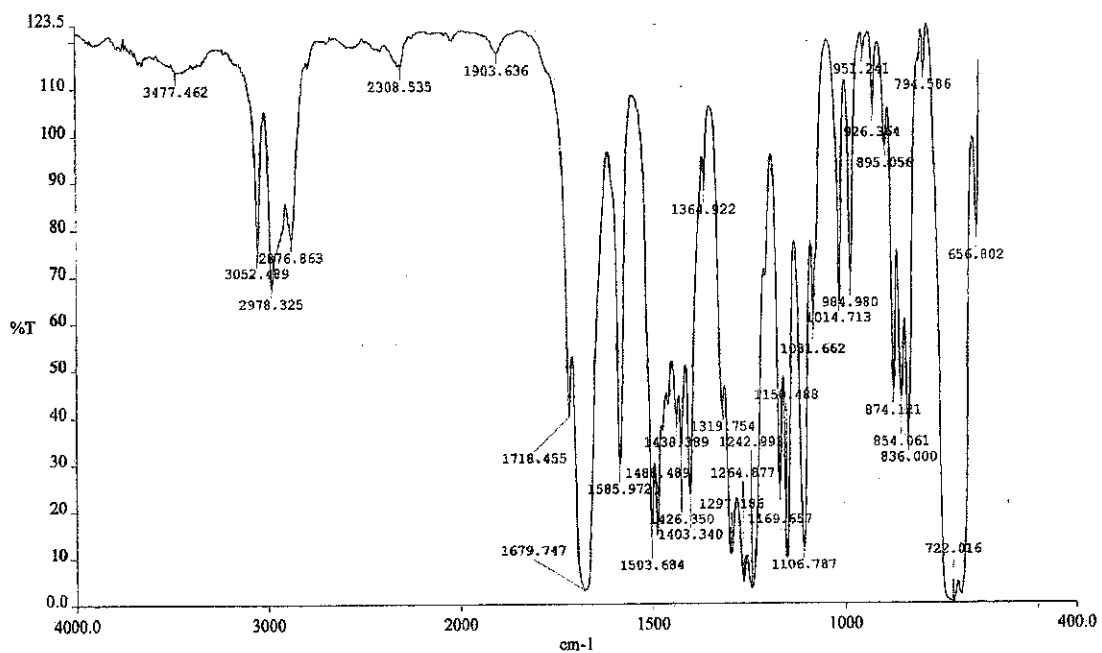


Figure 7: 90% PSF – 10% PI (80% DCM / 20% NMP)

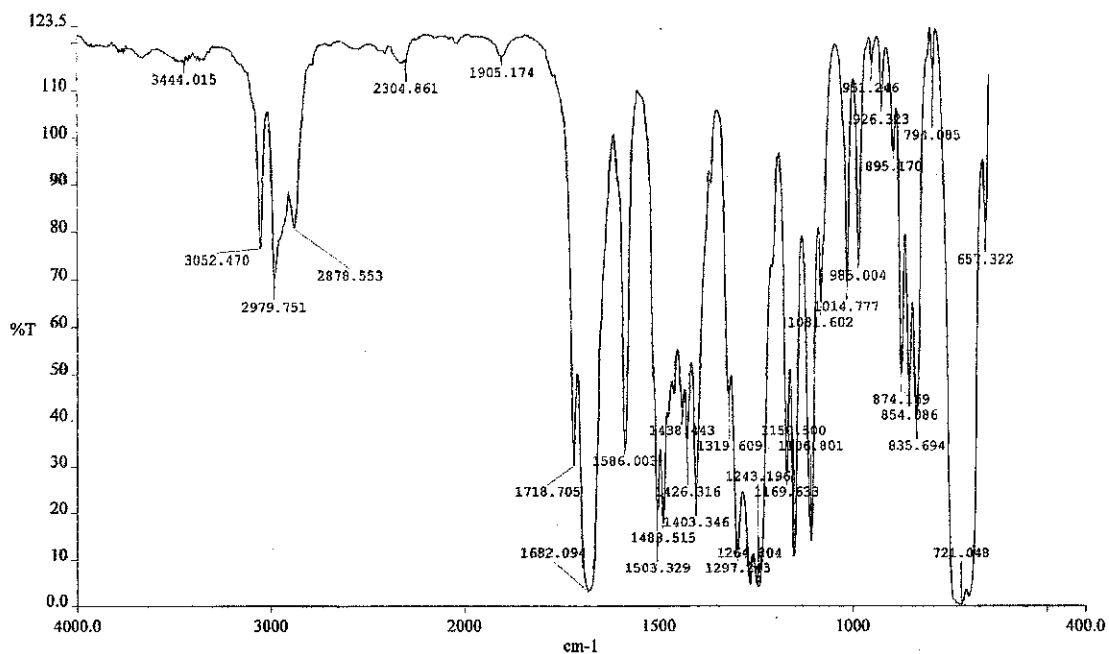


Figure 8: 85% PSF – 15% PI (80% DCM / 20% NMP)

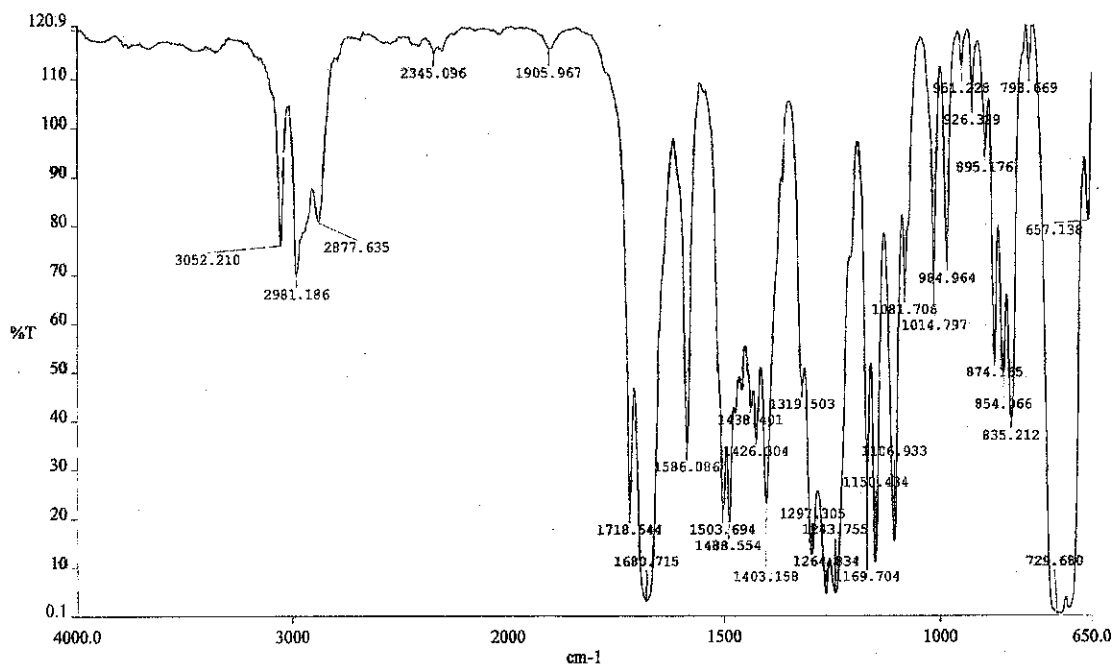


Figure 9: 80% PSF - 20% PI (80% DCM / 20% NMP)

## Appendix 14: FTIR Correlation Table

Functional Group	Molecular Motion	Wavenumber (cm <sup>-1</sup> )
alkanes	C-H stretch	2950-2800
	CH <sub>2</sub> bend	~1465
	CH <sub>3</sub> bend	~1375
	CH <sub>2</sub> bend (4 or more)	~720
alkenes	=CH stretch	3100-3010
	C=C stretch (isolated)	1690-1630
	C=C stretch (conjugated)	1640-1610
	C-H in-plane bend	1430-1290
	C-H bend (monosubstituted)	~990 & ~910
	C-H bend (disubstituted - E)	~970
	C-H bend (disubstituted - 1,1)	~890
	C-H bend (disubstituted - Z)	~700
C-H bend (trisubstituted)	~815	
alkynes	acetylenic C-H stretch	~3300
	C,C triple bond stretch	~2150
	acetylenic C-H bend	650-600
aromatics	C-H stretch	3020-3000
	C=C stretch	~1600 & ~1475
	C-H bend (mono)	770-730 & 715-685
	C-H bend (ortho)	770-735
	C-H bend (meta)	~880 & ~780 & ~690
	C-H bend (para)	850-800
alcohols	O-H stretch	~3650 or 3400-3300
	C-O stretch	1260-1000
ethers	C-O-C stretch (dialkyl)	1300-1000
	C-O-C stretch (diaryl)	~1250 & ~1120
aldehydes	C-H aldehyde stretch	~2850 & ~2750
	C=O stretch	~1725

ketones	C=O stretch	~1715
	C-C stretch	1300-1100
carboxylic acids	O-H stretch	3400-2400
	C=O stretch	1730-1700
	C-O stretch	1320-1210
	O-H bend	1440-1400
esters	C=O stretch	1750-1735
	C-C(O)-C stretch (acetates)	1260-1230
	C-C(O)-C stretch (all others)	1210-1160
acid chlorides	C=O stretch	1810-1775
	C-Cl stretch	730-550
anhydrides	C=O stretch	1830-1800&1775-1740
	C-O stretch	1300-900
amines	N-H stretch (1 per N-H bond)	3500-3300
	N-H bend	1640-1500
	C-N Stretch (alkyl)	1200-1025
	C-N Stretch (aryl)	1360-1250
	N-H bend (oop)	~800
amides	N-H stretch	3500-3180
	C=O stretch	1680-1630
	N-H bend	1640-1550
	N-H bend (1°)	1570-1515
alkyl halides	C-F stretch	1400-1000
	C-Cl stretch	785-540
	C-Br stretch	650-510
	C-I stretch	600-485
nitriles	C,N triple bond stretch	~2250
isocyanates	-N=C=O stretch	~2270
isothiocyanates	-N=C=S stretch	~2125
imines	R <sub>2</sub> C=N-R stretch	1690-1640
nitro groups	-NO <sub>2</sub> (aliphatic)	1600-1530&1390-1300

	-NO <sub>2</sub> (aromatic)	1550-1490&1355-1315
mercaptans	S-H stretch	~2550
sulfoxides	S=O stretch	~1050
sulfones	S=O stretch	~1300 & ~1150
sulfonates	S=O stretch	~1350 & ~11750
	S-O stretch	1000-750
phosphines	P-H stretch	2320-2270
	PH bend	1090-810
phosphine oxides	P=O	1210-1140

*Reference: Infrared Spectroscopy, IR Absorptions for Representative Functional Groups*  
, <http://www.chemistry.ccsu.edu/glagovich/teaching/316/ir/table.html>

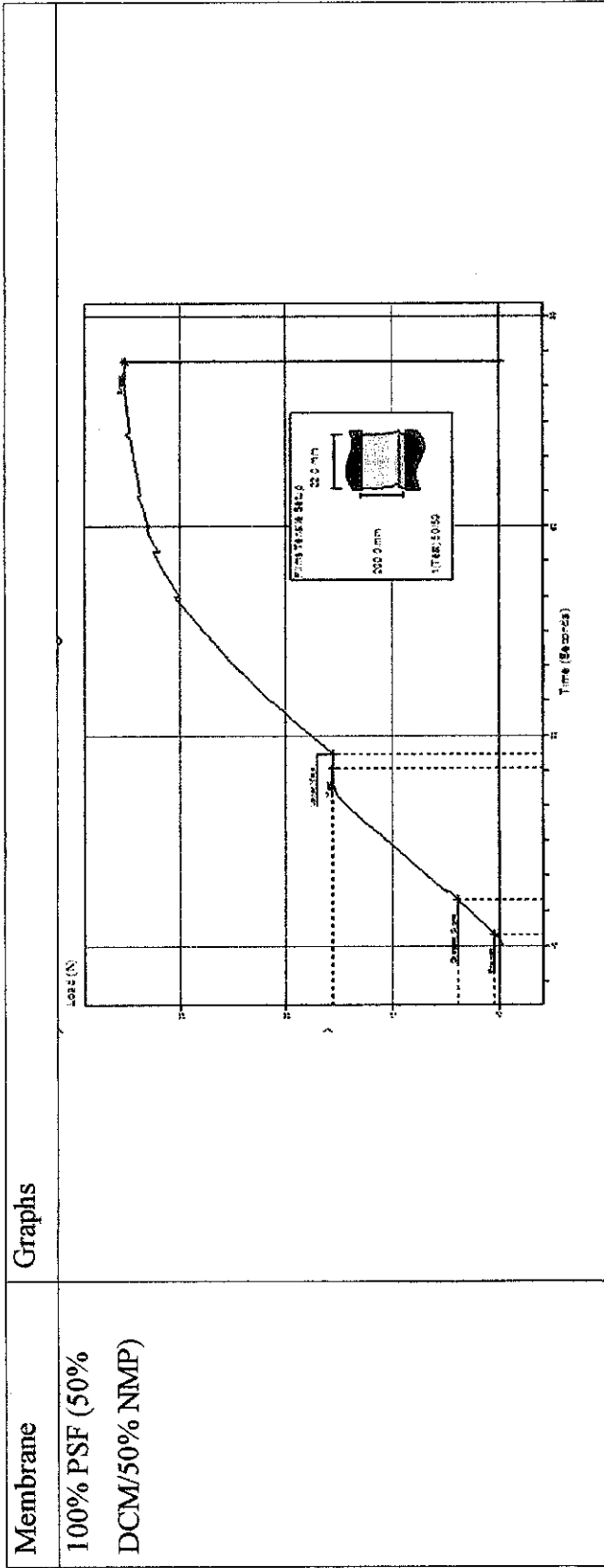
Appendix 15: Porosity Calculation

Membrane Thickness (Micrometer)

Area (cm<sup>2</sup>) 25

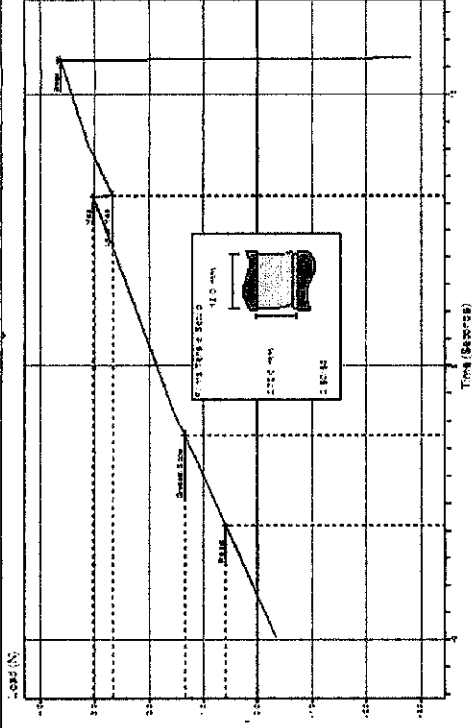
Solvents	Polymer	Thickness(μm)										Mass (gr)		Density,ρ	Porosity,ε	ε (%)		
		1	2	3	4	5	6	7	8	9	10	Average	Mass 1				Mass 2	Average
		100% PSF	315	323	321	321	323	316	315	319	329	335	321.7				0.32	0.33
95% PSF, 5% PI	307	298	305	339	303	304	319	332	307	324	313.8	0.2	0.23	0.43	0.801	0.932	93.16	
90% PSF, 10% PI	306	321	300	317	304	322	313	306	299	306	309.4	0.23	0.23	0.46	0.796	0.925	92.53	
85% PSF, 15% PI	272	277	289	328	307	303	275	306	311	301	296.9	0.32	0.31	0.63	0.791	0.893	89.27	
80% PSF, 20% PI	299	331	308	304	282	320	300	276	266	271	295.7	0.28	0.28	0.56	0.786	0.904	90.36	
100% PSF	248	249	210	256	269	217	214	221	207	287	237.8	0.35	0.3	0.65	1.240	0.912	91.18	
95% PSF, 5% PI	333	298	323	320	316	328	330	321	312	334	321.5	0.38	0.38	0.76	0.801	0.882	88.20	
90% PSF, 10% PI	297	255	269	271	252	257	303	283	252	253	269.2	0.41	0.39	0.80	0.796	0.851	85.07	
85% PSF, 15% PI	346	355	337	297	321	317	300	301	307	308	318.9	0.58	0.57	1.15	0.791	0.818	81.77	
80% PSF, 20% PI	290	284	290	290	285	284	298	307	301	286	291.5	0.58	0.58	1.16	0.786	0.797	79.75	

Appendix 16: UTM Test

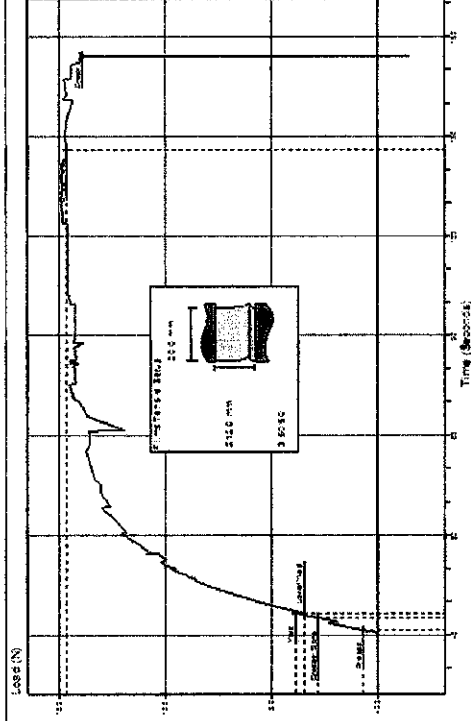




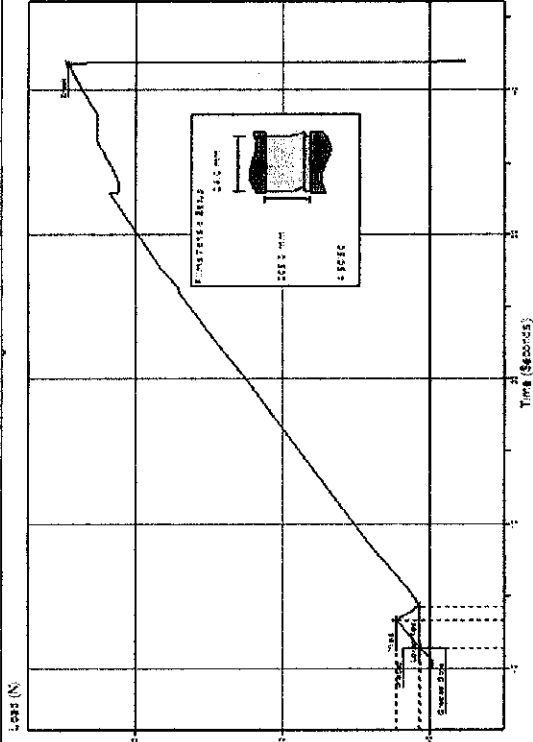
95% PSF - 5% PI  
 (50% DCM/50%  
 NMP)



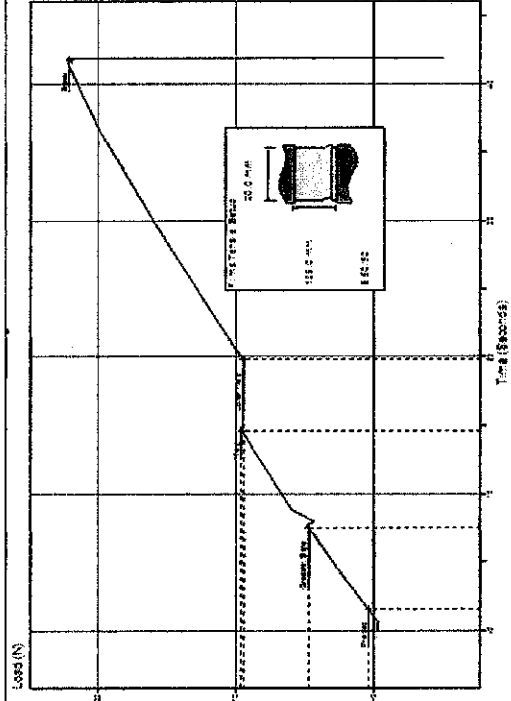
90% PSF - 10% PI  
 (50% DCM/50%  
 NMP)



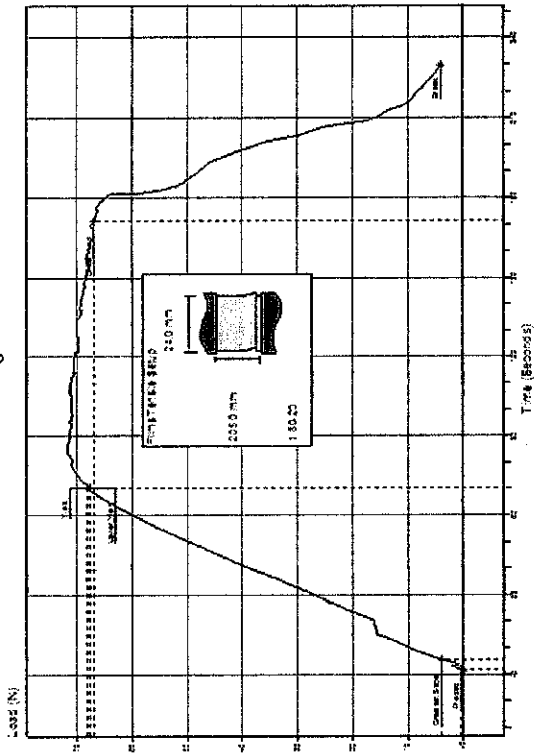
85% PSF – 15% PI  
(50% DCM/50%  
NMP)



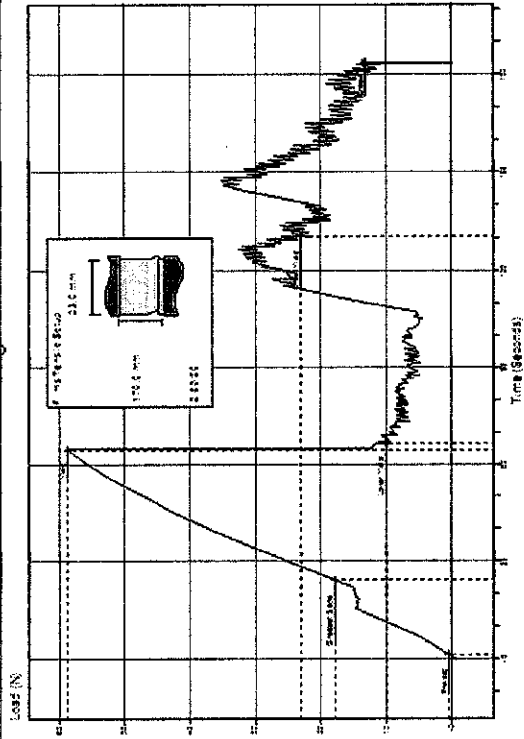
80% PSF – 20% PI  
(50% DCM/50%  
NMP)



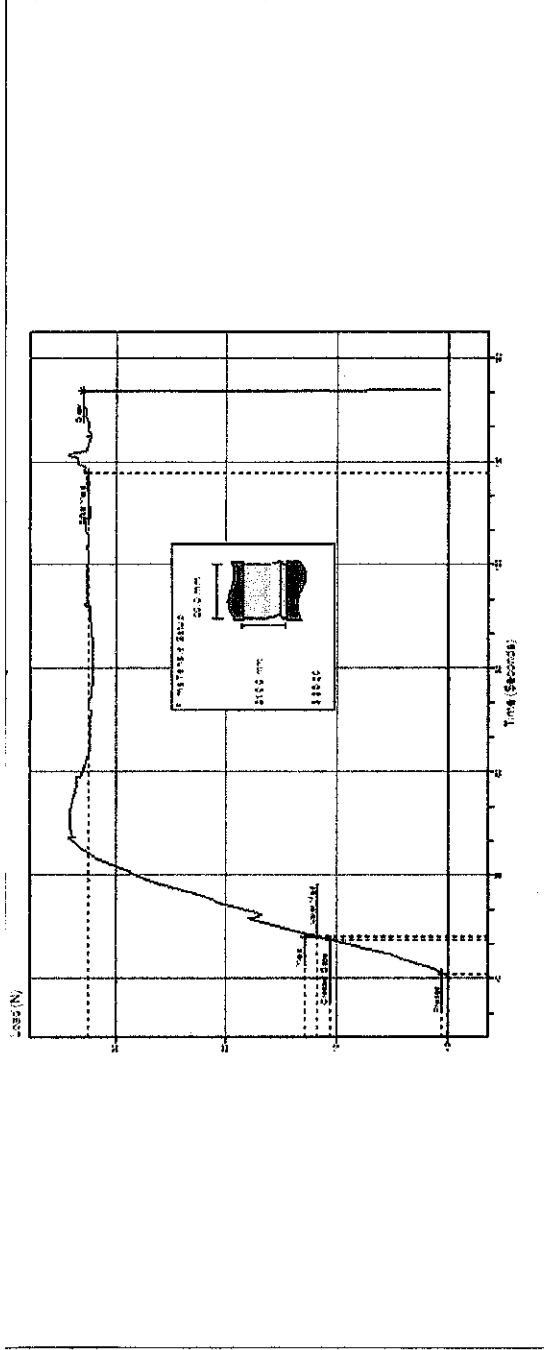
100% PSF (80%  
DCM/20% NMP)



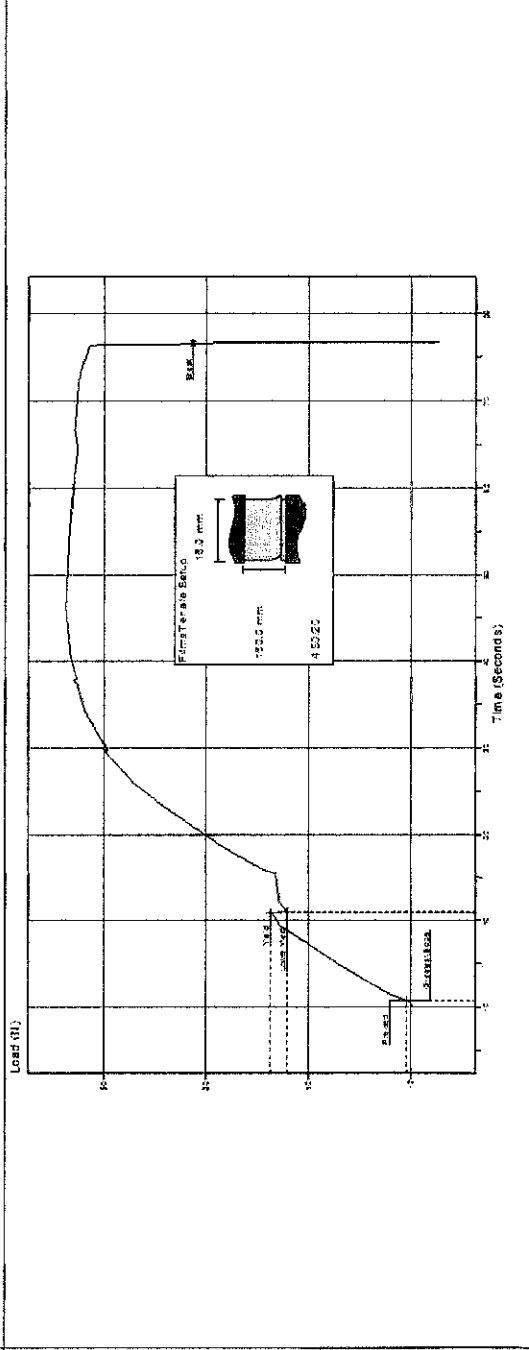
95% PSF - 5%  
PI(80% DCM/20%  
NMP)



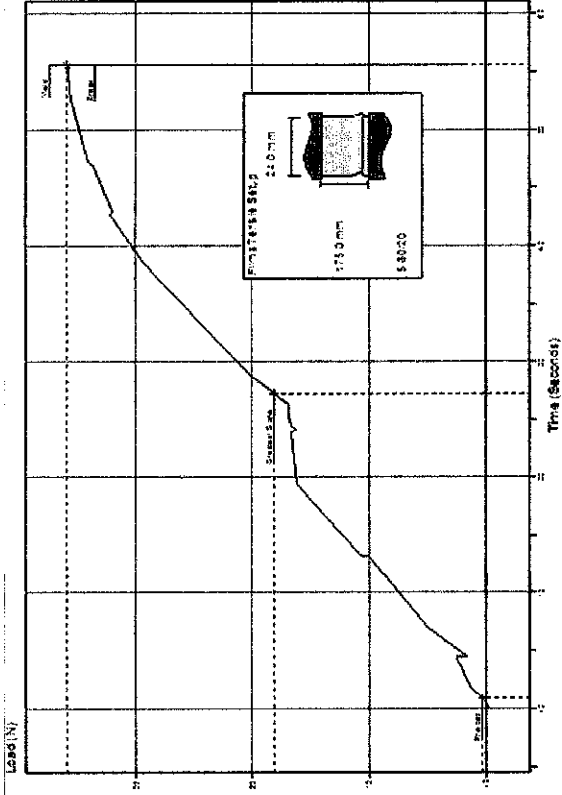
90% PSF - 10%  
PI(80% DCM/20%  
NMP)



85% PSF - 15%  
PI(80% DCM/20%  
NMP)



80% PSF - 20%  
PI(80% DCM/20%  
NMP)



## **Appendix 17: Weight Fraction Calculation**

### **Solvent Calculations**

Total Dope Solution = 25 g

Solvents (DCM and NMP) = 85%

Polymer (PI/PSF) = 15%

For 50% DCM / 50% NMP

Amount of DCM =  $0.5 \times 0.85 \times 25 = 10.625$  g

Volume =  $10.625 \text{ g} \times 1.325 \text{ g/cm}^3 = 8.01$  ml

Amount of NMP =  $0.5 \times 0.85 \times 25 = 10.625$  g

Volume =  $10.625 \text{ g} \times 1.030 \text{ g/cm}^3 = 10.31$  ml

### **Polymer Calculations**

For 95% PSF 5% PI

Amount of PI =  $0.05 \times 0.15 \times 25 = 0.1875$  g

Amount of PSF =  $0.95 \times 0.15 \times 25 = 3.5625$  g

# Appendix 18: Permeability Test Results

Membrane number	Solvent Ratio	Operation Pressure (bar)	CO <sub>2</sub> Permeation duration, t (s)	CH <sub>4</sub> Permeation duration, t (s)	Effective area, A (cm <sup>2</sup> )	Volume, V (cm <sup>3</sup> )	CO <sub>2</sub> Volumetric flow rate, Q (cm <sup>3</sup> /s)	CH <sub>4</sub> Volumetric flow rate, Q (cm <sup>3</sup> /s)	CO <sub>2</sub> Volumetric flow rate, Q (cm <sup>3</sup> (STP)/s)	CH <sub>4</sub> Volumetric flow rate, Q (cm <sup>3</sup> (STP)/s)	CO <sub>2</sub> Permeance, P/I (x10 <sup>-6</sup> cm <sup>3</sup> (STP) /cm <sup>2</sup> . s . cmHg)	CH <sub>4</sub> Permeance, P/I (x10 <sup>-6</sup> cm <sup>3</sup> (STP) /cm <sup>2</sup> . s . cmHg)	Selectivity CO <sub>2</sub> /CH <sub>4</sub>
100 % PSF		2	278	264	13.5	31	0.1115	0.0004	0.0881	0.0003	2.0848	0.1626	12.8201
		4	285	278	13.5	31	0.1088	0.0004	0.0859	0.0003	0.9918	0.0753	13.1684
		6	294	285	13.5	31	0.1054	0.0004	0.0833	0.0003	0.6213	0.0475	13.0867
		8	294	289	13.5	31	0.1054	0.0004	0.0833	0.0003	0.4660	0.0351	13.2704
		10	302	295	13.5	31	0.1026	0.0003	0.0811	0.0003	0.3533	0.0268	13.1871
95% PSF 5% PI		2	276	260	13.5	31	0.1123	0.0004	0.0887	0.0003	2.1151	0.1663	12.7174
		4	280	271	13.5	31	0.1107	0.0004	0.0875	0.0003	1.0275	0.0786	13.0661
		6	285	279	13.5	31	0.1088	0.0004	0.0859	0.0003	0.6612	0.0500	13.2158
		8	286	281	13.5	31	0.1084	0.0004	0.0856	0.0003	0.4924	0.0371	13.2640
		10	298	286	13.5	31	0.1040	0.0004	0.0822	0.0003	0.3629	0.0280	12.9564
90% PSF 10% PI	50/50	2	-	-	13.5	31	-	-	-	-	-	-	-
		4	-	-	13.5	31	-	-	-	-	-	-	-
		6	-	-	13.5	31	-	-	-	-	-	-	-
		8	-	-	13.5	31	-	-	-	-	-	-	-
		10	-	-	13.5	31	-	-	-	-	-	-	-
85% PSF- 15% PI		2	281	261	13.5	31	0.1103	0.0004	0.0872	0.0003	2.0405	0.1627	12.5391
		4	286	270	13.5	31	0.1084	0.0004	0.0856	0.0003	0.9849	0.0773	12.7448
		6	294	286	13.5	31	0.1054	0.0004	0.0833	0.0003	0.6213	0.0473	13.1327
		8	300	294	13.5	31	0.1033	0.0004	0.0816	0.0003	0.4476	0.0338	13.2300
		10	302	298	13.5	31	0.1026	0.0003	0.0811	0.0003	0.3533	0.0265	13.3212
80% PSF - 20% PI		2	286	265	13.5	31	0.1084	0.0004	0.0856	0.0003	1.9698	0.1575	12.5087
		4	290	273	13.5	31	0.1069	0.0004	0.0844	0.0003	0.9579	0.0754	12.7086
		6	298	288	13.5	31	0.1040	0.0004	0.0822	0.0003	0.6048	0.0464	13.0470
		8	302	296	13.5	31	0.1026	0.0003	0.0811	0.0003	0.4416	0.0334	13.2318
		10	310	302	13.5	31	0.1000	0.0003	0.0790	0.0003	0.3553	0.0255	13.1516

