DEVELOPMENT OF POLYETHERSULFONE–POLY VINYLIDENEFLUORIDE (PES-PVDF) THIN FILM COMPOSITE MEMBRANE FOR CO_2/N_2 GAS SEPARATION

MOHAMAD HADI BIN TAIRIN

DEGREE OF BACHELOR OF CHEMICAL ENGINEERING

UNIVERSITI MALAYSIA PAHANG

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MOHAMAD HADI BIN TAIRIN

A thesis submitted in fulfillment
of the requirements for the award of the Degree of
Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

FEBRUARY 2013

SUPERVISOR DECLARATION

“I/we hereby declare that I/we have read this thesis and in my/our opinion this thesis has fulfilled the qualities and requirements for the award of Degree of Bachelor of Chemical Engineering (GasTechnology)”

Signature : ……………………………...
Name of Supervisor I : Dr. Sunarti Bt Abdul Rahman
Position : URP Supervisor
Date : 18 February 2013

STUDENT DECLARATION

I declare that this thesis entitled “Development of Polyethersulfone–Poly Vinylidenefluoride (PES-PVDF) Thin Film Composite Membrane for Co_2/N_2 Gas Separation” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.”

Signature : ………………………………
Name : Mohamad Hadi Bin Tairin
Date : 18 February 2013

Special dedications to my mum and dad that always inspire, love and stand beside me,

and to my beloved friend.

Thank you for all your love, care and support.

ACKNOWLEDGEMENTS

Bismillahirrahmanirrahim and Alhamdulillah. Praise to God for His help and guidance that I finally able to complete this Undergraduate Research Project.

I would like to take this opportunity to express my sincere appreciation to all those people and organizations who contributed to this study. Firstly, thousands of thanks and appreciation goes to my supervisor, Dr. Sunarti Bt. Abdul Rahman, for her guidance, support, motivation, enthusiasm and willingness to teach and share her experience throughout this research project as well as her academic experience, have been invaluable to me.

I also gratefully acknowledge to Universiti Malaysia Pahang (UMP) for giving me the opportunity to take this degree course. The technical staffs of FKKSA especially Mr. Abdul Razak Abdul Hamid, Mr. Mohamad Zaki Bin Sahad, Mr. Mohd Masri Abdul Razak and Mr. Mahadhir Bin Muhammad also deserved special thanks for their assistance in supplying a good ideas, materials, apparatus, equipment, opinions and lend their hands during the research in progressing. I would like to apply most of forgiveness and apologize on my weakness and my mistake whether deliberately or accidently to all people that involved in this thesis.

Last but not the least, I would like to express my gratitude to my parents, my family, my friends and those who have directly or indirectly assisted me in the preparation of this thesis. I owe everything to them. Besides that, several people have knowingly and unknowingly helped me in the successful completion of this thesis.

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LIST OF ABBREVIATIONS

PES	-	Polyethersulfone
PVDF	-	Poly (vinylidene fluoride)
PEG	-	Polyethylene Glycol
PS	-	Polysulfone
PP	-	Polypropelyene
SEM	-	Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared
N_2	-	Nitrogen
CO_2	-	Carbon dioxide
NMP	-	N-methyl-2-pyrrolidone
TFC	-	Thin Film Composite
UF	-	Ultrafiltration
MF	-	Microfiltration
RO	-	Reverse Osmosis

LIST OF SYMBOL

P_i - Permeability for Gas component

Q - Volumetric Gas Flowrate

A - Effectiveness Membrane Area

ΔP - Pressure in System

l - Membrane Thickness

α - Selectivity

^oC - Digree Celcius

K - Kelvin

LIST OF APPENDICES

PEMBENTUKAN POLYETHERSULFONE–POLY VINYLIDENEFLUORIDE (PES-PVDF) BAGI KOMPOSIT FILEM NIPIS (TFC) UNTUK PEMISAHAN GAS KARBON DIOKSIDA ($C0_2$) DAN GAS NITROGEN (N_2)

ABSTRAK

Tujuan utama kajian ini adalah untuk menghasilkan komposit filem nipis (TFC) dengan menggunakan polietersulfon-poli (vinylidenefluoride) (PES PVDF) untuk pemisahan gas CO_2/N_2. Tujuan lain adalah untuk mengkaji segmen pada Poli (vinylidenefluoride) (PVDF) sebagai lapisan sokongan pada membran untuk meningkatkan kadar kebolehtelapan dan keterpilihan untuk pemisahan gas. Pertama, membran sokongan mestilah terdiri daripada vinylidenefluoride poli (PVDF), N-metil-2-pyrolidone (NMP) dan sedikit peratusan air. Larutan polymer dan pelarut yang merupakan larutan bagi sokongan untuk membran TFC telah disediakan dengan menggunakan kaedah konvensional dan elektrik pemanasan. Larutan untuk lapisan atas untuk kajian ini terdiri daripada PES, N-metil-2-pyrolidone (NMP) dan air atau heksana. Kemudian, larutan PES akan disalut pada PVDF membran yang telah siap dituang dan diratakan dengan menggunakan rod kaca. Lapisan untuk salutan dilaksanakan di atas plat kaca. Ujian penyerapan dijalankan dengan menggunakan gas karbon dioksida (CO_2) tulen dan gas nitrogen (N_2) tulen melalui TFC membran untuk melihat kebolehtelapan dan pemilihan gas masing-masing. Prestasi membran ini diukur berdasarkan kepada kebolehtelapan dan pemilihan untuk pemisahan gas CO_2/N_2. PVDF telah bertindak sebagai polimer asas, manakala N-metil Pyrrolidone (NMP) telah digunakan sebagai pelarut. TFC membran dianalisis menggunakan kaedah Mikroskop Imbasan Elektron (SEM) dan Sinaran inframerah transformasi Fourier (FTIR) untuk menentukan struktur dan kumpulan berfungsi yang wujud dalam membran. Gabungan antara liang-liang pada sokongan membran dan kepekatan larutan penyalut akan mencapai tahap terbaik dari segi kebolehpilihan dan kebolehtelapan masing-masing. Gas karbon dioksida (CO_2) perlu dipisahkan daripada gas bahan api untuk mengurangkan pelepasan gas karbon dioksida (CO_2) yang boleh menyebabkan isu-isu alam sekitar seperti pemanasan global, perubahan iklim dan kesan rumah hijau.

DEVELOPMENT OF POLYETHERSULFONE–POLY VINYLIDENEFLUORIDE (PES-PVDF) THIN FILM COMPOSITE MEMBRANE FOR CO_2/N_2 GAS SEPARATION

ABSTRACT

The main purpose for this study is to produce thin film composite (TFC) by using Polyethersulfone –poly (vinylidenefluoride) (PES–PVDF) for CO_2/N_2 gas separation. The other purpose is to investigate the segment of Poly (vinylidenefluoride) (PVDF) as the membrane support to improve the rate of permselectivity for gas separation. First, the support membrane was development consist of poly vinylidenefluoride (PVDF), N-methyl-2-pyrolidone (NMP) and water. The dope solution which is solution for support membrane for TFC membrane was prepared by using conventional and electrical heating method. The coating solution developed in this research consists of PES, N-methyl-2-pyrolidone (NMP) and water or hexane. Then, the PES solution was coated on the PVDF casted by using glass rod. The coating layer was performed on the glass plate. Permeation test was carried out by testing pure of CO_2 and N_2 through the TFC membrane to see the permeability and selectivity. We measure the performance of this membrane based on terms of permeability and selectivity for the CO_2/N_2 gas separation. PVDF was employed as a base polymer, while N-methyl pyrrolidone (NMP) was used as a solvent. The prepared TFC membrane was characterized using Scanning Electron Microscope (SEM) and Fourier Transform Infrared Radiation (FTIR) method to determine the structure and functional group of our membrane. The combination of support porosity and concentration of coating solution could lead to achieve the optimum of selectivity and permeability respectively. The CO_2 should be separated from the fuel gas to reduce the CO_2 emission that can cause of environmental issues like global warming, climate change and greenhouse effect.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

As energy costs rise, membrane technology for separating gases is likely to play an increasingly important role in reducing the environmental impact and costs of industrial processes. In addition, gas separation membrane units are smaller than other types of plants, like amine stripping plants, and therefore have relatively small footprints. A small footprint is important in environments such as offshore gas-processing platforms. Currently, gas separation membranes are most widely used in industry for CO_2 and water removal from natural gas. At the moment, the most widely used membrane materials for gas separation are polymers. Composite membrane including thin film composite (TFC) can be prepare by using dry and wet process. For example, in the dry process, there are the vapor depositions, the plasma-initiated polymerization and the radiation polymerization methods. In the wet process, there are polymer coating and spreding on water surface. Currently, among the types of support used for dip-coating are mostly Polysulfone (PSF) or Polyethersulfone (PES). However, Polypropelyene (PP) and polyvinylidenefluoride (PVDF) are very attractive materials as a hydrophobic support for forming a TFC membrane due to its high durability and resistance to chemicals, pH variations, and a substantially wide range of solvents. The economics of a gas separation membrane process is largely determined by the membrane's transport properties, which are permeability and selectivity for a specific gas in a mixture. Ideally, membranes should exhibit high selectivity and high permeability. For most membranes, however, as selectivity increases, permeability decreases, and vice versa.

1.2 PROBLEM STATEMENT

Membrane gas separation is a dynamic and rapidly growing field due to the high selectivity and fluxes achievable by membranes, low energy requirements, and simple, easy to operate modules. From the previous study, the formation of TFC membrane over PVDF substrate have a some weakness on the membrane characterization, strength and effectiveness of Polyethersulfone (PES) segment, and the rate of permeability and selectivity of the selected composite membrane Polyethersulfone–Poly (vinylidenefluoride) (PES-PVDF) for mixed CO_2/N_2 at varying pressure and feed concentration at ambient temperature. Now, we introduce method to improved permeability and selectivity for CO_2/N_2 gas separation.

1.3 RESEARCH OBJECTIVES

The first objective of this study are:to develop Poly-vinylidenefluoride (PVDF) membrane. The second objective are to produce thin film composite (TFC) by using Polyethersulfone–Poly (vinylidenefluoride) (PES–PVDF) polymer as membrane support for CO_2/N_2 separation. The last objectives of our research are to study the characteristic and performances of TFC membrane.

1.4 SCOPES OF STUDY

In order to achieve the objectives, the following scopes have been identified:

i. Study on production of TFC membrane preparation.
ii. Study on performances of TFC membrane for CO_2/N_2 gas separation using single gas permeation rig.
iii. Study on characteristics of the TFC membrane by using SEM and FTIR.

1.5 RATIONALE & SIGNIFICANCE

The rational of this study is to get the potential of (PES–PVDF) as basic polymers for TFC membrane development. The key problems are related to the selectivity/permeability ratio and the stability under process conditions. For such special polymers, which may have high cost, the manufacturing of thin film composite membranes and the processing of the polymer preparation from dope solutions, should be possible. Besides that, the production of TFC can be increased. Hence, it can give the beneficial to the company. In addition to the power generation industry, there have a number of different point sources which produce large CO_2 emissions. CO_2/ N_2 separation membranes can be used to create oxygen enriched air, which can be used in combustion, to get concentrated CO_2 flue gases.

CHAPTER 2

LITERATURE REVIEW

2.1 Background of the membrane

Membrane can define with different way of understanding based on different field research. The membranes also have many types and modules.

2.1.1 Definition

A membrane can be defined essentially as a semi-permeable barrier, which separates a fluid and restricts transport of various chemicals in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid, can carry a positive or negative charge or be neutral or bipolar (G. Srikanth, 2008).

2.1.2 Modules of membrane

We have three modules of membrane that commonly used in the field of gases separation industries. These modules are Spiral-Wound Modules, Hollow-Fiber Modules and Plate & Frame Modules. Each module has a different mechanical design and functions based on their applications.

2.1.2.1 Spiral-Wound Modules (brackish, UPW, wastewater, seawater)

The spiral wound module is a flat-sheet membrane sandwiched between feed and permeate spacers and wrapped around a central perforated tube that acts as the permeate channel. Membranes are manufactured as flat sheets and the membrane envelop inclusive of feed and permeate distributors is sealed on to the center tube and rolled around it to pack a large area into a small volume. They possess moderately high surface area per unit volume (900 m^2/m^3). Distributors between membrane layers promote turbulent flow to ensure low fouling and longer life (S. Sridhar and K. Sunitha, 2008). Figure 2.1 shows the basic mechanism of Spiral-Wound Modules.

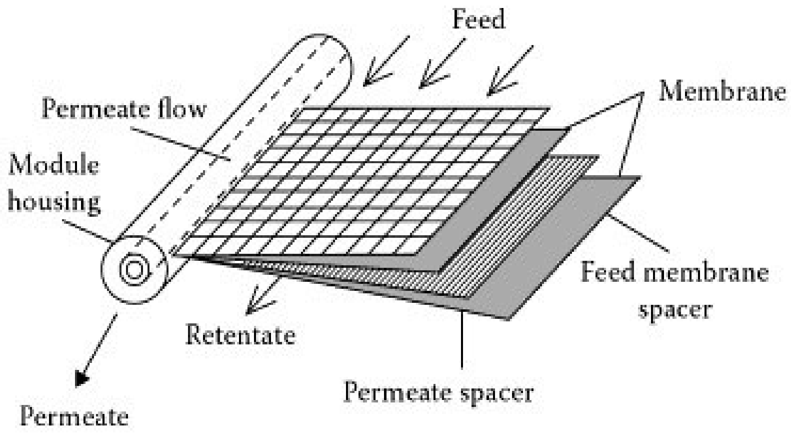


Figure 2.1: Spiral-Wound Modules

2.1.2.2 Hollow-Fiber Modules (RO, gas separations)

This type of module contains thousands of hollow fibers in a compact volume and sealed at the end and housed a shell. The feed solution either in radial or parallel mode with respect to the fibers depending on the permeate direction. Thus, configuring membranes into hollow fibers enables the packaging of large areas of membrane in very compact volumes. Higher membrane packing density in a module leads to lower production costs. Hollow fibers for PV can be produced by coating ultra-porous hollow of PAN, PES, or PSF with solutions of PVA, chitosan, CS, and so forth. The surface area obtained with HF membranes could go up to 10 000 m^2/m^3 (S. Sridhar and K. Sunitha., 2008). Figure 2.2 shows the basic mechanism of Hollow-Fiber Module.

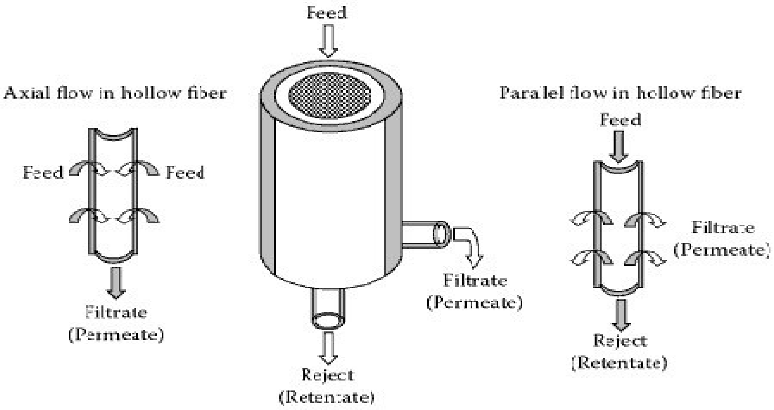


Figure 2.2: Hollow-Fiber Module

2.1.2.3 Plate & Frame Modules (filter presses, laboratory, MBRs)

A plate and frame module is similar to that of a filter press. The flat membranes are placed in a sandwich-like fashion with their feed sides facing each other. A suitable distributor is placed in between each feed and permeate compartment. The number of membrane sets needed for a given surface area furnished with feed and vacuum chamber distributors, sealing gaskets, and two end plates constitute one plate and frame module, and several such modules can be arranged in series or parallel. The main advantages of this module are its flexibility toward different separation tasks for instance, replaceable feed distributors for viscous media or in cases where high turbulence is needed. These modules are used for both organophilic as well as hydrophilic separations (S. Sridhar and K. Sunitha., 2008). Figure 2.3 shows the basic mechanism of Plate & Frame Modules.

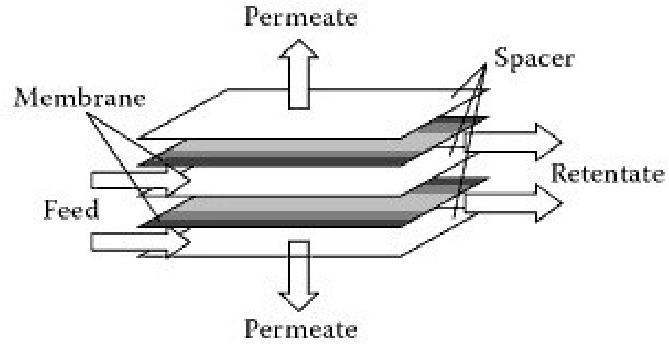


Figure 2.3: Plate & Frame Modules

2.1.3 Membrane process, type, material and application

Table 2.1: Membrane characterization (G. Srikanth, 2008)

Process	**Membrane type and pore radius**	**Membrane material**	**Process driving force**	**Applications**
Microfiltration	Symmetric macroporous, 0.1 – 1.0 microns	Cellulose nitrate or acetate, PVDF, polyamides, Polysulfone, PTFE, metal oxides, etc.	Hydrostatic pressure differences at approximately 10-30 psi	Bacteria and cyst filtration, clarification, potable water treatment, RO pre-treatment
Ultrafiltration	Asymmetric microporous, 0.001-0.1 microns	Polysulfone, polypropylene, nylon 6, acrylic copolymer	Hydrostatic pressure differences at approximately 30-100 psi	Separation of macromolecular solution, RO pretreatment, potable water treatment
Gas separation	Asymmetric homogeneous polymer	Polymer and copolymers	Hydrostatic pressure and concentration gradients	Separation of gas mixtures
Nanofilteration	Thin-film membrane	TFC	50-150 psi	Removal of hardness desalting

2.1.4 Structure of Membrane

Membrane for gas separation can divide by two type of structure. The first group is symmetric membrane that consists of porous and non-porous membrane. The other group is asymmetric membrane that consists of porous and composite membrane. Any groups have a different characteristic.

2.1.4.1 Symmetric Membrane

Symmetric membranes are the diameter of pores is constant throughout the cross section of the membrane, as membrane thickness causes draw to mass transfer.

2.1.4.2 Asymmetric Membrane

Asymmetric membranes the pore size at the surface have a different sixe compared with the holes at the bottom side. Large particles will not enter the body of the membrane so plugging is avoided. The asymmetric membranes were found to give smaller pore size compared to symmetric membranes. The orientation of asymmetric membranes provided different results for the mean pore size. The example of asymmetric membrane is from Thin-Film Composite (TFC) membranes. The application of this type of membrane is more to the gas separation.

(i) Porous Membrane

In porous membranes when gas transport takes place by viscous flow, no separation is achieved because the mean free path of the gas molecules is very small relative to the pore diameter (Maryam. et al. 2009). The example of porous symmetric membrane is alumina and other metal oxide membranes. Porous alumina ceramics are very well known and widely used as catalyst supports.

(ii) Non-Porous Membrane

Gas separation through nonporous membranes depends on differences in the permeability of various gases through a given membrane (D Richard. et al. 2011). Application of non-porous inorganic membranes is primarily for highly selective separation of gases such as hydrogen and oxygen. However, dense membranes have limited industrial application due to their low permeability compared to porous inorganic membranes.

2.1.5 Advantages of membrane

The membrane processes give certain advantages such as compactness and light in weight, low labour intensity, modular design permitting easy expansion or operation at partial capacity, low maintenance (no moving parts), low energy requirements and low cost especially so for small sizes (P.Bernardo et. al, 2009). Membrane processes can separate at the molecular scale up to a scale at which particles can actually be seen, this implies that a very large number of separation needs might actually be met by membrane processes. Membrane processes present basically a very simple flowsheet. There are no moving parts (except for pumps or compressors), no complex control schemes, and little ancillary equipment compared to many other processes. As such, they can offer a simple, easy-to-operate and low maintenance process option.

2.1.6 Disadvantages of membrane

The producing membrane that have high selectivity and high fluxes and that are mechanically stable is far more difficult in hollow-fiber form than with the flat sheets used in spiral-wound modules. The best membranes cannot be formed into hollow fibers (J. Zuo et. al, 2010). Membrane processes seldom produce 2 pure products, that is, one of the two streams is almost always contaminated with a minor amount of a second component. In some cases, a product can only be concentrated as a retentive because of osmotic pressure problems. In other cases the permeate stream can contain significant amount of materials which one is trying to concentrate in the retentive because the membrane selectivity is not infinite. Membrane processes can be saddled with major problems of fouling of the membranes while processing some type of feed streams. This fouling, especially if it is difficult to remove, can greatly restrict the permeation rate through the membranes and make them essentially unsuitable for such applications.

2.1.7 Gas permeation in a membrane

The permeation of gas molecules through polymers and the gas separation ability of polymers were observed and described over a century ago. In 1866, Thomas Graham demonstrated gas separation processes by showing that air can be enriched in O_2 by permeation through natural rubber polymeric membranes. Different gases pass through certain membranes at significantly different rates, thus permitting a partial separation. The rate of permeation is proportional to the pressure differential across die membrane and inversely proportional to the membrane thickness. The rate of permeation is also proportional to the solubility of the gas in the membrane and also to the diffusivity of gas through the membrane (Maryam. et al. 2009). Figure 5 shows the gas permeation process.

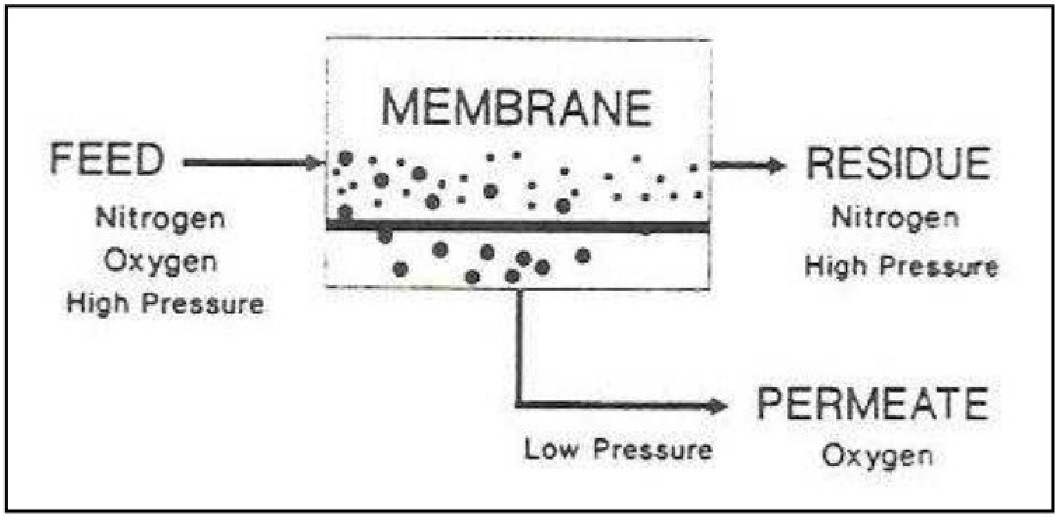


Figure 2.4: Gas permeation membrane process

(Source: Maryam. et al. 2009)

2.1.8 Mechanism of membrane separation process

Membrane devices for gas or vapor separation usually operate under continuous steady-state conditions with three streams. The feed stream is a high-pressure gas mixture passes along one side of the membrane. The molecules that permeate the membrane are swept using a gas on the other side of the membrane is called permeate stream. The non-permeating molecules that remain on the feed-stream side exit the membrane called as the retentate stream. In most of the membrane processes, the driving force is a pressure difference or a concentration (or activity) difference across the membrane. Parameters such as pressure, concentration (or activity) and even temperature may be included in one parameter, the chemical potential μ. Another driving force in membrane separations is the electrical potential difference. This driving force only influences the transport of charged particles or molecules (T. R. Maryam. et al. 2009).

2.1.8.1 Pressure Driven: (RO, NF, UF, MF, MBR, Gas)

Reverse Osmosis (RO) is a pressure driven membrane diffusion process for separating dissolved solutes. RO membranes have the smallest pore structure (Srikanth G., 1999). This membrane type is very popular and used. Configuration of this membrane is in spiral-wound or hollow fiber. The disadvantages of this membrane type are the flow limited by concentration polarization, fouling problems and need to pretreatment. The application of this membrane type is desalting of process water, desalination of brackish or seawater, concentration wastewater in paper pulping and production of ultrapure water for laboratories or electronic industry.

Nanofiltration (NF) is a form of filtration that uses membranes to separate different fluids or ions. Membranes used for NF are of cellulosic acetate and aromatic polyamide. NF is not effective on small molecular weight organics, such as methanol (Baker, R. W.,1995). This membrane is efficiently rejects, due to electrostatic interactions, charged particles and mainly multivalent ions. The applications of this membrane type are in water pretreatment, food industry and recovery of metals.

Ultrafiltration (UF) is used to separate a solution that has a mixture of some desirable components and some that are not desirable. UF is typically not effective at separating organic streams (Srikanth G., 1999). This is microporous membranes. The pore size is between 1 and 50 nm. The operating pressure is moderate high which is1 to 10 bar. Some advantages for this membrane are easy cleaning, long lifetime and available sterilization. The application of this membrane type is in food industry, wastewater treatment and also potentially useful in paper pulping and textile industry.

Microfiltration (MF) is a process of separating material of colloidal size and larger than true solutions. A microfiltration membrane is generally porous enough to pass molecules of true solutions, even if they are large (R. Ahmad et al. 2010). This type of separation processes is very popular and used. The pore size is between 0.05 and 10 μm (0.45 μm) and low operation pressure. The application of this type membrane is in bio-engineering, food industry, and wastewater treatment.

2.2 Membrane gas separation

2.2.1 History

The first scientific observation related to gas separation membrane was made by J. K. Mitchell, as early an 1831. He observed that natural rubber ballons in gas atmospheres with different compositions expanded with different velocities, depending on the nature of the gas: hydrogen filled expanded faster than air. Since in the 1990's, Generon, Praxair, and Medal had released new polymeric membrane with oxygen/nitrogen selectivities of 6 – 8. These membranes could produce more than 99 % nitrogen purity and offered a cost-competitive alternative to delivered liquid nitrogen for many small users. This application has grown to account for one-third of new nitrogen production, and currently, there are 5000 – 10,000 nitrogen systems operating worldwide. As of 2002, gas separation membrane equipment has grown into a $150 million/year market. The majority of the gas separations involve the separation of non-condensable gases, such as N_2 from air, CO_2 from CH_4, and H_2 from N_2, Ar or CH_4. Currently, many efforts are still underway to open up the market of condensable gases separations such as butane from methane, propylene from propane, and n-butane from isobutene (P.Bernardo et al., 2009).

2.2.2 Application of membrane gas separation

Currently, gas separation membranes are most widely used in industry for hydrogen separation, for example, hydrogen/nitrogen separation in ammonia plants and hydrogen/hydrocarbon separations in petrochemical applications.

Hydrogen recovery was among the first large-scale commercial applications of membrane gas separation technology. In fact, the ammonia reactor operates at high pressures (ca.130bar), thus providing the necessary driving force for separation. The H_2/N_2 membrane selectivity is high and the feed gas is free of contaminants. This technology has been extended to other situations for recovery of hydrogen from gas mixtures (H_2/CO or H_2/CH_4 ratios adjustment for syngas production) and has been successfully competing with cryogenic distillation and Pressure Swing Adsorption (PSA) processes (T.M. Abdulreza, 1999).

Polymeric membranes are today more developed and commercially available for CO_2 separation. Rubbery polymers have attracted greater interest for the separation of CO_2 from H_2 due to higher flux rates and high selectivity (Reza Abedini and Amir Nezhadmoghadam, 2010). Polymeric membranes have been developed for variety of industrial applications including gas separation. Gas membranes are now widely used in variety of application, as shown in Table 2.2.

Table 2.2: Application of Membrane for Gas Separation

Common gas separation	Application
O_2/N_2	Oxygen enrichment, inert gas separation
H_2/Hydrocarbons	Refinery hydrogen recovery
H_2/N_2	Ammonia purge gas
H_2/CO	Syngas ratio adjustment
CO_2/Hydrocarbons	Acid gas treatment, landfill gas upgrading
H_2S/Hydrocarbon	Sour gas treatment
He/Hydrocarbon	Helium separation
Hydrocarbons/Air	Hydrocarbons recovery, pollution control
H_20/Air	Air dehumidification

2.2.3 Characteristics of membrane for gas separation

The performance of a membrane is in general characterized by its flux, selectivity, morphology, and filtration performance and fouling analysis. The gas separation properties of membranes depend upon:

- The material (permeability, separation factors)
- The membrane structure and thickness (permeance)
- The membrane configuration (flat, hollow fiber) and
- The module and system design.

Both membranes permeability and selectivity influence the economics of a gas separation membrane process (P.Bernardo.et. al, 2009).

2.2.4 Types of membrane gas separation

Normally, membrane gas separation can be classified by four types of membrane. These types are commonly used in the industrial membrane gas separation.

2.2.4.1 Polymer

The main rubbery and glassy polymers employed for gas separation membranes are listed in Table above (P.Bernardo.et. al, 2009).

Table 2.3: Polymer in gas separation

Most Important Glassy and Rubbery Polymers Used in Industrial Membrane Gas Separation	
Rubbery polymers	Glassy polymers
- Poly (dimethylsiloxane) - Ethylene oxide/propylene oxide - Amide copolymers	- Cellulose acetate - Polyperfluorodioxoles - Polycarbonates - Polyimides - Poly (phenylene oxide) - polysulfone

2.2.4.2 Solubility-Controlled Membranes

Solubility controlled membranes, sometimes referred to as "reverse-selective membranes", preferentially allow large gas or vapor molecules to permeate in a gaseous mixture containing smaller molecules. These membranes find application in the separation of CO_2 from lighter gases, in VOCs removal from permanent gas streams, in monomer recovery from the exhaust of polymerization reactors, and are studied for the removal of higher hydrocarbons from methane (P.Bernardo.et. al, 2009).

2.2.4.3 Mixed Matrix Membranes

Mixed matrix membranes (MMMs) are a well-known route to enhance the properties of polymeric membranes. Their micro structure consists of an inorganic material in the form of micro or nanoparticles (discrete phase) incorporated into a polymeric matrix (continuous phase). The use of two materials with different flux and selectivity provides the possibility to better design a gas separation membrane, allowing the synergistic combination of polymers easy process ability and the superior GS performance of inorganic materials (P.Bernardo.et. al, 2009).

2.2.4.4 Zeolite Membranes

Zeolite membranes in principle might separate continuous mixtures on the basis of differences in the molecular size and shape, but also on the basis of different adsorption properties. The separation ability of a micro porous membrane can be described by the inter play of the mixture adsorption equilibrium and the mixture diffusion in away similar to the solubility diffusion model established for describing the permeation behavior of dense organic polymer membranes (P.Bernardo.et. al, 2009). Zeolite membranes have uniform, molecular-sized pores, and they separate molecules based on differences in the molecules’ adsorption and diffusion properties. Zeolite membranes are thus well suited for separating liquid-phase mixtures by pervaporation, and the first commercial application of zeolite membranes has been for dehydrating organic compounds.

2.2.5 Mechanism of membrane gas separation

Membrane devices for gas or vapor separation usually operate under continuous steady-state conditions with three streams. The feed stream is a high pressure gas mixture and passes along one side of the membrane. The second stream is the molecules that permeate the membrane are swept using a gas on the other side of the membrane. The third stream is the non-permeating molecules which are that remain on the feed-stream side exit the membrane as the retentive stream. A pressure difference across the membrane drives the permeation process (S. Sridhar et al, 2007).

2.2.6 Factors affecting membrane performance

The membrane performances are much related to feed conditions. The factor effecting to the membrane performances are feed composition and concentration, feed and permeate pressure and relation between permeability and selectivity of gas separation.

2.2.6.1 Feed Composition and Concentration

A change in feed composition will directly affect the sorption phenomena (degree of swelling) at the gas-membrane interface as envisaged by the sorption-diffusion principle. Since the diffusion of gaseous components in the membrane is dependent upon the concentration of the components (or solubility of the components), the permeation characteristics are greatly influenced by the feed composition (S. Sridhar et al. 2007).

2.2.6.2 Feed and Permeate Pressure

The driving force in gas separation is the partial pressure gradient across the membrane. The flow of a component, say I, across the membrane can thus occur only if the partial pressure (product of mole fraction and total pressure) of component I at the feed side of the membrane is greater than the partial pressure of the same component at the permeate side (S. Sridhar et al. 2007).

2.2.7 Relation between permeability and selectivity for gas separation

A high permeability and selectivity can be achieved by conducting a permeation test towards the gases. However, in the reality, a high permeability contributes to low selectivity and vice versa. The gas permeability (P) was calculated using Eqn (1) and expressed in Barrer [1 Barrer = 1 × 10−10 (cm^3 (STP) cm) / (cm^2 scmHg)]. The gas permeability (*P*) was calculated using this equation:

$$P = \frac{Vl}{At\ \Delta P} = (\mathrm{cm}^3\ (\mathrm{STP})\ \mathrm{cm}) / (\mathrm{cm}^2\ \mathrm{scmHg}) \qquad (1)$$

The permeance (P/l) for TFC membranes was calculated using Eqn (2) and expressed in GPU [1 GPU = 1 × 10^{-6} cm^3 (STP) / (cm^2 scmHg)].

$$\frac{P}{l} = \frac{V}{At\ \Delta P} = (\mathrm{cm}^3\ (\mathrm{STP})\ \mathrm{cm}) / (\mathrm{cm}^2\ \mathrm{sHg}) \qquad (2)$$

Where l is the thickness of membrane in cm, A is the effective membrane area in cm^2, V the volume (cm^3) displaced in time t (s) ,and ΔP is the transmembrane pressure expressed in cmHg. The selectivity (α) is expressed as the ratio of two pure gas permeance (in case of TFC membranes) or of permeabilities (incase of dense membranes). Simplify from above equation,

$$\frac{P}{l} = \frac{Q}{A\,\Delta P} = (\text{cm}^3\ (\text{STP})\ \text{cm}) / (\text{cm}^2\ \text{sHg}) \qquad (3)$$

Where the volumetric flowrate, Q in specific unit (cm^3/sec).

Gas diffusivity depends on the ability of small gas molecules to undergo diffusive jumps, which occur when thermally driven, random, cooperative polymer segmental dynamics from transient gaps, large enough to accommodate penetrants, in the immediate vicinity of the gas molecules. Like solubility, diffusivity depends on the membrane operating conditions. Moreover, gas diffusivity is also sensitive to properties such as penetrant size, polymer morphology and polymer segmental motions (A. L. Ahmad. et al. 2009).

2.3 TFC membrane for gas separation

Thin film composite (TFC) membranes have found large scale applications in various membrane separation processes including reverse osmosis, pervaporation and gas separation. Permeate flow through the composite membrane may be controlled by the mass transfer resistance of the coating film layer, the under laying porous support membrane or a combination of at least two type of polymer (S.K. Karode et al. 1995).

2.3.1 Application TFC membrane for gas separation

Thin film composite (TFC) membranes have found large scale applications in various membrane separation processes including reverse osmosis, pervaporation and gas separation.

2.3.2 Advantages TFC membrane for gas separation

The membrane processes give certain advantages such as compactness and light in weight, low labour intensity, modular design permitting easy expansion or operation at partial capacity, low maintenance (no moving parts), low energy requirements and low cost especially so for small sizes (P.Bernardo et. al, 2009).

2.3.3 Disadvantages TFC membrane for gas separation

One of the major problems confronting the use of membrane based gas separation processes in a wide range of applications is the lack of membranes with high pressure normalized flux and high selectivity. During fabrication, certain factors need proper attention in order to produce a good gas separation membrane (W. J. Koros et al. 2000).

2.3.4 PES-PVDF TFC membrane to CO_2/N_2 separation

PES-PVDF membrane were prepared by the phase inversion process which is a well-known process for preparation a variety of asymmetric membranes with specific condition of their preparation (W. Lishun et. al, 2006).

2.3.4.1 TFC Membrane preparation

PVDF/PES blend membranes were prepared by the dry/wet phase inversion process which is well known process for preparation a variety of asymmetric membranes. Organic acids were used to form Lewis acid–base complexes in polymer/solvent casting solutions. These complexes are stable in the casting solution but can easily break-up into smaller parts in the gelation bath (J. Kurdi, A.Y. Tremblay, 2000).

2.3.4.2 Dope solution preparation

PES/PVDF flat membranes were prepared by dry/wet phase inversion via immersion precipitation method. Dope solution or casting solution was made by first dissolving PVDF (polymer), EG (non-solvent) and NMP (solvent) in this solution at around 60°C for 4h with mechanical stirring at 200 rpm. EG was added as the non-solvent into the PVDF dope solution to enhance flux because it is a known pore forming agent and can be leached out easily during the precipitation and subsequent solvent exchange. The homogeneous polymer solution was kept stagnant to remove bubbles. The solution was sprinkled and cast on a glass plate substrate and then was moved to the non-solvent bath for precipitation at room temperature. The prepared membranes were washed and stored in water bath for at least 2 hour to leach out the residual solvents. As the final stage, membrane was dried by placing between two sheets of filter paper for 24 h at room temperature. (S.A. Hashemifard et. al, 2011).

Table 2.4: Dope solution formula after titration (A. F. Ismail et. al, 2006)

Components (%)	Dope formulation (polymer solutions)				
	D1 (%) (%)	D2 (%)	D3 (%)	D4 (%)	D5
Polyethersulfones (PES)	20.24	20.34	20.34	20.34	20.34
N-Methyl-2-pyrrolidone (NMP)	75.51	73.51	71.51	69.51	67.51
Distilled water (H2O)	3.15	3.15	3.15	3.15	3.15
Polyvinylpyrrolidone (PVP K30)	1.00	3.00	5.00	7.00	9.00

Table 2.5: Composition of casting solution for PES/PVDF blend membrane preparation (Minggang Zhang et. al, 2009)

Membrane	PES		PVDF	LiCl	NMP
	(g)	(wt %)	(g)	(g)	(g)
PVDF	0.00	0.67	15.00	4.50	85.00
0.1 PES/PVDF	0.10	1.33	14.90	4.50	85.00
0.3 PES/PVDF	0.30	2.00	14.70	4.50	85.00
0.5 PES/PVDF	0.50	3.33	14.50	4.50	85.00
1.0 PES/PVDF	1.00	6.67	14.00	4.50	85.00

2.3.4.3 Membrane fabrication (casting) process

The polymeric solutions can be casted into flat sheet membranes. The solution is subjected to ultrasonification process for several hours to ensure removal of air bubbles before casting the membrane. Membranes are casted on a glass plate using the casting knife, which is measured and fixed at 200 μm. Immediately after casting, the glass plate with the solution film was immersed into the coagulation bath of distilled water at room temperature. The phase inversion process takes place, and after a few minutes, a thin polymeric film is separated out from the glass. The prepared film is then immersed again in the coagulation bath in 40 °C. The formed layer is then stored in distilled water for 48 h to allow the water-soluble components in the film to be leached out. As the final stage, the film is washed again with distilled water and is dried by the filter paper for at least 48 h at room temperature. All membranes are then inspected for defects and good areas are chosen for evaluation (Idris et al., 2008).

2.3.4.4 Membrane dip-coating process

For this study, PES is the thickness of interfacial polymerization selective layer (top layer) while the PVDF is the porous support. For PES substrate membrane, were contacted with methanol and chloroform/methanol mixtures of 18, 42 and 66 wt. % chloroform respectively, and were dried after draining the solvent from the membrane surface. Membranes were dried in a vacuum oven overnight at room temperature before analysis. The solvent exposure and the drying were carried out similar to that PVDF-PES composite membrane preparation. Then, gas stream was determined for each membrane after one hour of compaction at 2069 kPa gauge (300 psig) (Takeshi et al., 2001).

2.3.5 Effect to environment

Global warming has been identified as one of the world's major environmental issues. While it is impossible to completely stop the effects of anthropological global warming, it is possible to mitigate these effects via a variety of options. One such option is the reduction of greenhouse gas emissions by the capture of carbon dioxide from flue gases followed by underground sequestration. For this technology to become widespread, new methods of capturing carbon dioxide must be devised. Nowadays, the membrane gas separation is the one of the number of industrial process that can be used to reduce the emissions of greenhouse gases (Clem E. Powell and Greg G. Qiao, 2006). For a membrane to be useful for the capture of carbon dioxide, it should possess a number of properties, namely:

- High carbon dioxide permeability.
- High carbon dioxide/nitrogen selectivity,
- Thermally and chemically robust,
- Resistant to aging,
- Cost effective, and
- Able to be cheaply manufactured into different membrane modules.

In addition to the power generation industry, there are a number of different point sources which produce large CO_2 emissions. CO_2/ N_2 separation membranes can be used to create oxygen enriched air, which can be used in combustion, to get concentrated CO_2 flue gases. CO_2 can also be separated from fuel gases leading to lower CO_2 emissions (Colin A. S. 2008).

CHAPTER 3

Research Methodology

3.0 Membrane preparation

PVDF/PES blend membranes were prepared by the dry/wet phase inversion process which is well known process for preparation a variety of asymmetric membranes. Polyvinylidene fluoride (PVDF) is valued for its toughness, stability, and distinct engineering advantages. For example, if we need a polymer that will withstand exposure to harsh thermal, chemical, or ultraviolet conditions, PVDF offers superior stability similar to the performance of fluoropolymers in these environments. Generally, Polyethersulfone (PES) is widely used for gas separation membranes. Besides, they are principally to the favorable characteristics of wide pH tolerance, wide temperature limits, easy to fabricate membranes in a wide variety of configurations and module and also have a wide range of pore sizes. The PVDF powder must be dried before start prepare for the dope solution. The main purpose for drying process is to produce the PVDF powders which have a less humidity and to avoid moisture on the PVDF powder. Figure 3.1 shows the membrane preparation for overall process flow.

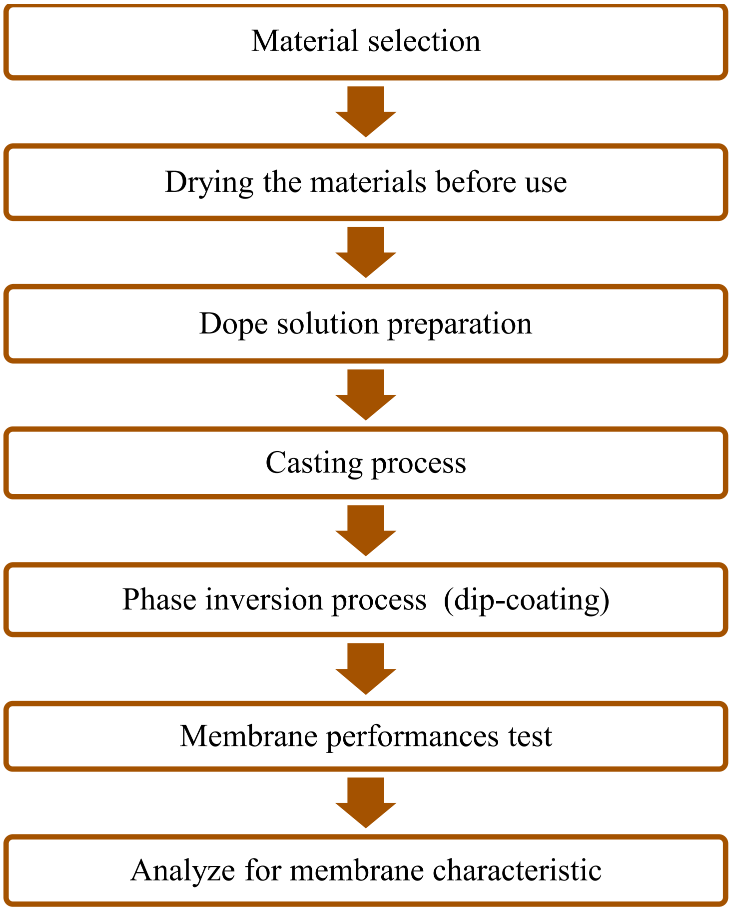


Figure 3.1: Membrane preparation for overall flow process

3.1 Materials

Polyethersulfone (PES) in powder and Poly (vinylidene fluoride) (PVDF) was obtained from Sigma Aldrich (M) Sdn Bhd. The solvents used for membrane making are N-Methyl Pyrrolidone (NMP), hexane, methanol solution and deionized water. Table 3.1 and Table 3.2 shows the physical and chemical properties for the N-Methyl Pyrrolidone (NMP) and Poly Vinylidene Fluoride (PVDF).

Table 3.1: Physical and chemical properties for N-Methyl Pyrrolidone (NMP)

N-Methyl-2-pyrrolidinone (NMP)	
Synonyms	: 1-Methyl-2-pyrrolidinone
Formula	: C_5H_9NO
Molecular Weight	: 99.13 g/mol
Appearance	: Form : liquid : Colour: colourless
pH	: 7.7 - 8.0
Melting point	: -24 ^{o}C
Boiling point	: 202 °C
Boiling range	: 81 - 82 °C at 13 hPa
Flash point	: 91 °C - closed cup
Vapour pressure	: 0.39 - 0.43 hPa at 20 °C
Relative density	: 1.028 g/mL at 25 °C

Table 3.2: Physical and chemical properties for Poly Vinylidene Fluoride (PVDF)

Poly Vinylidene Fluoride (PVDF)	
Synonyms	: Polyvinylidene difluoride
Formula	: $(C_2H_2F_2)_n$
Molecular Weight	: 0
Appearance	: Form : Solid (powder) : Colour: Whitish or Translucent
pH	: $\geq$ 11
Melting point	: 160 ~ 170 °C
Boiling point	: 149 °C
Boiling range	: 140-150 °C
Vapour pressure	: 15 mm Hg (32 °C)
Relative density	: 1.78 g/mL at 25 °C

3.2 Preparation for dope solution

The polymer can be dissolved using two different methods: the conventional electrical heating (CEH) or the recently developed Microwave Heating (MH) method (Idris et al., 2008). But, for this research we choose the conventional electrical heating (CEH) which is mechanical stirrer and heater for our method.

3.2.1 Dope solution of PVDF and coating solution of PES

Dissolved PVDF (polymer) and NMP (solvent). The dissolution process was carried out in 1-L, four-necked, round-bottomed vessel with stirrer and condenser placed over the electrical thermal heater. Obtained the wt. % between polymer and solvent. PVDF/NMP (15 wt% /85 wt %). The dope temperature was kept constant at range temperature of 60^{o}C - 90 ^{o}C and the mechanical stirrer was set at 450 rpm. The dissolution may take 4 to 7 hour to complete homogenous depending on the type of formulating used. After the solution was fully homogenous, the dope solution was cooled and keeps the bottle. The homogeneous polymer solution in the bottle was immersed into the Ultrasonic water bath to remove the bubbles.

3.3 Membrane casting process

Membranes are casted on a glass plate using the glass rod. The membrane casted was leaving for 3 minute on the glass plate after casting for dry process. Then, immersed the glass plate containing membrane that has been cast into the coagulant bath of distilled water for 8 minutes to complete the dry and wet phase inversion process. Measured and fixed that membrane casted at 200 μm. The prepared film is then immersed again in the coagulation bath at 25 °C for 15 minutes to remove the residual of NMP by-product. Leave it for 15 minutes

3.4 Membrane dip-coating process

For this research, PES is the thickness of selective layer (top layer) while the PVDF is the porous membrane support. PVDF are very attractive materials as a hydrophobic support for forming a TFC membrane due its high durability and resistance to chemicals, pH variations, and a substantially wide range of solvents. For the first step of this process, casting again the PES /NMP and methanol or water mixture of 18, 23 and 28 wt.% PES respectively on the skin layer of PVDF that we are casted already. Leave for 8 minute to completing the top layer formation of TFC membrane. Then, the excess solvent was drained from the membrane surface by immersed in the coagulant bath of distilled water for 15 minute. The PES/PVDF composite membrane was thoroughly washed with deionized water to eliminate excess methanol or hexane when we used as an non-solvent to replace the water. And the last once is put the resulting composite membrane in the ambient temperature for 12 hours before analysis.

3.5 Membrane gas permeation test

The prepared membrane was analyzed by using Gas Permeation Test. The parameter that we need to evaluate is the effect of the various permeates pressure on the various concentration of PES in the coating solution for our based PVDF membrane.

3.6 Membrane characterization

We have two common methods that we can use for the membrane characterization. The both method is Fourier Transform Infrared Radiation (FTIR) and Scanning Electron Microscopy (SEM).

(i) Fourier Transform Infrared Radiation (FTIR)

Fourier Transform Infrared Radiation (FTIR) is a qualitative analysis that detects the chemical bonds, molecular structure, and functional groups in a sample by producing an infrared absorption spectrum. When a sample absorbs infrared light, the absorbed light energy is converted into atomic bond vibrations. Specific groupings of bonded atoms, located within a materials molecular structure, absorbed infrared light within loosely defined frequency ranges. The defined absorption frequency range remains fairly constant and is not significantly dependent on the material type. FTIR of a PV membrane helps in studying intermolecular interactions and transport mechanisms. Modification in the PV membrane could be confirmed through shifts in peaks, absence of old peaks, emergence of new peaks, and reduction in transmission.

(ii) Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a method that uses electrons rather than light to form an image. SEM also produces images of high resolution, which is means that closely spaced features can be examined at high magnification. Morphology of surface, cross-section, pore diameter, and pore size distribution can be analyzed.

CHAPTER 4

RESULT & DISCUSSION

4.1 Effect of various concentration of coating solution on the membrane gas permeation

A high permeability and selectivity can be achieved by conducting a permeation test towards the gases. However, in the reality, a high permeability contributes to low selectivity and vice versa. To handling the gas permeation, we use water that was diluted with a small amount of soap and produced a foaming solution. We inserted the foaming solution into the titration tube that was completed installed on the Gas Permeation equipment. To measure the gas permeance of the CO_2/N_2 gas through the TFC membrane, we observed and calculated the volumetric flowrate of the gas in the titration tube. The result for the volumetric flowrate that we collected was attached in the Appendix A and Appendix B at behind this report.

The result for CO_2 gas permeance and N_2 gas permeance for TFC membrane can be refer from the Appendix C and Appendix D. This is PVDF polymer as a membrane support and coated by various concentration of PES polymer as a coating solution.

4.1.1 Effect of different pressure and different concentration of coating solution on the gas permeance for CO_2 gas.

The optimum polymer concentration for casting solution had been determined in order to achieve defect-free and ultrathin-skinned asymmetric membranes for gas separation. Referring to the graph on Figure 4.1, the average gas permeance for PVDF uncoated is higher than the average gas permeance for PVDF coated by various concentration of PES. It's due to the porosity of the membrane surface. The PVDF uncoated membrane have a large size of pores while the PVDF coated have a smallest pore sizes. The pores size was affected on the gas performance especially on their permeability. Our approach is to bring the coating solution as close as possible to the state of phase separation by adding water as non-solvent.

Table 4.1 : CO_2 Gas permeance (GPU)

Membrane Type	Pressure, *P* (cmHg)	Volumetric flowrate (cm^3/sec)	Gas permeance (GPU)
PVDF	37.503	3.720	1262.95
	75.006	6.257	1062.13
	112.509	9.187	1039.67
	150.012	18.068	1533.53
PVDF coated by 18 % PES	37.503	0.307	104.228
	75.006	2.467	418.778
	112.509	4.126	466.931
	150.012	6.821	578.938
PVDF coated by 23 % PES	37.503	0.482	163.641
	75.006	4.163	706.676
	112.509	6.824	772.257
	150.012	12.412	1053.47
PVDF coated by 28 % PES	37.503	0.706	239.689
	75.006	3.412	579.193
	112.509	5.794	655.694
	150.012	8.303	704.724

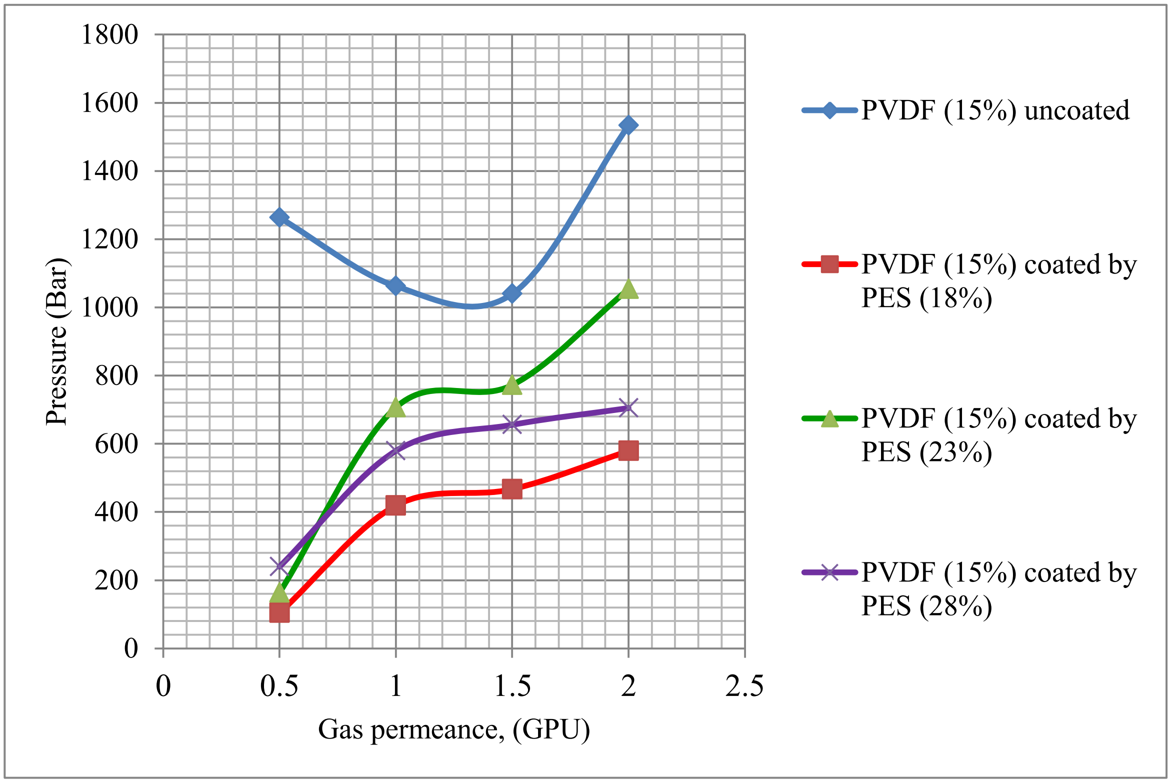


Figure 4.1 : CO_2 gas permeance (GPU) VS. Pressure (bar)

4.1.2 Effect of different pressure and different concentration of coating solution on the gas permeance for N_2 gas.

The Table 4.2 shows the result for N_2 gas permeance in GPU unit at different pressure. It can be seen that there is slight increase in N_2 permeance with increasing the feed pressure from 0.5 bar to 2.0 bar. By the way, the increasing concentration of coating solution, the N_2 permenace is also increased. The result can be seen from 18% PES to 23% PES.

Table 4.2 : N_2 Gas permeance (GPU)

Membrane Type	Pressure, *P* (cmHg)	Volumetric flowrate (cm^3/sec)	Gas permeance (GPU)
PVDF	37.503	4.720	1602.456
	75.006	7.257	1231.888
	112.50	11.18	1266.008
	150.01	21.06	1788.165
PVDF coated by 18 % PES	37.503	0.257	87.252
	75.006	2.167	367.852
	112.50	4.325	489.451
	150.01	7.121	604.401
PVDF coated by 23 % PES	37.503	0.397	134.783
	75.006	4.113	698.189
	112.50	7.824	885.425
	150.01	11.41	968.603
PVDF coated by 28 % PES	37.503	0.606	205.739
	75.006	2.952	501.107
	112.50	5.234	592.321
	150.01	7.763	658.891

Based on the graph from Figure 4.2, we assumed that the decrease in gas permenace between PVDF uncoated and PVDF coated by PES was due to the membrane compaction. The compaction would decrease the amount of free volume and subsequently reduce the mobility of the penetrating molecules. The compaction may produce a thickening of the skin layer due to densification of material in the support layer immediately adjacent to the skin layer, which results in the decrease in gas permance. The compaction can cause by the membranes were pressurized at high pressure.

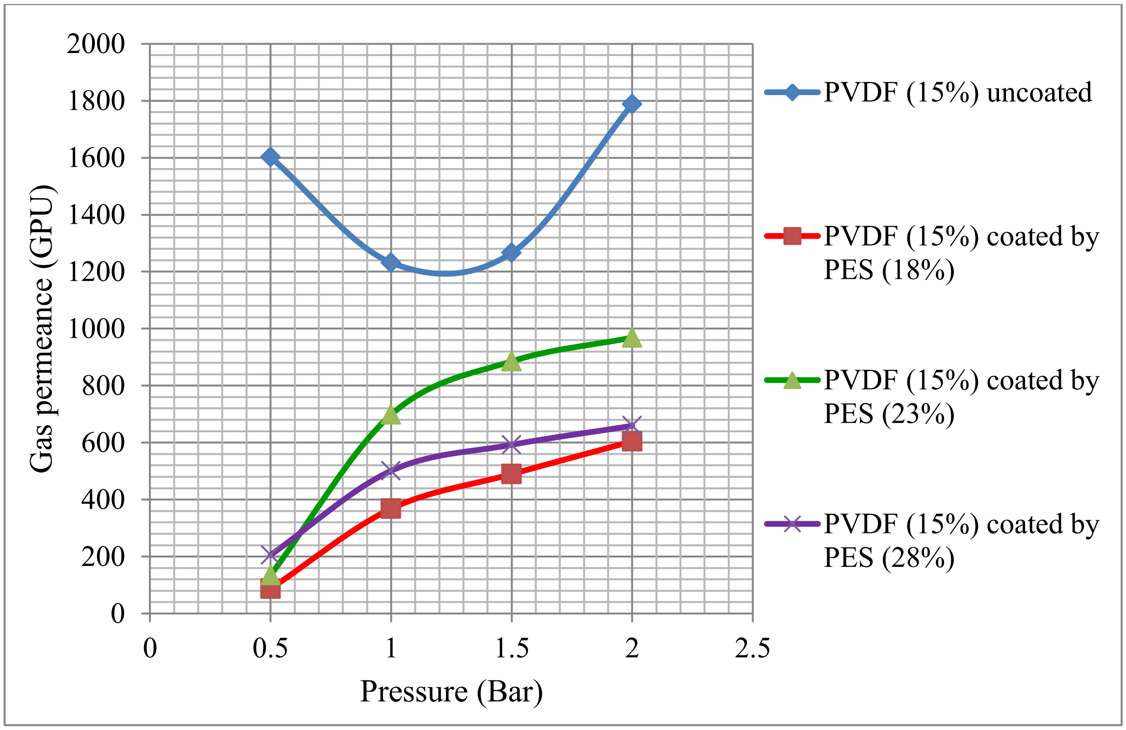


Figure 4.2 : N_2 gas permeance (GPU) VS. Pressure (bar)

Most of the PVDF uncoated membranes seem to exhibit higher permeance but a selectivity is lower than 1 without exception. It's because a large number of pores (defects) were formed and the free volume was enhanced in the skin layer. Skin layer pores are defined as passageways that allow communication between upstream and downstream side of the membrane. PVDF as a membrane support usually contain few defect, which are attributed to the incomplete coalescence on the composed skin layer. Thus, the performance of gas separation will be decrease because the membrane surface was dominated by surface porosity. The effect of the weaknesses that exist on the surface porosity of PVDF membrane, a standard coating procedure was then applied to seal the skin layer defects.

Table 4.3 : The relationship between the gas permeance and the selectivity

Membrane Type	Pressure, (*Bar*)	The permeance (P/*l*) CO_2 (GPU)	The permeance (P/*l*) N_2 (GPU)	Selectivity (α) (CO_2/N_2)
PVDF	0.5	1262.95	1602.45	0.7881
	1.0	1062.13	1231.88	0.8622
	1.5	1039.67	1266.00	0.8223
	2.0	1533.53	1788.16	0.8576
PVDF coated by 18 % PES	0.5	104.22	87.252	1.1946
	1.0	418.77	367.85	1.1384
	1.5	466.93	489.45	0.9540
	2.0	578.93	604.40	0.9579
PVDF coated by 23 % PES	0.5	163.64	134.78	1.2141
	1.0	706.67	698.18	1.0122
	1.5	772.25	885.42	8.7219
	2.0	1053.47	968.60	10.876
PVDF coated by 28 % PES	0.5	239.68	205.73	1.1650
	1.0	579.19	501.10	1.1558
	1.5	655.69	592.32	1.1070
	2.0	704.72	658.89	1.0696

Referring to the Table 4.3, the different concentration of coating solution of PES will produce the different result on the performance of gas permeation. Coating reduced the gas permeance while enhancing the membrane selectivity by caulking the pinholes or defects on the membrane outer dense skin layer. The selectivity of the gas separation can decrease due to the membrane compaction, membrane fouling and have too many defects on the skin layer of membrane surface.

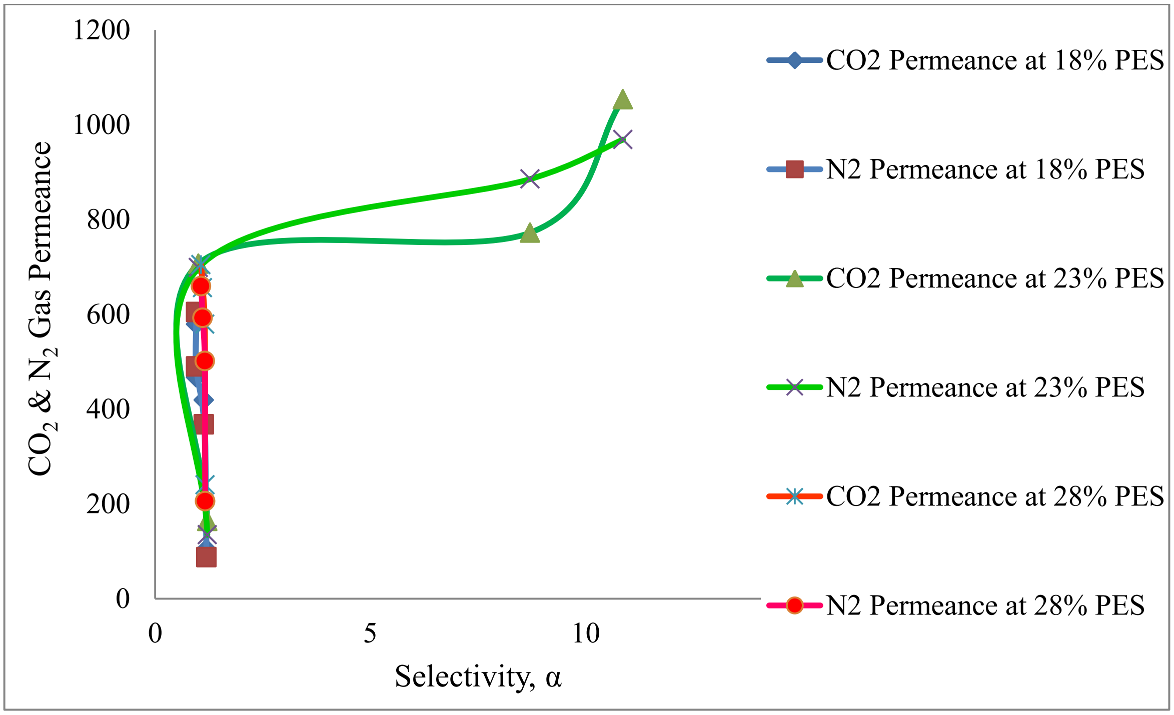


Figure 4.3 : Gas Permeance vs. Selectivity

The Figure 4.3 shows the high performance of PVDF/PES thin film composite (TFC) membranes with high selectivity and by low gas permeance are obtained. The performance of gas separation will be decrease because the membrane surface was dominated by surface porosity and membrane compactness. The compactness can defined as a compression of the membrane structure under a trans membrane pressure difference causing a decrease in membrane permeability due to the mechanical deformation of the solid polymer. This is a common phenomenon during application of polymeric membrane. The compactness was due to the membrane were pressurized at high pressure for the long time.

4.2 PES/PVDF for TFC membrane characterizations

We have two common methods that we can use for the membrane characterization. The both method is Fourier Transform Infrared Radiation (FTIR) and Scanning Electron Microscopy (SEM). Fourier Transform Infrared Radiation (FTIR) is a qualitative analysis that detects the chemical bonds, molecular structure, and functional groups in a sample by producing an infrared absorption spectrum. Scanning Electron Microscopy (SEM) is a method that uses electrons rather than light to form an image. SEM also produces images of high resolution, which is means that closely spaced features can be examined at high magnification. Morphology of surface, cross-section, pore diameter, and pore size distribution can be analyzed.

4.2.1 Identification of functional group in the PES/PVDF for TFC membrane

The FTIR spectrum displayed new absorption bands in the region of aliphatic stretching vibration of the modified TFC membrane which is coating by PES polymer is (2998 – 2875 cm^{-1}), a region lacking absorption bands in the spectrum of the original membrane. Because the spectrum of PES has no bands in the area below 3065 cm^{-1}, where the stretching vibrations of aliphatic hydrocarbons are located, we were able to detect the presence of new polymeric hydrocarbon chains grafted on to the surface of the membrane.

Aromatic bands at 1278 cm^{-1} and 1146 cm^{-1} are characteristic for PES is highlighted. Two weak bands at 1385 cm^{-1} and 1365cm^{-1} are due to methyl groups and are present exclusively in the spectrum of Polyethersulfone (PES).

Table 4.4 : Sulfones and Sulfonates Group for aliphatic bands

Aliphatic Bands		
Functional Group	**Molecular Motion**	**Wavenumber (cm^{-1})**
Sulfones	S=O stretch	3000 – 2700
Sulfonates	S=O stretch	3015 – 2700
	S-O stretch	2000 – 1750

Table 4.5 : Sulfones and Sulfonates Group for aromatic bands

Aromatic Bands		
Functional Group	**Molecular Motion**	**Wavenumber (cm^{-1})**
Sulfones	S=O stretch	1300 – 1150
Sulfonates	S=O stretch	1300 – 1175
	S-O stretch	1000 – 750

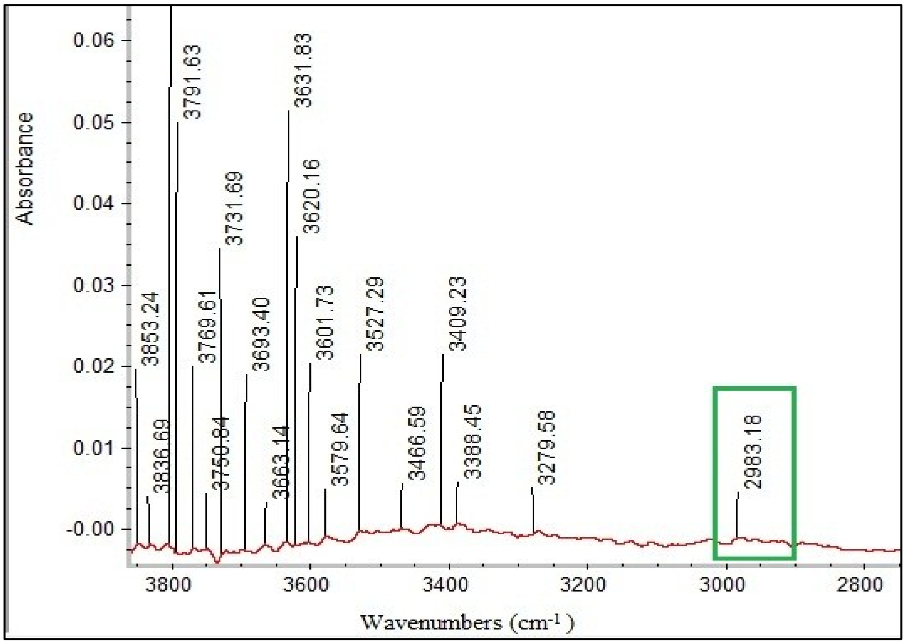


Figure 4.4 (a) : PVDF (15%) coated by PES (18%)

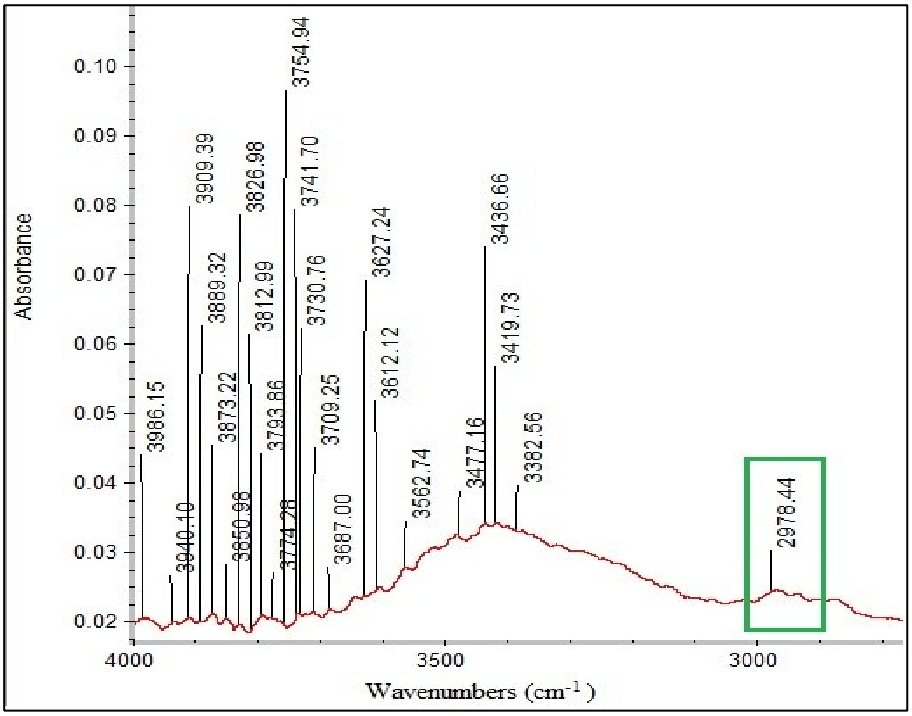


Figure 4.4 (b) : PVDF (15%) coated by PES (23%)

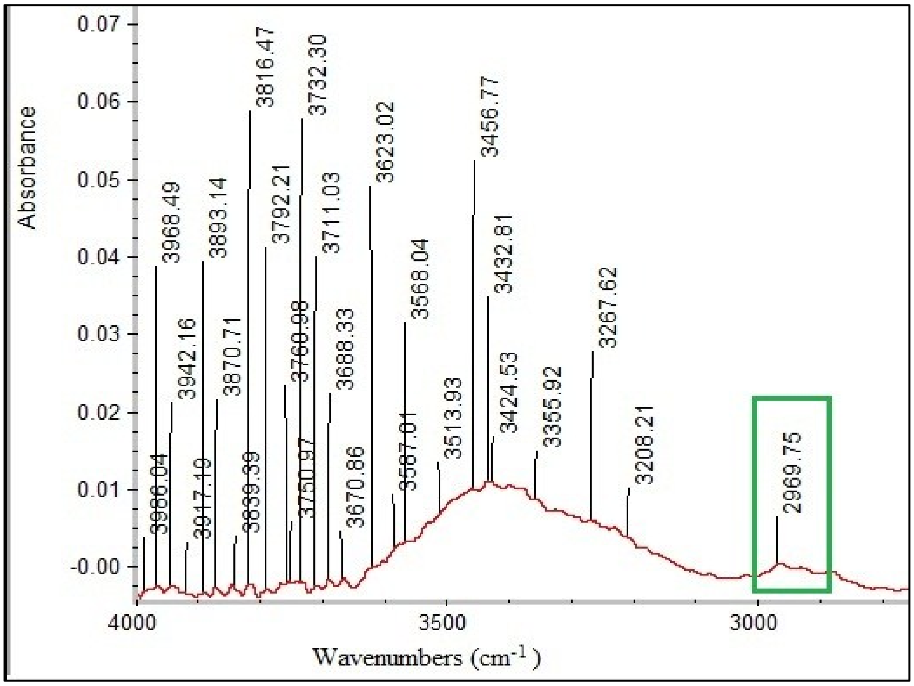


Figure 4.4 (c) : PVDF (15%) coated by PES (28%)

We also need to identify the functional group of amines in PES/PVDF for TFC membrane. Primary amines produce two N-H stretch absorptions, secondary amides only one, and tertiary none. The peak of amines that we have been to analyze was highlight with blue color.

Table 4.6 : Amines Group

	Stretching Vibrations		
Functional Group	**Wavenumber (cm^{-1})**	**Intensity**	**Molecular Motion**
Amines	3400 – 3500 (dilute solution)	Weak	N-H (1^{o} – amines), 2 bands
	3300 – 3400 (dilute solution)	Weak	N-H (2^{o} – amines)
	1000 – 1250	Medium	C – N

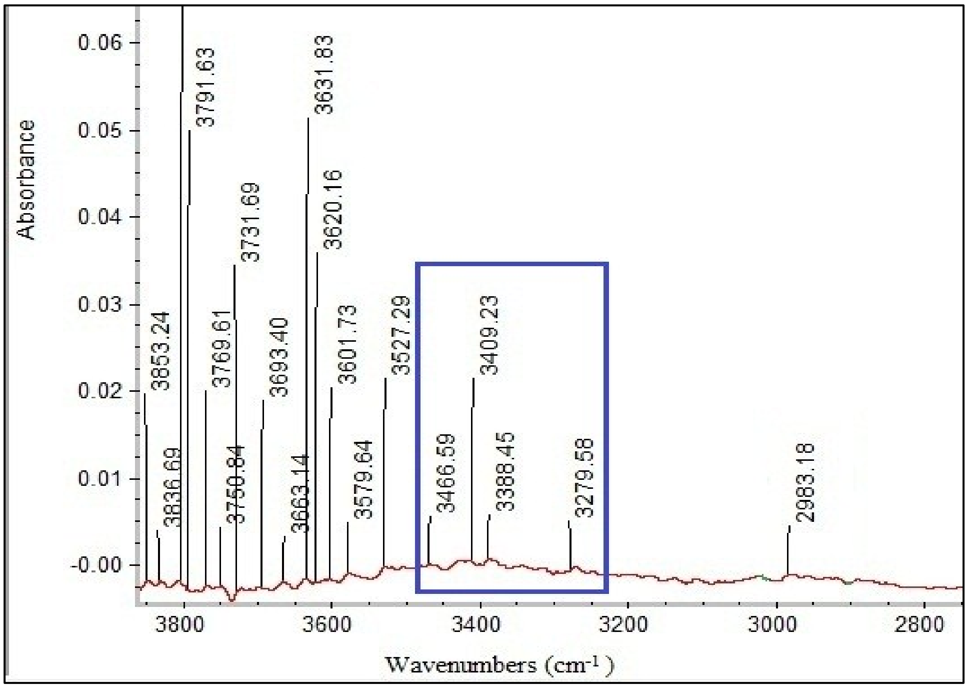


Figure 4.5 (a) : PVDF (15%) coated by PES (18%)

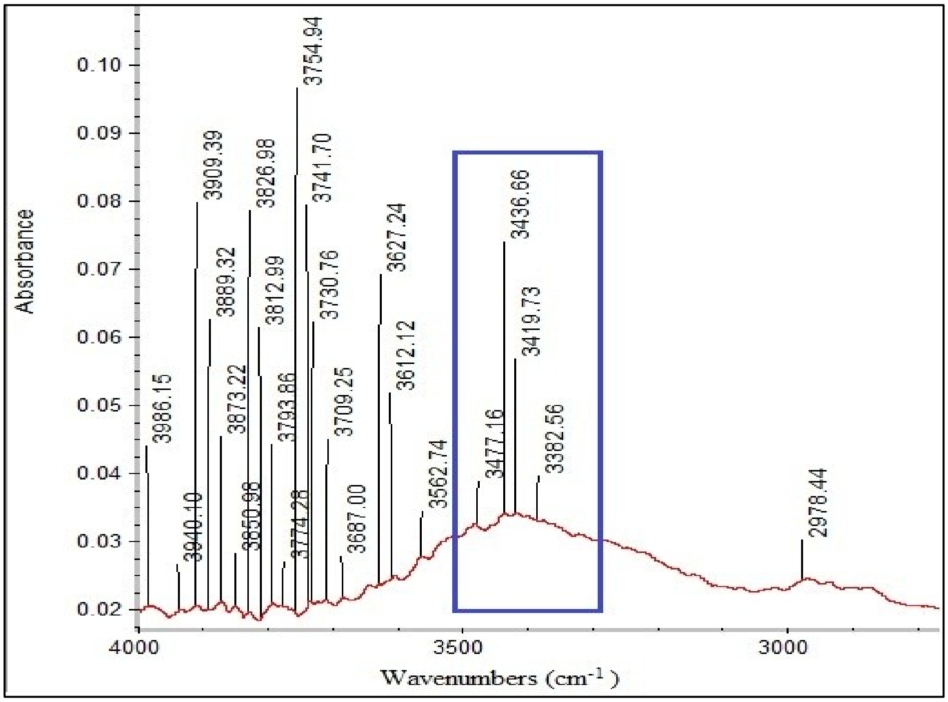


Figure 4.5 (b) : PVDF (15%) coated by PES (23%)

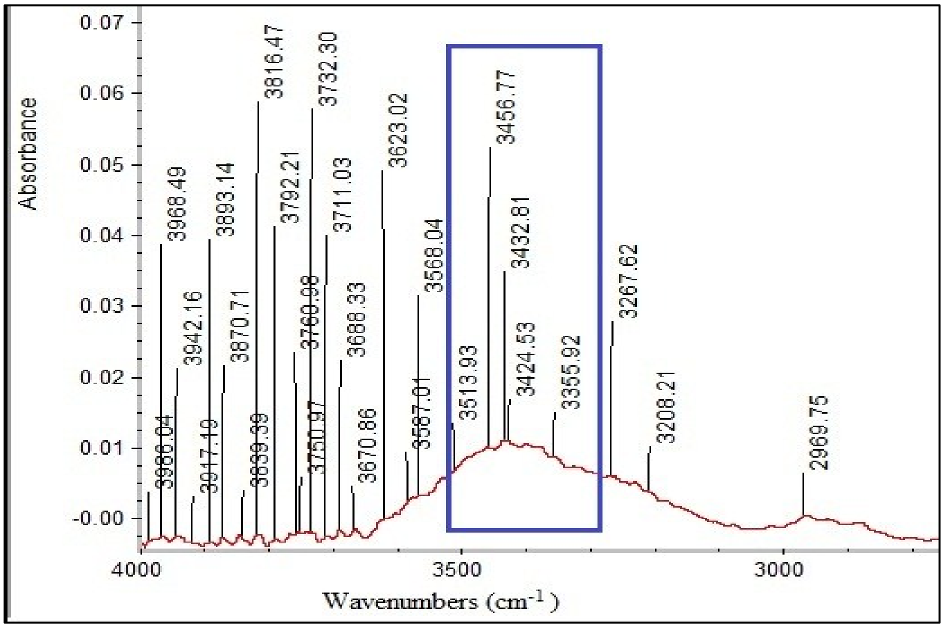


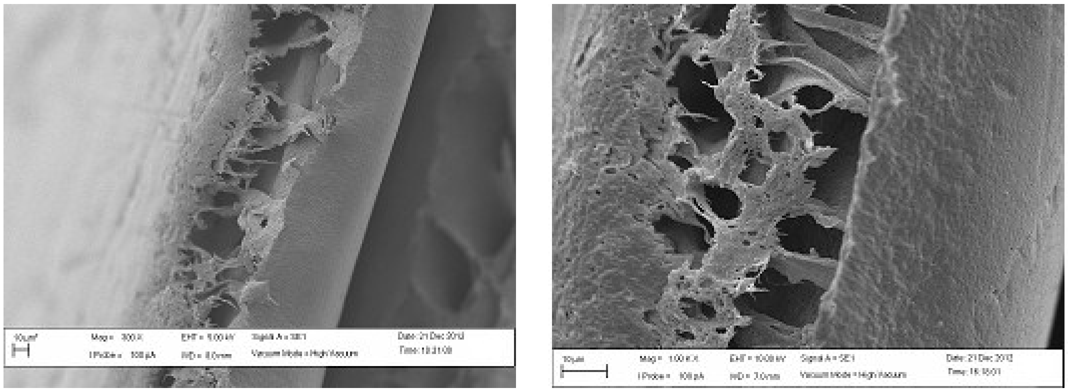
Figure 4.5 (c) : PVDF (15%) coated by PES (18%)

4.2.2 Effect of different concentration coating solution on membrane morphology

The optimum polymer concentration for coating solution had been determined in order to achieve defect-free and ultrathin-skinned membranes for gas separation. The addition of non-solvents in the polymer solution has been shown to play an important method in the development of membrane structure with improved separation performance. The more intense the interaction of solvent with non-solvent and the solubility of solvent to polymer will decrease. Normally, the weak interaction between Polyethersulfone (PES) as a solvent and water as a non-solvent promotes the formation of big polymer aggregates. According to Ismail and Lai, a coating solution with higher polymer concentration exhibits weaker interaction between solvent and non-solvent. This thermodynamically indicates that addition of non-solvent can induce the more enhance coagulation. For PES, water is a strong non-solvent, which means that coagulation process take place faster when the polymer solution is brought through contact with water and formed the finger-like structure. According to L. Broens et. al, the finger-like structure is formed by spinodal decomposition with unbalanced localized stresses from surface tension, solvent coagulant agglomeration and radial convective flows of the internal and external coagulation. With an increase of PES concentration from 18% to 23%, the internal surfaces become more microporous while the pore size reduced. The result can be referring to the Figure 4.7 (a), Figure 4.7 (b) and Figure 4.7 (c). Referring to the result in Figure 4.8, the microporous structure in the internal surface become less while the pore size increase with an increase of water concentration in the coating solution. Besides, the formation of finger-like structure also depends on viscosity of the dope solution. This means that the membrane morphology is strongly affected by the amount of non-solvent in the composition of both dope and coating solution of membranes.

Figure 4.6, Figure 4.7 and Figure 4.8 shows the result for SEM images for cross-section view for TFC membrane based PVDF polymer with coated by various concentration of PES coating solution. All displayed similar cross-sectional structures. There are long finger-like and wide finger-like macro-voids extending from the skin layer to the support region. Most likely, formation of micro-voids at the sub-layer is caused by liquid-liquid dimixing occurred as increasing the polymer concentration.

The PVDF polymer membrane support that was coated by 18 % PES polymer for the lowest polymer concentration can be clearly seen in Figure 4.6. Referring to the SEM images at the Figure 4.6, Figure 4.7 and Figure 4.8, the formation of finger-like structure was determined in coating solution contained 18 wt.%. We can see that the structure of the membrane is large long finger-like macro-voids. Besides, the formation of finger-like structure also depends on the viscosity of the coating solution.

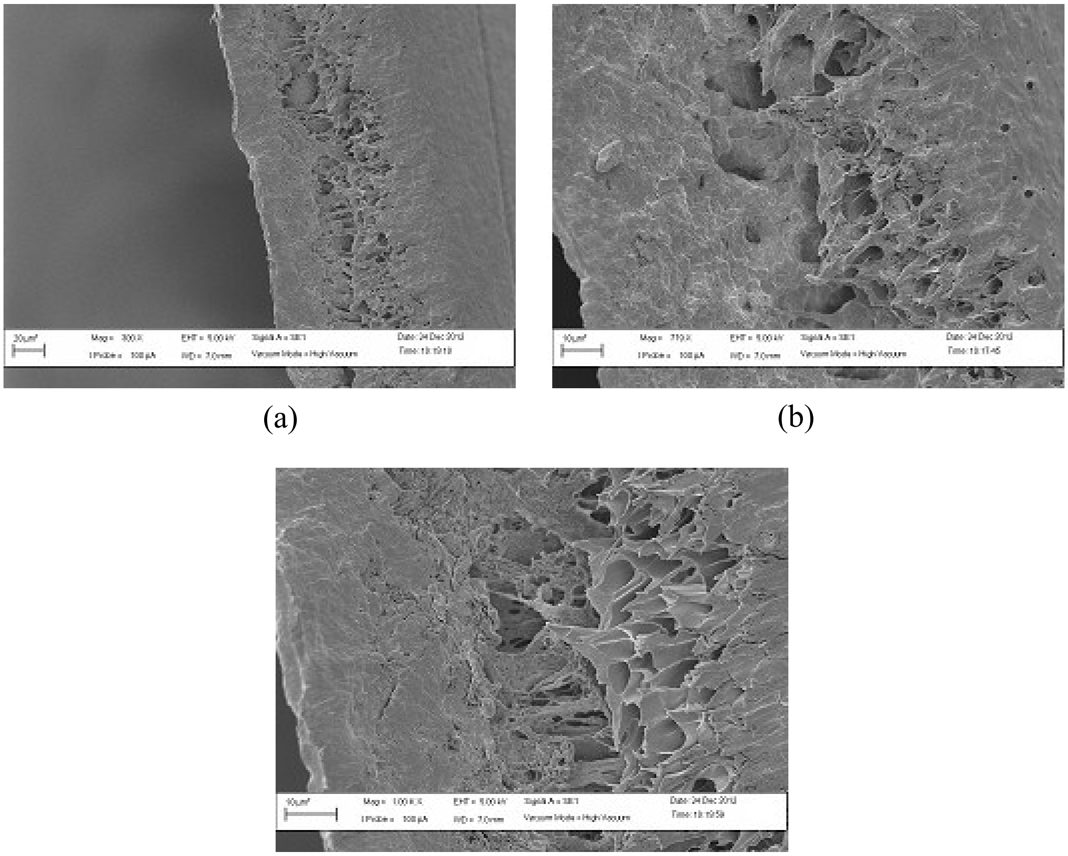


(a) (b)

Figure 4.6 (a) shows the result for PVDF coated by 18% PES at magnification 300X.

Figure 4.6 (b) shows the result for PVDF coated by 18% PES at magnification 1000X.

PES polymer as compared with 23 wt.% PES polymer which no finger-like structure formed in the cross-section of Thin Film Composite (TFC) membrane. Whereas much smaller and shorter macro-voids for the highest polymer concentration.


(a) (b)

(c)

Figure 4.7 (a) shows the result for PVDF coated by 23 % PES at magnification 300X.

Figure 4.7 (b) shows the result for PVDF coated by 23 % PES at magnification 779X.

Figure 4.7 (c) shows the result for PVDF coated by 23 % PES at magnification 1000X.

But, for this research, we recognized the optimum concentration of PES that we use as the coating solution of TFC membranes. Referring to the result from the Figure 4.8 (a). (b), (c) and (d), the morphology at higher concentration of PES in the coating solution can cause of larger size of pores. Larger size of pores can be determined as a defect of the membrane structures. Consequently, the membrane morphology changed from larger to smaller macro-voids. Besides, the appropriate amount of non-solvent (water) in polymer solution enhanced the formation of microvoids while too much of non-solvent suppressed their formation because the delayed dimixing in the growth stage is inhibited. This means that the membrane morphology is strongly affected by amount of water as a non-solvent.

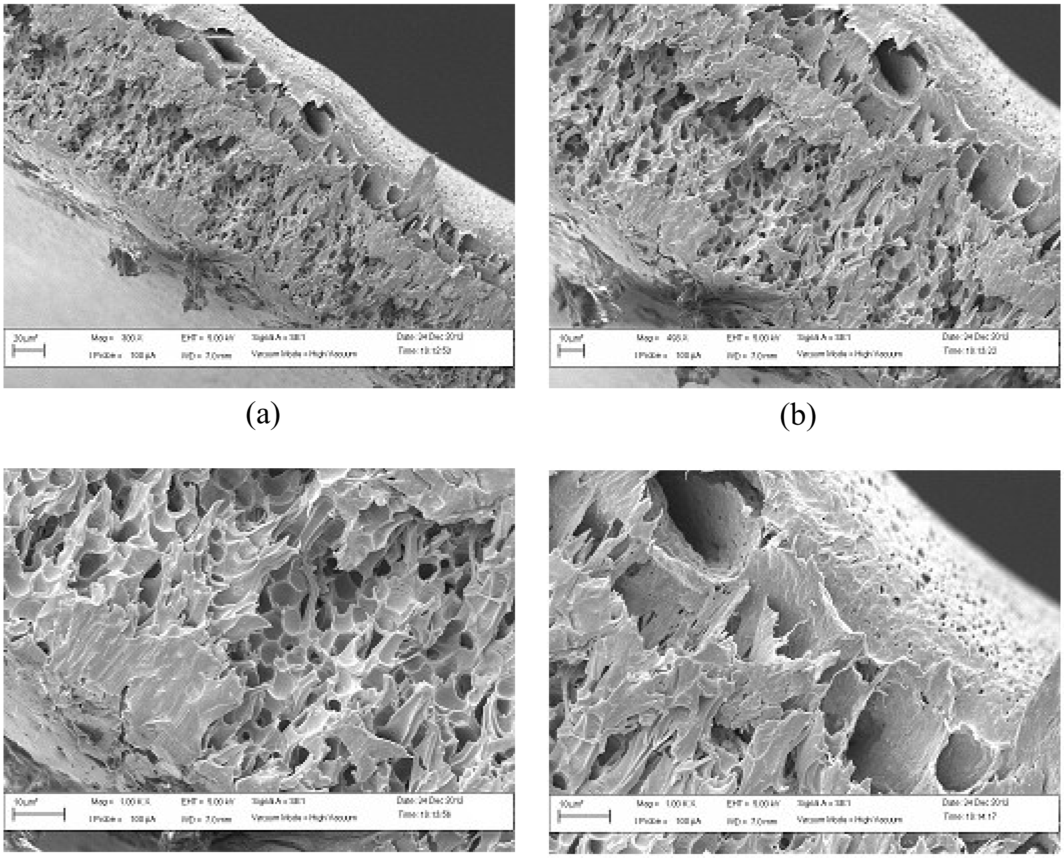

(a) (b) (c) (d)

Figure 4.8 (a) shows the result for PVDF coated by 28 % PES at magnification 300X. **Figure 4.8** (b) shows the result for PVDF coated by 28 % PES at magnification t 493X. **Figure 4.8** (c) and (d) shows the result for PVDF coated by 28 % PES at magnification 1000X.

CHAPTER 5

5.1 CONCLUSION

The systems of thin film composite membrane (TFC) membranes are highly applicable for separation of gases mixture. The combination of support porosity and concentration of coating solution was lead to achieve the optimum of selectivity and permeability respectively. The optimum polymer concentration for coating solution had been determined in order to achieve defect-free and ultrathin-skinned asymmetric membranes for gas separation. Consequently, the membrane morphology changed from larger to smaller macro-voids following the increasing concentration of coating solutions. Now, the high performances PVDF/PES for TFC membrane with high selectivity with by optimum percent of PES concentration as a coating solution are obtained. For the environmental effects, CO_2/N_2 separation membranes can be used to create oxygen enriched air, which can be used in combustion, to get concentrated CO_2 flue gases. CO_2 can also be separated from fuel gases leading to lower CO_2 emissions. Finally, it can improve the quality of life instead of reduce the industrial costing for flue gas treatment process.

5.2 RECOMMENDATION

Based on the study conducted, some recommendations are given for future work.

1. PVDF polymer is very compatible to become a support for TFC membrane because PVDF polymer have a wide temperature limits and easy to fabricate membranes in a wide variety of configurations
2. Asymmetric thin film composite membrane should be prepared with a variety of polymer, solvent and coagulation medium in order to generalize membrane formation process.
3. Dry and wet phase inversion method should be used during the casting process because this method is suitable for casting dope solution with and without additive.

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APPENDIX A

VOLUMETRIC FLOWRATE (Q) OF CO_2 GAS PERMEATE THROUGH THE TFC MEMBRANE

CO_2 Gas Permeatation Test

Membrane Type	Pressure Supply (bar)			
	0.5	1.0	1.5	2.0
	Volumetric flowrate , Q (cm³/sec) = $\dfrac{Volume\ displacement,\ cm^3}{Time, sec}$			
Main Support				
PVDF	3.623	6.309	8.969	18.348
	3.839	6.410	10.10	17.699
	3.731	6.230	9.132	16.807
	3.690	6.079	8.547	19.417
Average value =	3.720	6.257	9.187	18.068
PVDF coated by 18 % PES	0.307	2.413	4.115	6.734
	0.267	2.571	4.057	6.920
	0.338	2.451	4.184	6.711
	0.311	2.430	4.158	6.873
	0.313	2.472	4.115	6.863
Average value =	0.307	2.467	4.126	6.820
PVDF coated by 23 % PES	0.500	4.124	6.452	11.904
	0.466	4.175	6.711	12.422
	0.478	4.158	6.969	12.738
	0.489	4.202	6.873	11.834
	0.476	4.141	7.117	13.158
Average value =	0.482	4.160	6.824	12.412
PVDF coated by 28 % PES	0.709	3.413	5.814	7.463
	0.720	3.478	5.764	8.511
	0.697	3.372	5.848	8.547
	0.715	3.407	5.730	8.696
	0.707	3.328	5.814	8.299
Average value =	0.706	3.400	5.794	8.303

APPENDIX B

VOLUMETRIC FLOWRATE (Q) OF N_2 GAS PERMEATE THROUGH THE TFC MEMBRANE

N_2 Gas Permeatation Test

Membrane Type	Pressure Supply (bar)			
	0.5	1.0	1.5	2.0
	Volumetric flowrate , Q (cm^3/sec) = $\frac{Volume\ displacement,\ \ cm^3}{Time, sec}$			
Main Support				
PVDF	4.623	7.309	11.971	21.348
	4.839	7.410	11.101	21.699
	4.731	7.230	11.132	21.807
	4.690	7.079	11.547	21.417
Average value =	4.720	7.257	11.187	21.068
PVDF coated by 18 % PES	0.258	2.172	4.367	7.017
	0.263	2.446	4.073	7.168
	0.255	2.278	4.367	6.873
	0.257	2.018	4.264	7.194
	0.258	2.148	4.435	7.813
Average value =	0.257	2.167	4.329	7.117
PVDF coated by 23 % PES	0.397	4.132	7.936	11.696
	0.392	4.175	7.605	11.050
	0.400	4.338	7.968	11.173
	0.408	4.057	8.065	11.765
	0.412	4.336	7.936	10.989
Average value =	0.387	4.246	7.813	11.429
PVDF coated by 28 % PES	0.608	3.072	5.155	7.519
	0.629	3.086	5.376	7.663
	0.596	2.963	5.420	8.032
	0.598	2.937	5.195	7.634
	0.609	3.012	5.076	8.163
Average value =	0.604	2.950	5.235	7.752

APPENDIX C

CO_2 GAS PERMEANCE AT DIFFERENT PRESSURE

Membrane Type	Pressure, *P* (cmHg)	Thickness *l* (cm)	Effective area A (cm^2)	Volumetric flowrate , Q (cm^3/sec)	Gas permeance (cm^3 (STP) / (cm^2 scmHg) (P / *l*) CO_2
PVDF	37.503	0.013208	78.5398	3.720	0.001262953
	75.006	0.013208	78.5398	6.257	0.001062137
	112.509	0.013208	78.5398	9.187	0.001039673
	150.012	0.013208	78.5398	18.068	0.001533537
PVDF coated by 18 % PES	37.5030	0.026416	78.5398	0.307	0.000104228
	75.0060	0.026416	78.5398	2.467	0.000418778
	112.509	0.026416	78.5398	4.126	0.000466930
	150.012	0.026416	78.5398	6.821	0.000578938
PVDF coated by 23 % PES	37.5030	0.026416	78.5398	0.482	0.000163641
	75.0060	0.026416	78.5398	4.163	0.000706676
	112.509	0.026416	78.5398	6.824	0.000772257
	150.012	0.026416	78.5398	12.412	0.001053479
PVDF coated by 28 % PES	37.5030	0.026416	78.5398	0.706	0.000239689
	75.0060	0.026416	78.5398	3.412	0.000579193
	112.509	0.026416	78.5398	5.794	0.000655694
	150.012	0.026416	78.5398	8.303	0.000704724

APPENDIX D

N_2 GAS PERMEANCE AT DIFFERENT PRESSURE

Membrane Type	Pressure, *P* (cmHg)	Thickness *l* (cm)	Effective area A (cm^2)	Volumetric flowrate (cm^3/sec)	Gas permeance (cm^3 (STP) / (cm^2 scmHg)) (P/ *l*) N_2
PVDF	37.503	0.013208	78.5398	4.720	0.001602456
	75.006	0.013208	78.5398	7.257	0.001231888
	112.509	0.013208	78.5398	11.187	0.001266008
	150.012	0.013208	78.5398	21.068	0.001788165
PVDF coated by 18 % PES	37.5030	0.026416	78.5398	0.257	0.000087252
	75.0060	0.026416	78.5398	2.167	0.000367852
	112.509	0.026416	78.5398	4.325	0.000489451
	150.012	0.026416	78.5398	7.121	0.000604401
PVDF coated by 23 % PES	37.5030	0.026416	78.5398	0.397	0.000134783
	75.0060	0.026416	78.5398	4.113	0.000698189
	112.509	0.026416	78.5398	7.824	0.000885425
	150.012	0.026416	78.5398	11.412	0.000968603
PVDF coated by 28 % PES	37.5030	0.026416	78.5398	0.606	0.000205739
	75.0060	0.026416	78.5398	2.952	0.000501107
	112.509	0.026416	78.5398	5.234	0.000592320
	150.012	0.026416	78.5398	7.763	0.000658891

APPENDIX E (POLYETHERSULFONE IN GEL FORM)

APPENDIX F (DOPE SOLUTION OF PVDF AND PES)

APPENDIX G (THIN FILM COMPOSITE (TFC) MEMBRANE)

APPENDIX H (GAS PERMEATION RIG)