DEVELOPMENT OF PVDF/PEG THIN FILM COMPOSITE MEMBRANE FOR CO_2/N_2 GAS SEPARATION

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A thesis submitted to the Faculty of Chemical and Natural Resources Engineering in partial fulfillment of the requirement for the Degree of Bachelor of Engineering in Chemical Engineering (Gas Technology)

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SUPERVISOR’S 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 (Gas Technology)"

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Date : 18th February 2013

STUDENT’S DECLARATION

I declare that this thesis entitled " Development of PVDF/PEG TFC 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."

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In the name of ALLAH, Most Gracious, Most Merciful

Dedicated to my beloved parents my father, mother, sisters and brothers.

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First and foremost, I praised to Allah S.W.T, the Almighty for the strength and health that He gives me to initiate my steps in all my way until I have finished up my undergraduate research project within due course of time . Additionally, I also want give my pleasure to God because enabling me to prepare my thesis within the short time instead of exploring, understanding, gaining more knowledge which related to my research study as well.

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DEVELOPMENT OF PVDF/PEG TFC MEMBRANE FOR CO_2/N_2 FOR GAS SEPARATION

ABSTRACT

This research study develops polyvinylidenefluoride-poly ethylene glycol (PVDF/PEG) thin film composite (TFC) membrane for CO_2/N_2 gas separation. Asymmetric thin flat sheet membrane was prepared by dry wet phase inversion process consisting 15 %w/v of (PVDF) as the support layer polymer, 82 %w/v of N-methyl-2-pyrrolidone (NMP) as the solvent and 3 %w/v of distilled water as the non-solvent. Different concentration of poly (ethylene glycol) (PEG) polymer acts as the top film was study with 10 %, 15%, and 20% by using dip-coating method. The morphological structures of produced membranes were examined using Scanning Electron Microscopy (SEM). The Fourier Infrared Spectroscopy (FTIR) analysis also conducted in order to characterize the existence of the chemical bonding type in the membrane. The performance of the membrane was examined by conducting the gas permeation test. Pure carbon Dioxide (CO_2) and pure nitrogen (N_2) were used as the test gases by using feed ration range from 0.5 to 1.5 bars. As expected by the morphological structure, 10% PVDF/PEG (TFC) membrane showed the best performance compared to 15% and 20% PVDF/PEG TFC membrane. The selectivity of CO_2/N_2 was (1.01 at 0.5 bar), (1.07 at 1.0 bar) and (1.08 at 1.5 bar) for 20% PVDF/PEG TFC membrane, (1.02 at 0.5 bar), (1.11 at 1.0 bar) and (1.22 at 1.5 bar) for 15% PVDF/PEG TFC membrane, (1.03 at 0.5 bar), (1.27 at 1.0 bar), (1.43 at 1.5 bar) for 10% PVDF/PEG TFC membrane. From the investigation, PVDF/PEG (TFC) membrane was pointed the higher performance of selectivity and permeability behavior and hereby supposedly selected for future membrane development. The concentration of top layer membrane was discovered to affect the morphological structure which will preferentially affect the performance of the PVDF/PEG TFC membrane. Therefore, from the study conducted the most suitable asymmetric (TFC) membrane to developed high performance with concentration in range of 10% PVDF/PEG TFC membrane.

PENGHASILAN PVDF/PEG KOMPOSIT NIPIS MEMBRAN UNTUK PEMISAHAN CO_2/N_2 GAS

ABSTRAK

Penyelidikan ini adalah untuk menghasilkan fluoride polyvinylidene-polietilena glikol (PVDF/PEG) filem nipis komposit (TFC) membran untuk CO_2/N_2 pemisahan gas. Asimetrik nipis lembaran rata membran telah disediakan oleh fasa kering/basah inversi yang terdiri daripada 15% w/v (PVDF) sebagai sokongan lapisan polimer, 82% w/v N-metil-2-pyrrolidone (NMP) sebagai pelarut dan 3% w/v air suling sebagai bukan pelarut. Kepekatan (PEG) polimer yang berbeza bertindak sebagai filem atas adalah kajian bagi 10%, 15%, dan 20% dengan menggunakan celup kaedah salutan. Struktur morfologi membran yang dihasilkan telah diuji dengan menggunakan Pengimbas Mikroskop Electron (SEM). Fourier Transform Spektroskopi Inframerah (FTIR) juga dilakukan untuk mengesan kewujudan jenis ikatan kimia dalam membran. Prestasi membran telah diperiksa dengan menjalankan ujian penyerapan gas. Karbon dioksida (CO_2) dan nitrogen (N_2) telah digunakan sebagai gas ujian dengan menggunakan pelbagai tekanan dengan 0.5 hingga 1.5 bar. Seperti yang dijangka oleh struktur morfologi, 10% PVDF/PEG (TFC) membran menunjukkan prestasi yang terbaik berbanding dengan 15% dan 20% PVDF/PEG TFC membran. Kepilihan CO_2/N_2 adalah (1.01 pada 0.5 bar), (1.07 pada 1.0 bar) dan (1.08 pada 1.5 bar) untuk 20% PVDF/PEG TFC membran, (1.02 pada 0.5 bar), (1.11 pada 1.0 bar) dan (1.22 pada 1.5 bar) untuk 15% PVDF/PEG TFC membran, (1.03 pada 0.5 bar), (1.27 pada 1.0 bar), (1.43 pada 1.5 bar) 10% PVDF/PEG TFC membran. Mengikut kajian yang dijalankan, PVDF/PEG (TFC) membran telah menunjukkan prestasi yang lebih tinggi ketelapan pemilihan ini dipilih untuk penghasilan membran pada masa akan datang. Kepekatan membran lapisan atas telah dikesan boleh menjejaskan struktur morfologi terutamanya.menjejaskan prestasi PVDF/PEG filem nipis komposit membran. Dengan itu, daripada kajian yang dijalankan, asimetrik (TFC) membran yang paling sesuai dan berpontensi tinggi adalah konsentrasi 10% PVDF/PEG filem nipis komposit membrane.

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LIST OF ABBREVIATIONS

CO_2 - Carbon Dioxide
N_2 - Nitrogen
TFC - Thin Film Composite
PEG - Polyethylene Glycol
PVDF - Polyvinylidenefluoride
SEM - Scanning Electron Microscopy
FTIR - Fourier Transform Infrared Ray
wt - Weight
v - Volume
V - Volume
P - Permeance
Q - Flow Rate
l - Thickness of Membrane
ΔP - Trans-membrane Pressure
T - Time Displacement
A - Effectiveness Membrane Area
NMP - N-Methyl-1-Pyrrolidone
α - Selectivity
IR - Infrared Ray
Pj - Permeability of another Gas Component
Pi - Permeability of One Gas Component

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Gas separation by applying membrane technology plays an important role in minimizing the environmental impacts and cost for industrial processes specifically. According to Freeman (2005) at the moment, the most widely used membrane materials for gas separation are polymers. The economics of a gas separation membrane process is widely determined by the membrane's transport properties. Ideally, membranes should exhibit high selectivity and high permeability. Each gas component in a feed mixture has a characteristic permeation rate through the membrane. The rate is determined by the ability of the component to dissolve in and diffuse through the membrane material.

Recently, separation of carbon-dioxide from power plant flue gas and sequestration as liquid carbon dioxide into salt domes is a target of research programs around the world. The uses of selective membranes to separate carbon dioxide from flue gas have been suggested. The design process uses membranes with very high permeance and selectivity. Very low cost membrane and membrane modules are needed to make this process viable (Driolli, 2009).

Currently, development of thin film composite (TFC) membrane is one of the advance trends in material development for better gas separation membrane performance. Thin film composite (TFC) gas separation membranes useful in the separation of oxygen, nitrogen, hydrogen, water vapor, methane, carbon dioxide, hydrogen sulfide, lower hydrocarbons, and other gases are disclosed. Synthesis of membrane is one of the interesting parts. The most technically used membrane is made from organic polymer via phase separation methods. The phase-inversion process consists of the induction of phase separation in a previously homogeneous polymer solution either by temperature change, by immersing the solution in a non solvent bath (wet process) or exposing it to a non-solvent atmosphere (dry process) (Driolli, 2009).

1.2 Problem statement

The progress in the field of gas separation was grown mostly through the basic concepts of solution-diffusion implementation. The factor of membrane performance variables are selectivity and permeability. In gas separation, membrane selectivity is utilized to match up to the separating capability of a membrane for two or more species. Usually, the relationship between these aspects of membrane performance is directly proportional to each other; high selectivity membranes have more permeability and vice versa. Membrane application driven by development of gas separation technology has some problems that must be solved before commercially use. One of the major problems related in gas separation processes is the better membrane are required to change market economics significantly. Therefore, by developing (TFC) membrane is in order to provide good separating characteristics and mechanical strength rather than relying upon a single polymer membrane in improving the gas separation performance. This is the major study need to approach in this field to make the membrane capable in expanding what market significantly required.

1.3 Objective of Research

Based on the problem statement described in the previous section, the following were the objectives of this research:

1) To synthesis thin film composite (TFC) membrane.
2) To test the performance of thin film composite (TFC) membrane.
3) To analysis the physical and chemical properties of (TFC) membrane.

1.4 Scopes of the Study

In this research, there are several scopes of the study in order to achieve the above objective mentioned which are:

1) Synthesizing (TFC) membrane from PVDF as a support by using dry/wet phase inversion.

2) Conducting an experiment to study on (TFC) membrane performance using single gas permeation test.
3) Characterizing the membranes morphology by using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Ray (FTIR).

1.5 Rationale and Significant

The higher selectivity of membrane is the target of membrane separation process. Thus, the synthesis of (PVDF/PEG) thin film composite (TFC) membrane is one of the ways to enhance the membrane performance for gas separation process to be economically and effectively driven to the advance development applicable and reliable nowadays.

- In term of productivity and membrane performance:

✓ This research has been done to test the performance of (TFC) membrane. The better distribution of thin film permeability behavior towards carbon dioxide and nitrogen gas through the membrane increased the selectivity of the gas separation. Flat asymmetric thin film composite membrane exhibited highly selectivity than plain membrane based on the characterization of (TFC) membrane performance by using Scanning Electron Microscopy (SEM) device which analyzed the morphology of the (TFC) membrane, permeation test which demonstrated the permeability and selectivity performance and chemical and physical properties of (TFC) membrane by using Fourier Transform Infrared Ray (FTIR) accordingly.

- In term of economical aspect:

- ✓ The cost is significantly lower than the polymer replacement and energy cost associated with traditional technologies. The improvement in developing membrane and pretreatment design contribute a longer useful membrane life, which further recovers operating costs.

- In term of environmental aspect:
- ✓ Membrane systems do not involve the periodic removal and handling of spent solvents or polymers. Instead of that, incinerationn process can be performed for the items which do not require proceeding through disposal process.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition and Development of Membrane

A Membrane is a selective barrier that allows the separation of certain species in a fluid by combination of separating and sorption diffusion mechanism. Separation is achieved by selectively permeating one or more components of a stream through the membrane while avoiding the passage of one or more other components as shown in Figure 2.1 which illustrate the membrane separation principle. Besides that, membranes can selectivity separate components over an extensive range of particle sizes and molecular weights, from macromolecular materials such as starch and protein to monovalent ions. Economically, membranes have accepted as an important place in chemical technology and are used in a wide range of applications.

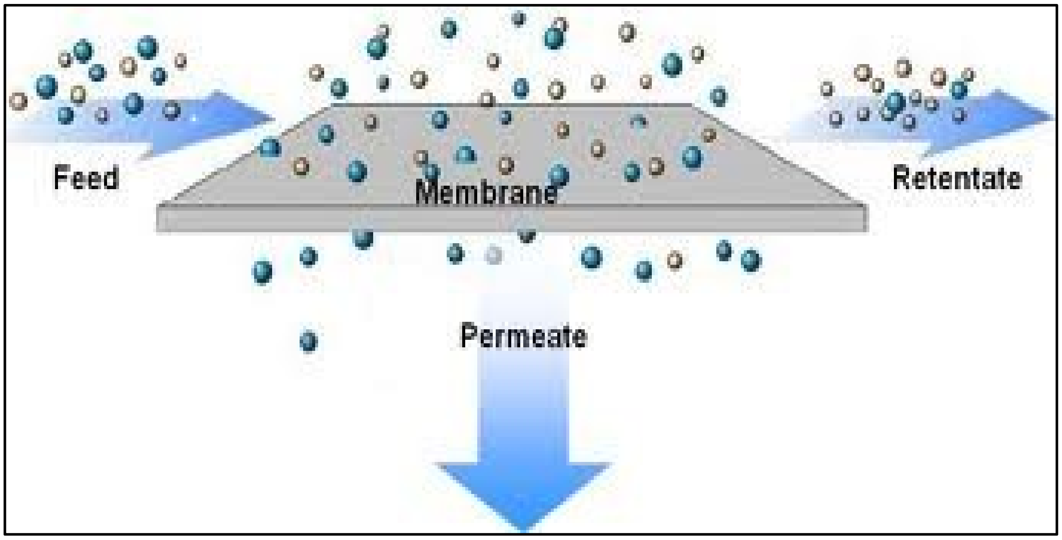


Figure 2.1: Illustrate the Membrane Separation's Principle

Indeed, membrane media is the determining component of a diffuser. It controls the operating and long term performance capabilities of the diffuser, allowing operation at a reasonable head loss and release of fine, discrete gas bubbles. Proper membrane material selection is critical in achieving desired results. Polymeric compounds are selected and engineered to produce desired surface properties, material stability, as well as environmental and chemical resistance. Then, optimum performance of a flexible membrane often directly correlates with proper membrane compound selection. On other word, improvement and advances in membrane technology have been expanding in many industrial sector; chemical, petrochemical, mineral and metallurgical, food, biotechnology, pharmaceutical, electronics, paper, pulp and water and many more applications.

2.2 Classification of Membrane Separation Processes

Membrane separations are in competition with physical methods of separation such as selective adsorption, absorption, solvent extraction, distillation, crystallization and cryogenic gas separation. Transport of selected species through the membrane is achieved by applying a driving force across the membrane. This gives a broad classification of membrane separations in the way or mechanism by which material is transported across a membrane. The flow of material across a membrane has to be kinetically driven, by the application of mechanical, chemical or electrical work (Hughes and Scott, 1996).

Certainly, membrane structure can be classified into two types which are symmetric and asymmetric ones. The functional of the membrane will depend on its structure and it is slightly different in term of physical and chemical properties as this essentially determines the mechanism of separation and thus the application.

2.2.1 Symmetric Membrane

Symmetric membrane is defined as a uniform structure which having the same chemical and physical structure throughout the hole and also called as an isotropic membrane. Generally, there are three types of symmetric membranes which are with cylindrical pores, porous and non-porous. Figure 2.2 show the schematic illustration of symmetrical membrane for microporous and nonporous dense structure.

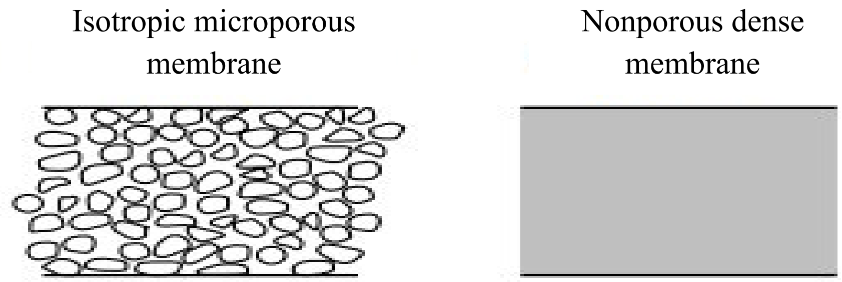


Figure 2.2: Schematic Illustration of symmetrical Membrane

2.2.1.1 Microporous

Microporous membranes are the simplest of all the symmetric membranes in term of operation. They are primarily used in filtration process. Micro porous membranes have defined pores or hole and separation is achieved by a sieving action (Hughes and Scott, 1996).

2.2.1.2 Nonporous

Nonporous mostly used in membrane separations involving molecules of the same size, gases and liquids. A driving force will take an action for diffusion through the membrane to occur. Usually, this membrane is used for gas separation.

2.2.1.3 Electrical charged

Electrically charged membranes can be dense or micro porous, however are most commonly very finely micro porous, with the pore walls carrying fixed positively or negatively charged ions. A membrane with fixed positively charged ions is known as an anion- exchange membrane and a membrane containing fixed negatively charged ions is called a cation-exchange membrane.

2.2.2 Asymmetric Membrane

Asymmetric membranes are characterized by non-uniform structure consisting of an active top layer supported by a porous sub layer. Asymmetric membranes are produced either by phase inversion from single polymers or as composite structure. Significantly, asymmetric membranes are classed as diffusion membranes and are used in reverse osmosis, gas permeation and pervaporation (Hughes and Scott, 1996). Figure 2.3 demonstrate the schematic illustration of asymmetric membrane.

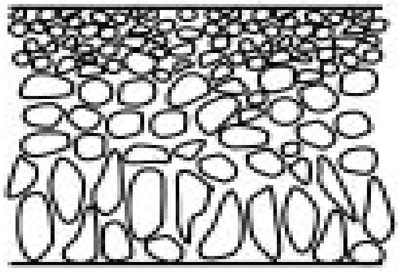


Figure 2.3: Schematic Illustration of Asymmetric Membrane

2.2.2.1 Thin film Composite Membrane

Thin film composite membrane was developed as an alternative means of producing a thin separating layer on top of a more porous support layer. The advantage of the (TFC) is that the role of the active, separating layer and the support can be separated, and each part made from optimum polymer, rather than relying upon a single polymer to provide both good separating characteristics and mechanical strength (Naylor, 1996). Figure 2.4 show the schematic demonstration of TFC membrane.

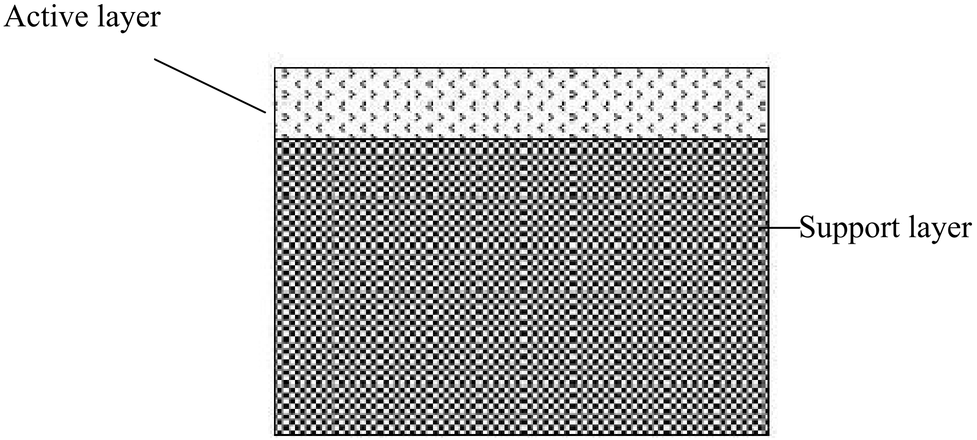


Figure 2.4: Schematic Illustration of Thin Film Composite Membrane

2.2.2.2 Liquid Membrane

Liquid membranes is a membrane which containing carriers to facilitate selective support for gases or ions. The mobile carriers which held by capillary action in the pores of a microporous film can be employed to improve single bulk material properties.

2.3 Membrane Module

Significantly, large surface areas are required for industrial applications of membrane processes. Therefore, a practical solution for providing this large surface area is packing the membranes into small unit is called as module. The module is the base for membrane process design and installation. During the process, a stream feed enters the module with a specific content at a specific flow rate. There are two streams which separate the feed stream when passing through the membrane module which are a retentate stream and permeate stream. The retentate stream is the part which retains in the feed stream while the permeate stream is the part that passes through the membrane. Typically, plate and frame module, spiral-wound module, tubular module and hollow-fiber module are largely used for industrial application.

2.3.1 Plate and Frame Module

The structure is simple where the arrangement placed in a sandwich-like fashion with their feed sides facing each other. The membrane permeate is collected from each support plate. The spacer surface is made uneven in order to promote turbulence of the feed fluid and minimize concentration polarization. The module diameter is about 20-30cm. The total membrane area in one module is up to 19m^2, depending of the height of the module (Wang et al, 2006). Figure 2.5 shows the structure of plate and frame membrane module.

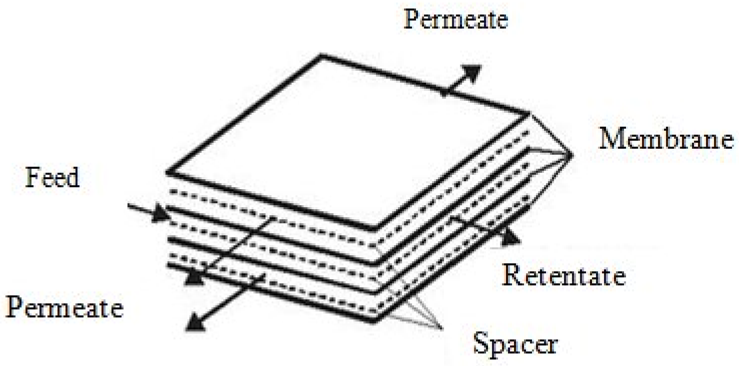


Figure 2.5: The Structure of Plate and Frame Membrane Module (technologyreport.mecadi.com)

2.3.2 Spiral-wound Module

The spiral-wound is in fact a plate-and-frame system wrapped around a central collection pipe, similar to a sandwich roll. Membrane and permeate-side spacer material are then glued along three edges to build a membrane envelope. The feed flows axial through the cylindrical module parallel along the central pipe and the permeate flows radially toward the central pipe (Wang et al, 2006). Figure 2.6 shows the structure of spiral-wound membrane module.

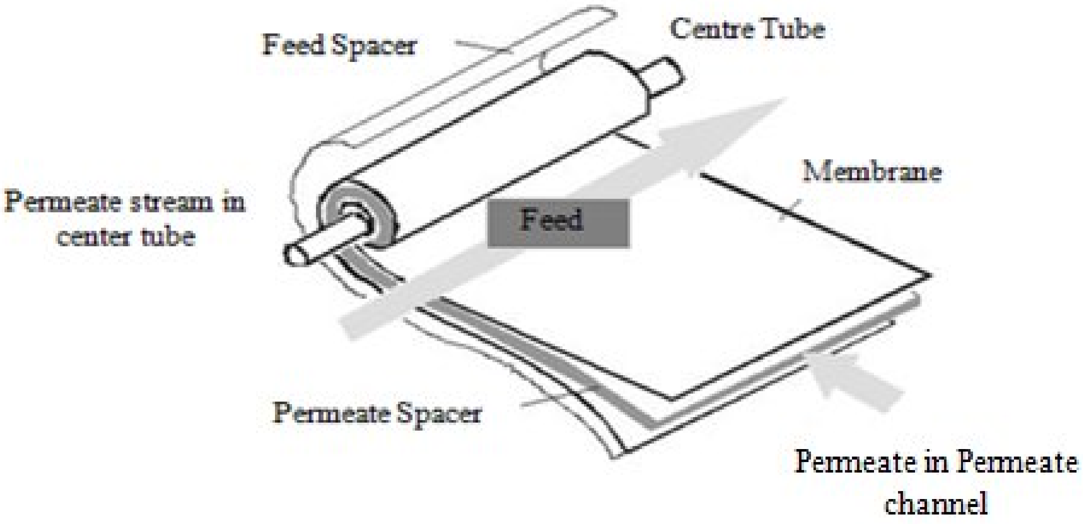


Figure 2.6: The Structure of Spiral-wound Membrane Module (technologyreport.mecadi.com)

2.3.3 Tubular Module

In this type of module, a number of membranes of tubular shape are encasing in a container. The feed solution always flows through the center of the tubes while the permeate flows through the porous supporting tube into the module housing (Wang et al, 2006). Figure 2.7 demonstrate the view of tubular membrane module.

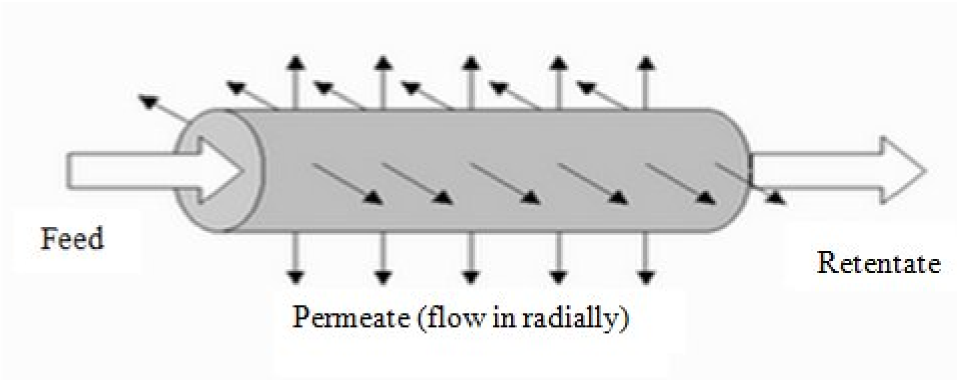


Figure 2.7: The View of Tubular Membrane Module (technologyreport.mecadi.com)

2.3.4 Hollow Fiber Module

Hollow-fiber modules consist of a large number of fibers assembled together in a module. The membrane is self-supporting for this module. There two basic types of arrangement for this module which are inside-out arrangement and outside-out arrangement (Wang et al, 2006). Figure 2.8 shows the view of hollow fiber membrane module.

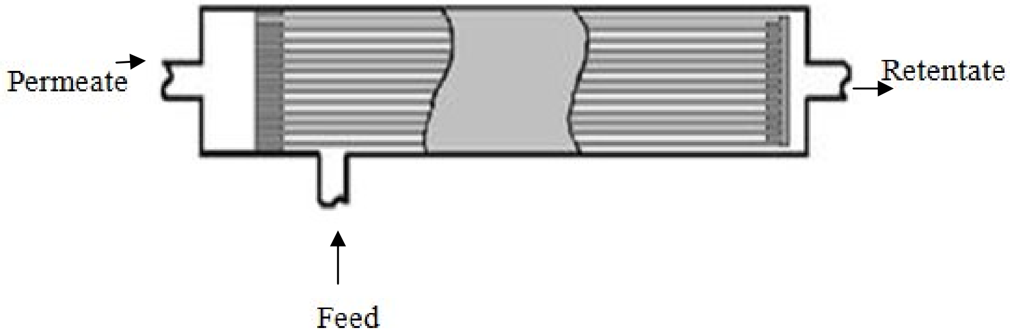


Figure 2.8: The View of Hollow Fiber Membrane Module (technologyreport.mecadi.com)

2.4 Polymeric Membrane

Polymeric membranes are still dominating a very wide range of industrial applications. In term of advantages, many different types of polymeric materials are commercially available and large variety of different selective barriers that is, porous, nonporous, charged and affinity can be prepared by versatile and robust methods (Hughes and Scott, 1996).

2.4.1 Polyvinylidenedifluoride (PVDF)

The material is a popular choice for ultrafiltration and microfiltration membranes. It offers similar pH and temperature limits as polysulphone, but has a higher tolerance to oxidizing agents such as chlorine. It is available as an anisotropic membrane formed by phase inversion. (PVDF) also shows a clear advantage in performance over polysulphone membranes, with fluxes of up to double those of similar membranes. Besides that, (PVDF) are very attractive materials as a hydrophobic support for forming a (TFC) membrane due to its outstanding properties such as high mechanical strength, thermal stability, chemical resistance, and high hydrophobility compared to other commercialized polymeric materials. The excellent thermal stability of (PVDF) has made it interesting as a membrane in a wide range of industrial applications (Hughes and Scott, 1996). PVDF is certainly used as insulation on some kinds of electrical wires, tactile sensor arrays manufacturing and production of composite electrodes for lithium ion batteries.

2.4.2 Polyethylene Glycol (PEG)

Polyethylene Glycol, (PEG) is a condensation polymer of ethylene oxide and water which are present in many organic solvent. Lee et al (1995) stated that PEG offers a hydrophilic surface property, a large excluded volume, and unique coordination with surrounding water molecules in an aqueous medium. Other than that, (PEG) has been extensively investigated for the separation of various mixtures, and scientific researchers have been made to modify (PEG) membrane in different ways to enhance it performance. PEG mostly used in pharmaceutical products.

2.4.3 Polysulphone

This membrane can be used for ultrafiltration and microfiltration membranes which has good chemical and temperature stability. It also shows some tolerance to oxidizing agents such as chlorine, prolonged exposure, or contact with high concentrations can cause cracking of the membrane film (Hughes and Scott, 1996). Polysulfone used as dielectric in capacitors, copolymer, water waste recovery, food beverage processing and gas separation.

2.4.4 Polyacrylonitrile

Membranes made from this material, either alone or as a copolymer and often claimed to be hydrophilic and to exhibit a wider tolerance to solvents than some of the other membranes. It is produced using the phase inversion technique and is available for separations in the ultrafiltration range (Hughes and Scott, 1996). Commonly used for fishing rods, pressure vessels , copolymers such as styrene-acrylonitrile (SAN) and acrylonitrile butadiene styrene (ABS) plastic.

2.4.5 Other Polymers

The above list does not cover all of the materials in use for membrane. New polymer and additives are continually being introduced into the market according to the manufacturer in producing and make a notice to public for what polymer that they have developed,

2.5 History of Membrane Gas Separation

Gas separation has become a major industrial application of membrane technology only during the past 20 years, but the study of gas separation has a long history. Systematic studies began with Thomas Graham who, over a period of 20 years, measured the permeation rates of all the gases then known through every diaphragm available to him. This was so small task because his experiments had to start with synthesis of the gas. Graham gave the first description of the solution-diffusion model, and his work on porous membranes led to Graham's law of diffusion. Through the remainder of the nineteenth and the early twenties centuries, the ability of gases to permeate membranes selectively had no industrial or commercial use. The concept of the perfectly selective membrane was, however, used as a theoretical tool to develop physical and chemical theories, such as Maxwell's kinetic theory of gases (Baker, 2004).

2.6 Membrane Gas Separation Process

(Baker, 2004) defined that most gas separation processes require that the selective membrane layer be extremely thin to achieve economical fluxes. Typical membrane thicknesses are less than 0.5µm and often less than 0.1µm. Early gas separation membranes were adapted from the cellulose acetate membranes produced for reverse osmosis by the Loeb- Sourirajan phase separation process. These membranes are produced by precipitation in water; the water must be removed before the membranes can be used to separate gases. However, capillary forces generated as the liquid evaporates cause collapse of the finely microporous substrate of the cellulose acetate membrane, destroying its usefulness. This problem has been overcome by a solvent exchange process in which the water is exchanged for an alcohol, then for hexane. The surface tension forces generated as liquid hexane evaporated are much reduced, and dry membrane is produced. Membranes produced by this method have been widely used by Grace (now GMS, a division of Kvaener) and Separex(now a division of UOP) to separate carbon dioxide from methane in natural gas.

2.6.1 Nitrogen Separation from High-Nitrogen Gas

Drioli (2009) mentioned that a second application of rubbery membranes in natural gas processing is separation of nitrogen from high-nitrogen gas. Pipeline gas must normally contain less than 4% nitrogen, but the pipeline operator will often accept high-nitrogen if sufficient low-nitrogen gas is available to dilute the off-spec gas. When dilution is not possible, cryogenic, adsorption or membrane treatment of the gas is required.

2.6.2 Carbon Dioxide Gas Separation

Processes requiring the separation of carbon dioxide from gas streams include purification of sour gases, removal of CO2 from biogas and separation of carbon dioxide in enhanced oil recovery processes. Although other processes such as chemical absorption have been used extensively, membranes have a number of advantages for certain applications such as in CO2 removal from natural gas on offshore production platforms where lightweight and minimal maintenance favor their adoption (Hughes and Scott, 1996).

2.7 CO_2 and N_2 gas separation in produced PVDF/PEG for TFC membrane

PVDF/PEG is one of the (TFC) membrane inventions that progressively to enhance the best performance for carbon dioxide, (CO_2) and nitrogen gas, (N_2) separation in the term of purification of gas separation from this undesired gas compound. The surface modification will be performed on the thin film composite membrane in order to improve the permeation of gas in more effective contact. (PVDF) is one of the fluorocarbon polymer that have higher impact strength, pure thermoplastic fluoropolymer, highly non reactive and many more. For the membrane solvent, (PEG) act as the attachment together with (PDVF) polymer group. Other than that, (PVDF) also is one of the good substrate materials with high chemical stability and permeability. The combination of (PVDF) with poly ethylene glycol, (PEG) has attached special attention due to the advantages of not only better thermal stability and better compressive strength and chemical resistance characteristic contributed by (PVDF).

CHAPTER 3

METHODOLOGY

This chapter covers the type of materials used to develop the asymmetric thin film composite membrane which comprising of the experimental procedures and method used to test this (TFC) membrane. In Surface, there are three steps involve in TFC membrane development. They are (1) Preparation of the membrane dope solution, (2) membrane fabrication to form asymmetric flat sheet membrane support and (3) Dip coating to form a thin film layer on flat sheet membrane support. The selection of suitable membrane material also plays an important role in achieving the best performance in membrane separation process. Figure 3.1 shows the research design for this TFC membrane development process.

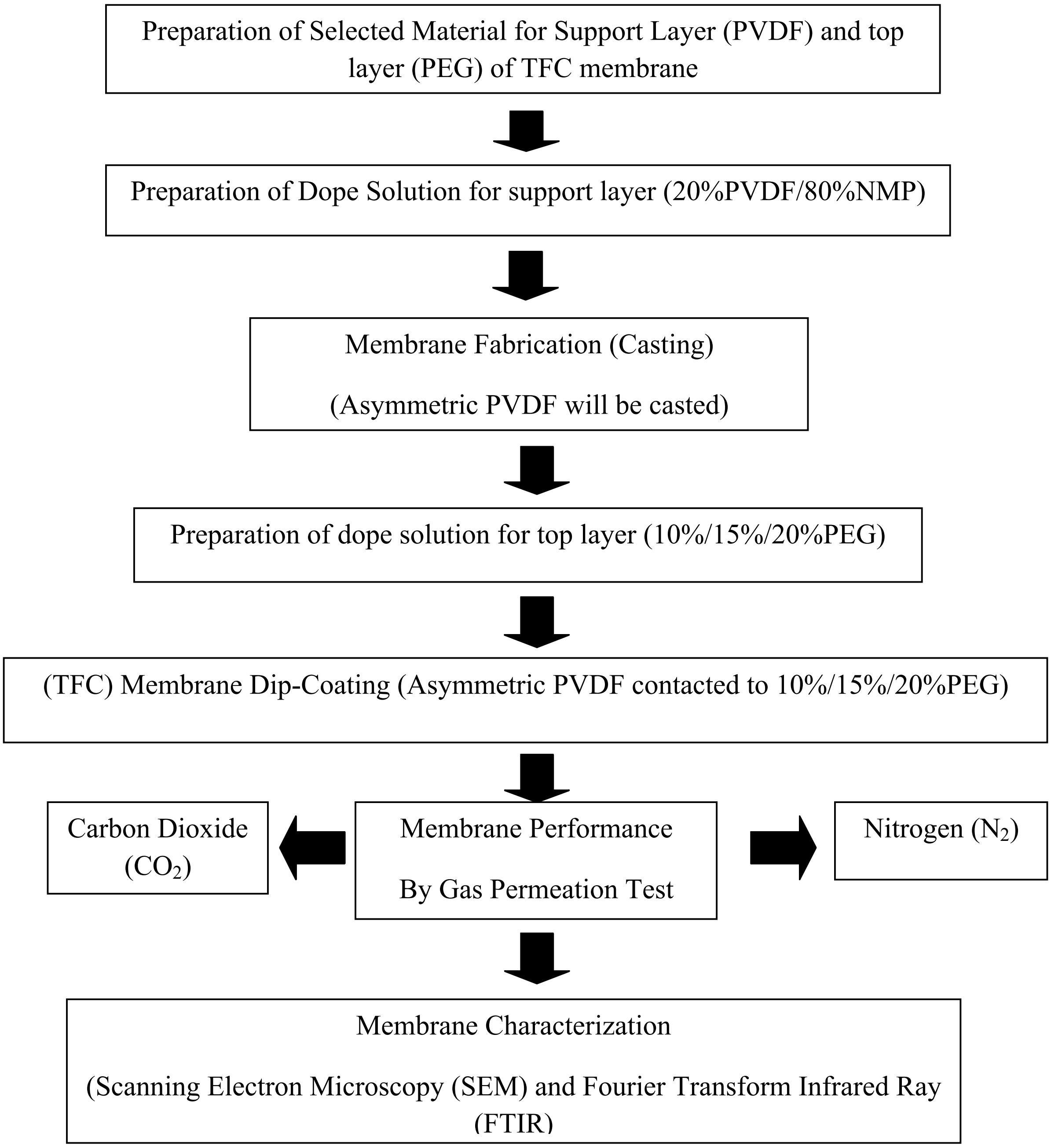


Figure 3.1: Illustrate the Research Design

3.2 Material Selection

In thin film composite membrane development, selection of suitable polymer and its solvent is an important aspect. This section will discuss about the selection of the materials and the interesting criteria that had been performed by this materials.

3.2.1 Polymer selection

3.2.1.1 Polyvinylidenefluoride (PVDF)

Polyvinylidenefluoride (PVDF) will be selected to be the polymer in this research. (PVDF) is a semi-crystalline polymer containing a crystalline phase and rubbery phase. The crystalline phase provides thermal stability and the rubbery phase has flexibility towards membranes. (PVDF) is stable while it is attacked by most of the corrosive chemicals and organic compounds including acids, alkaline, strong oxidants and halogens. Besides that, the hydrophobicity of this polymer provides a potential application in the membrane-based gas absorption and oil or water separation. Figure 3.1 shows the molecular structure of Polyvinylidenefluoride (PVDF) and Table 3.1 shows the physical, mechanical and thermal properties of (PVDF).

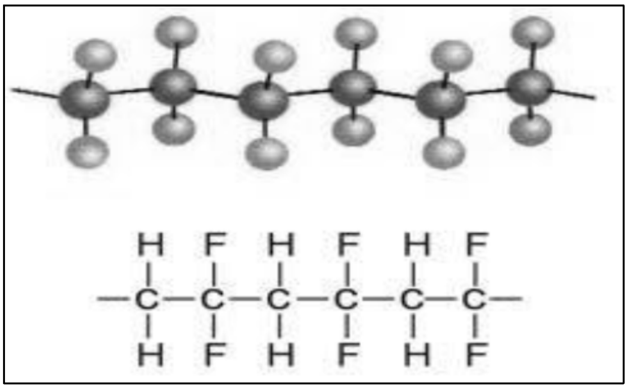


Figure 3.2 Molecular Structure of Polyvinylidenefluoride (PVDF)

Table 3.1 Physical, mechanical and thermal properties of Polyvinylidenefluoride (www.polymerprocessing.com)

Properties	**Value**
Molecular weight of repeat unit (g/mol)	64.03
Amorphous density at 25°C (g/cm^3)	1.74
Crystalline Density at 25°C (g/cm^3)	2.00
Glass transition Temperature(°C)	-38
Tensile strength (yield) (MPa)	11.7-141
Modulus of Elasticity(Gpa)	0.2-7.0
Elongation at break (%)	4.5-800
Compressive strength (yield) (MPa)	3.0-172
Thermal conductivity (Wm^{-1} K^{-1})	0.11-0.3
Crystallization Temperature (°C)	12-142

3.2.1.2 Polyethylene Glycols (PEG)

Polyethylene glycols (PEG200) will be selected to be the barrier layer which will be placed on a porous support of (PVDF) based. (PEG) are cheap oligomers that are easily available with a molecular weight ranging from 62g mol^{-1} (ethylene glycol monomer) up to 40 000 gmol^{-1}. PEGs are inherently neutral molecules soluble in water and a wide range of organic solvents. Table 3.2 shows the physical properties of Polyethylene glycols (PEG 200).

Table 3.2 Physical properties of Polyethylene glycols (PEG200) (msdssearch.dow.com)

Physical properties	**Value**
Range of average molecular weight	190-210
Range of average hydroxyl number, (mg KOH/g)	535-590
Density, (g/cm3) @ 20°C	1.1238
Melting or freezing range, ° C	sets to glass below -65
pH at 25°C, 5% aqueous solution	4.5-7.5
Physical form	Liquid

3.2.2 Solvent Selection

3.2.2.1 N-Methyl-2- Pyrrolidone (NMP)

N-methyl-2-Pyrrolidone which known as (NMP) is aprotic solvent which high in solvency and low volatility. It is colorless, high boiling point, high flash point, low vapor pressure liquid and carries a mild amine-like odor.(NMP) has high chemical and thermal stability and is completely miscible with water at all temperature. (NMP) can serve as co-solvent with water, alcohols, glycol ethers, ketones, and aromatic/chlorinated hydrocarbons. (NMP) is both recyclable by distillation and readily biodegrable.(www.lyondellbasellcom). Table 3.3 shows the physical properties of 1-methyl-2-Pyrrolidone.

Table 3.3 Physical Properties of N-methyl-2-Pyrrolidone (www.polymerprocessing.com)

Component	Value
Density (g/cm3)	1.03
Solubility in water (%)	100
Viscosity (cP)	1.70
Molecular weight (g/mol)	99.1
Boiling point (°C)	202

3.2.2.2 Ethanol

Ethanol is a clear, colorless liquid. Its functional group is a hydroxyl group,-OH which bonded to a carbon atom. Table 3.4 shows the physical properties of ethanol which will be used as PEG solvent.

Table 3.4 Physical Properties of Ethanol (www.infoplease.com)

Component	Ethanol (Industrial Grade)
Molecular Weight MW (g/mol)	46.0684
Melting Point (°C)	-117.3
Boiling Point (°C)	78.5
Density (kg/m^3)	789

3.2.3 Coagulant Medium

3.2.3.1 Methanol

Methanol is the simplest alcohol, and is a light, volatile, colorless and flammable liquid. Commonly, it is used as an antifreeze, solvent, fuel and as a denaturant for ethanol. Table 3.5 shows the physical properties of methanol.

Table 3.5: Physical Properties of. Methanol (www.infoplease.com)

Component	**Methanol (Industrial Grade)**
Molecular Weight MW (g/mol)	32.04
Melting Point (°C)	-98
Boiling Point (°C)	65.04
Density (kg/m^3)	790

3.2.4 Non Solvent

3.2.4.1 Distilled Water

Distilled water will be use as non solvent additives. Table 3.6 shows the physical properties of non solvent additives.

Table 3.6: Physical Properties of Non solvent Additives (www.infoplease.com)

Component	**Distilled Water**
Molecular Weight MW (g/mol)	18.02
Melting Point (°C)	0
Boiling Point (°C)	100
Density (kg/m^3)	998

3.2.5 Test Gases

In this study, two types of gases which are pure oxygen and pure nitrogen will be used as test gases. Table 3.6 shows physical properties of pure oxygen and nitrogen.

Table 3.7 Physical Properties of test Gases

Component	**Carbon dioxide (CO_2)**	**Nitrogen (N_2)**
Kinetic diameter	3.3	3.64
Molecular weight (g/mol)	44.01	28
Molecular speed (cm/s)	44	47500
Viscosity (mPa.s)	15.4	20.7

3.3 Dope Solution Preparation

The polymer Polyvinylidenefluoride (PVDF) will dry first in the vacuum oven at 90 °C for 24 hours before preparing the dope solution. The weighted PVDF was poured into the NMP solvent and stirred to ensure the mixture is well mixed. The solution was stirred for 5 hours. The non-solvent (distilled water) will be added drop by drop into the mixture and stir for 2 hours. After all, the polymer solution consists of 15%w/v PVDF, 82%w/v NMP and 3%w/v distilled water were formed as a dope solution significantly. Then, the dope solution was placed in a storage bottle and degassed by using ultrasonic bath to remove any trace of bubbles. Figure 3.3 show the dope solution apparatus set up.

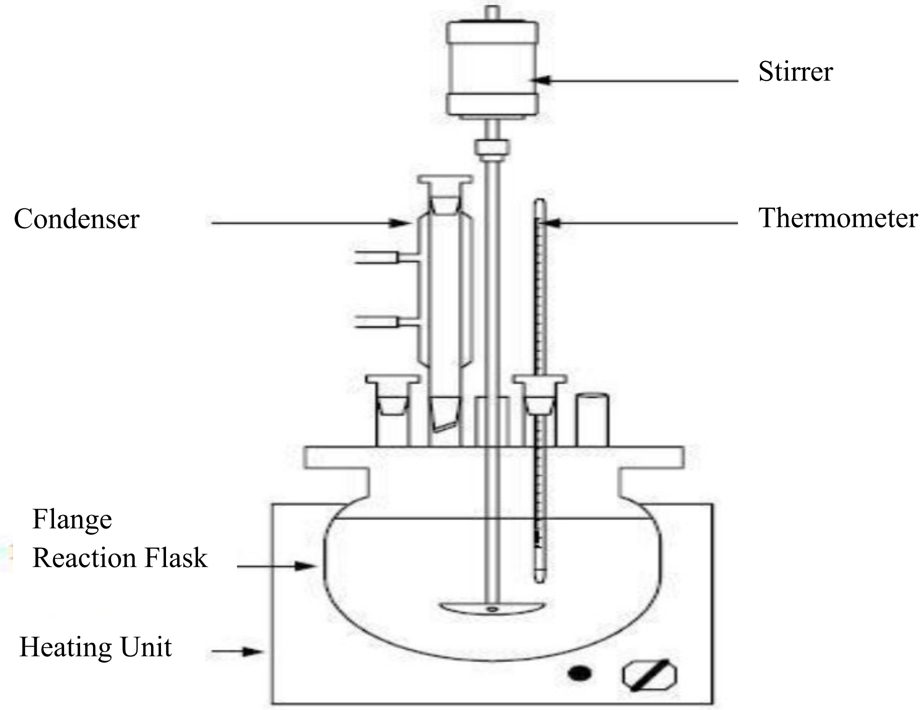


Figure 3.3 Dope Solution Preparation Set up

3.4 Membrane Fabrication (Casting)

The Dry / Wet Phase Inversion method was used in order to get the asymmetric PVDF. Free flat membrane was obtained by casting the polymer solution on a glass plate. PVDF support was casted at 25^{o}C where approximately 15%wt% PVDF will be placed onto a glass plate. The dope solution was extended on a gas plate by using glass rod under a room temperature. Then, the glass was immersed immediately into the coagulation bath consists of water as a coagulation medium. The support film was dried in a vacuum oven for 2 hours at 60^{o}C and then immersed in methanol. Then, the dense homogenous membrane was rinsed with water. After that, the PVDF support membrane was dried at 80^{o}C in a vacuum oven (Nunes, 2006).

3.5 Membrane Dip-Coating

In order to get thin film layer of (PEG) to develop (TFC) membrane, three different range of weight per volume percentage for 10%, 15% and 20%w/v (PEG) were allowed to contact to the (PVDF) support layer which fabricated already in the previous step. Then, (PVDF/PEG) Thin film (TFC) membrane will be formed and can be used for gaseous separation experiments directly (Nunes, 2006).

3.6 Gas Permeation Test

The pure CO_2/N_2 gas permeation was tested by using the gas permeation test apparatus separately. The test was done under the ambient temperature (30°C) and feed pressure about 0.5, 1.0 or 1.5 bar gauge. A soap bubble flow meter in the gas permeation system was the important part to measure the gas permeation rate. Figure 3.4 shows the gas permeation test apparatus and Figure 3.5 illustrates the cross-sectional view of assembled permeation cell and gas Flow Direction.

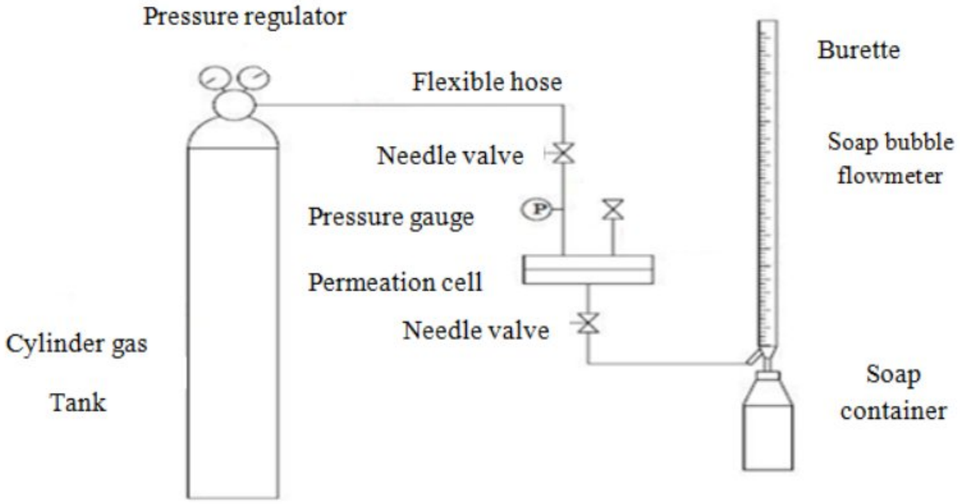


Figure 3.4: Gas Permeation Test Apparatus (Cheer, 2002)

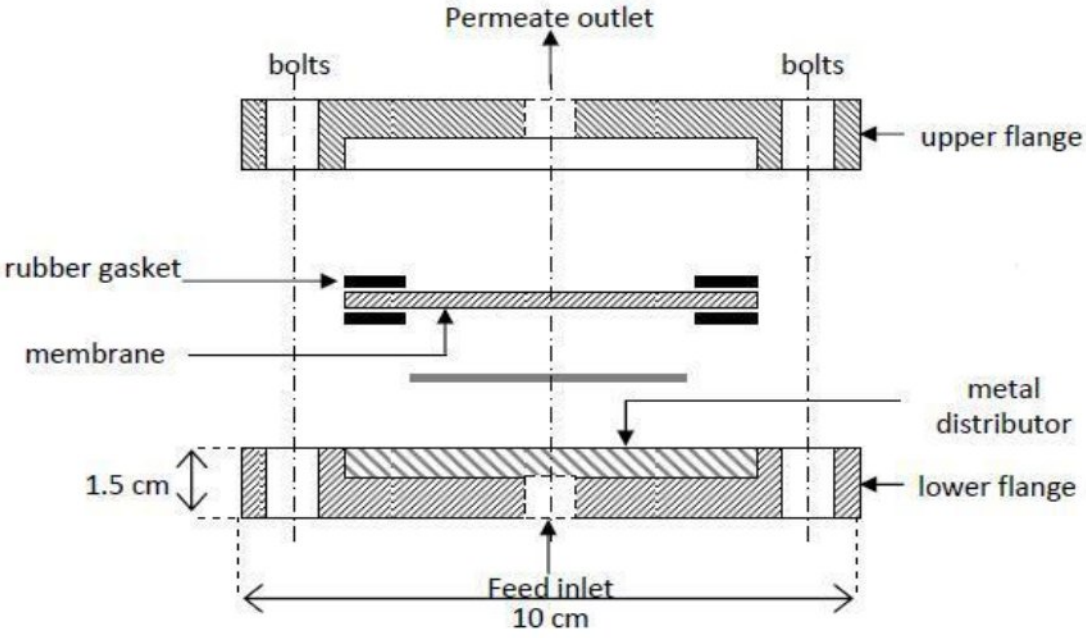


Figure 3.5: A cross-Sectional View of Assembled Permeation Cell and Gas Flow Direction (Cheer, 2002)

The permeability rate and selectivity of the membrane towards Carbon Dioxide, (CO_2) and Nitrogen, (N_2) has been evaluated by used the following Eqn (3.1) and Eqn (3.2):

$$P_i = \frac{Q}{A\Delta P} = \frac{P_i}{l} \qquad \text{Eqn (3.1)}$$

Where: Q = Gas Flowrate (cm^3/s)

A = Effective membrane area (cm^2)

ΔP = Transmembrane pressure in system (cm Hg)

P_i = Permeability for Gas Component ($cm^3/s.cm^2.cm$ Hg)

l = Thickness of membrane in cm

1 GPU = 1×10^{-6} $cm^3/s.cm^2.cm$ Hg (The calculated permeability should be converted in GPU unit).

The selectivity can be calculated by using Eqn.(4.2):

$$\alpha = \frac{P_i}{P_j} \qquad \text{Eqn (3.2)}$$

α : Selectivity

P_i : Permeability of one gas component

P_j : Permeability of another gas component

3.7 Membrane Characterization

3.7.1 Scanning Electron Microscope (SEM)

In order to identify the membrane morphology of PVDF/PEG, SEM (Philips SEMEDAX, XL40, and PW6822/10) has been used preferentially. First of all, PVDF/PEG has been cut into small pieces and immersed into the nitrogen liquid. Then it will be coated with gold by sputter coating under vacuum condition. Then, SEM device was analyzed the morphology of the PVDF/PEG.

3.7.2 Fourier Transform Infrared Ray (FTIR)

FTIR (Thermo fisher scientific Nicolet) drives a spectral snapshot on the structure of membrane and the specific molecular functional group which important to show us the effect of different solvent used in membrane to the membrane structure. In term of analyze, the FTIR results was displayed changes of the functional groups and elements in the membranes when they are heated from room temperature to high temperature.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Effect of Different Concentration on Membrane Performance for Gas Separation

In this research, the gas permeability and selectivity through the membrane is evaluated by conducting gas permeation test. The permeation rate and selectivity were calculated using Eqn (3.1) and Eqn (3.2) which expressed in Barrer [1 Barrer = 1×10^{-10} (cm^3 (STP) cm)/ ($cm^2 s cmHg$)].

Table 4.1: Gas Permeance and Selectivity for Based PVDF Membrane and PVDF/PEG TFC Membrane

Membrane	Feed Pressure (cm Hg)	Permeance (GPU)		Selectivity, α (CO_2/N_2)
		CO_2	N_2	
PVDF	37.50	4465.26	4583.32	0.97
	75.01	4753.34	4944.75	0.96
	112.51	4180.24	4445.06	0.94
20% PVDF/PEG	37.50	5072.41	5044.75	1.01
	75.01	5046.35	4677.89	1.07
	112.51	4465.26	4110.28	1.08
15% PVDF/PEG	37.50	5098.74	5053.58	1.02
	75.01	5098.74	4604.79	1.11
	112.51	4961.40	4076.17	1.22
10% PVDF/PEG	37.50	5560.51	5377.87	1.03
	75.01	5824.25	4576.19	1.27
	112.51	5488.03	3822.40	1.43

Permeability and selectivity of TFC membrane developed using same PVDF based support and different concentration of selective top layer (PEG) shown in Table 4.1. Separation behavior occurs at the selective layer of the membrane and the based support later acts as the mechanical strength of the membrane. From Table 4.1, (10% w/v) PVDF/PEG TFC show the highest selectivity CO_2/N_2 separation factor of 1.43 with CO_2 permeance of 5488.03 GTU at room temperature. PVDF/PEG provides highest carbon dioxide permeability through the membrane compared to PVDF based membrane specifically. The high selectivity of CO_2/N_2 could be enlightened by the high solubility of CO_2 in the PEG. Interestingly, having TFC membrane with PEG as the selective layer improved the selectivity against nitrogen.

Indeed, the flexible and polar (PEG) structure is very attractive for the polar CO_2 molecules compared to N_2 molecules.

4.2 Effect of Different Feed Pressure on Membrane Performance for Gas Separation

The gas separation behavior is verified by plotting a graph of the permeation rate for Carbon dioxide (CO_2) and Nitrogen (N_2) and also CO_2/N_2 selectivity ratio for each membrane developed from different concentration (%w/v) of PVDF/PEG TFC membrane against the feed pressure variation. Figure 4.1 show a graph of permeation rate of CO_2 versus feed pressure, Figure 4.2 show a graph of permeation rate of N_2 versus feed pressure and the selectivity for CO_2/N_2 of PVDF/PEG TFC membrane and based PVDF membrane is presented in Figure 4.3 respectively.

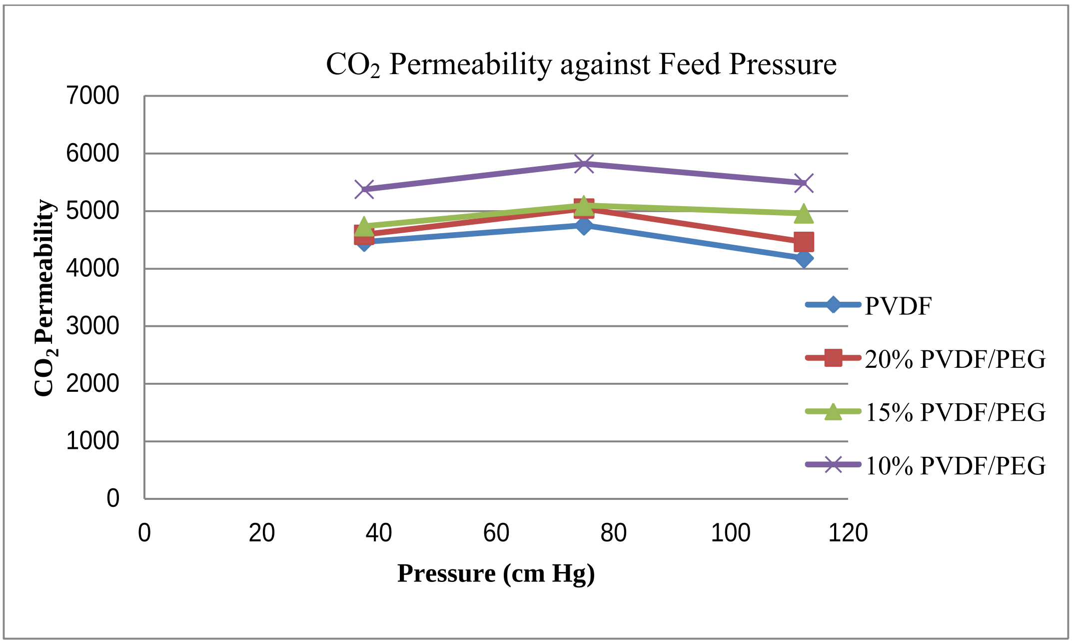


Figure 4.1: CO_2 Permeance of TFC Membranes and Based Membrane Developed Against Feed Pressure

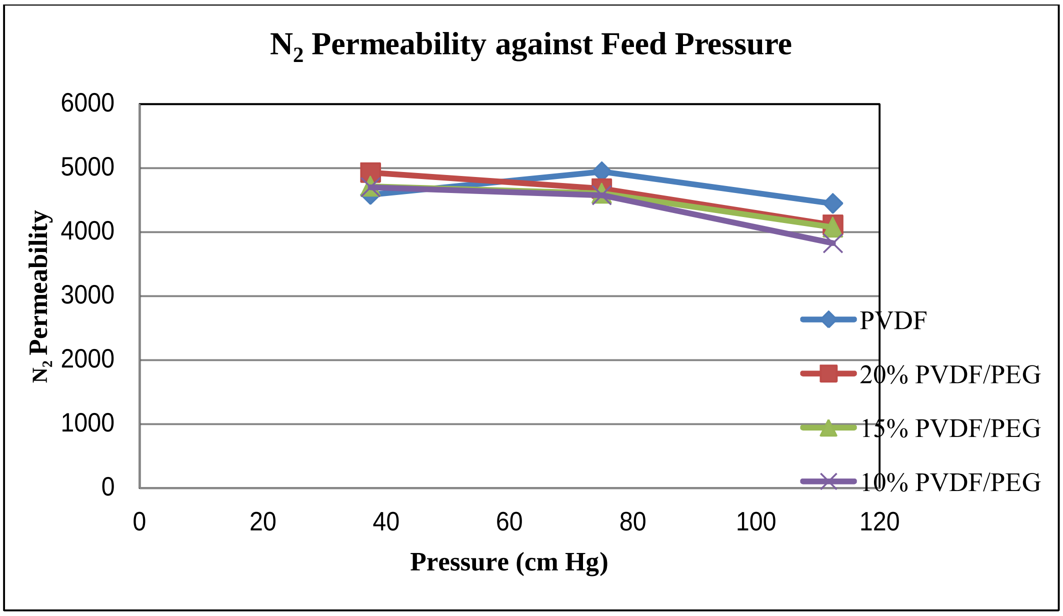


Figure 4.2: N_2 Permeance of TFC Membranes and Based Membrane Developed Against Feed Pressure

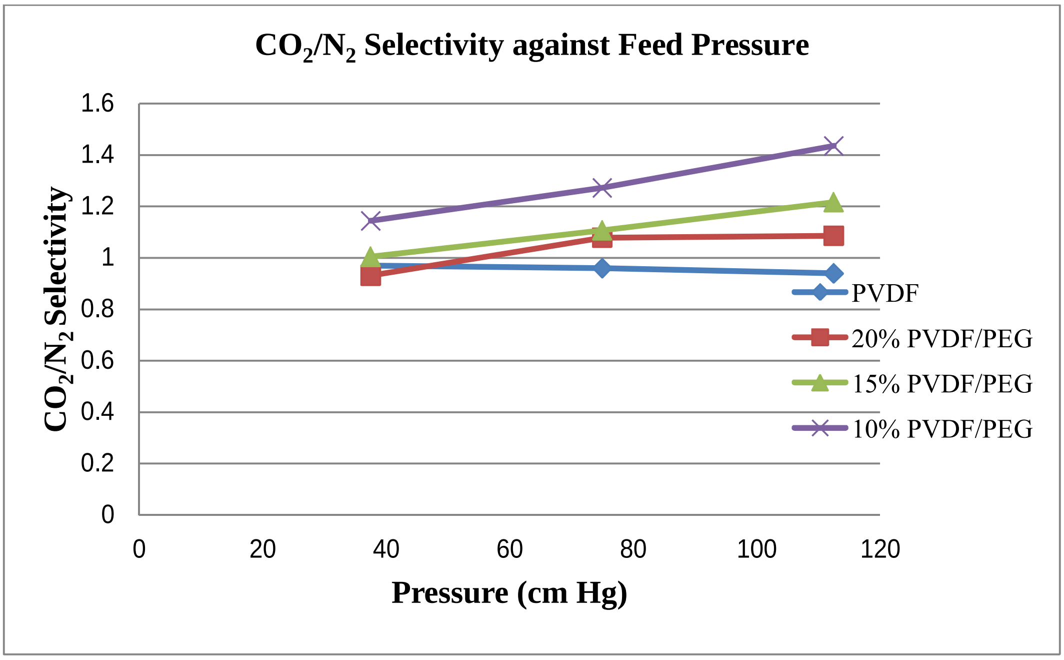


Figure 4.3: A Graph of CO_2/N_2 Selectivity of PVDF Membrane and PVDF/PEG Membranes Developed Against Feed Pressure

According to Figure 4.1, CO_2 permeance values increase in the order of PVDF membrane < 20% PVDF/PEG TFC membrane < 15% PVDF/PEG TFC membrane < 10% PVDF/PEG TFC membrane. In term of permeation, the differences of permeance rate among membrane developed from difference range of weight percentage of PEG selective layer on PVDF based membrane and plain PVDF membrane could be justified by referring to their morphologies structure respectively. Surface porosity, pore size and wetting resistance are important parameters which significantly affect the CO_2 permeability performance (Mansourizadeh and Ismail, 2012). From Figure 4.2, plain PVDF membrane demonstrates the highest N_2 permeability rate compared to other developed TFC membrane. The plain PVDF membrane presented the higher N_2 permeance than the other membranes due to the open structure with large finger-likes and good surface porosity (Mansourizadeh and Ismail, 2012). Permeation rates could be affected by the interaction of a gas mixture on the membrane and also feed and permeate pressure whereas the membrane structure can change under pressure variation.

Both of graph in Figure 4.1 and Figure 4.2 shows declined trend when high pressure was applied because of membrane compactness. The high pressures required in the applications tend to cause compaction of the membrane, which in turn reduced membrane permeability (Lawson, Hall and Lloyd, 1994).

On the other hand, carbon dioxide, CO_2 and nitrogen, N_2 are both gases which acted as gas penetrant. In fact, CO_2 is the fast gas penetrant and N_2 is the slow gas penetrant. Fast gases permeate through the membrane wall more readily than slow gases. The ability of a membrane to separate two gases is determined by their selectivity, the ratio of the permeability of the two gases. Figure 4.3 observed that, the selectivity is highest for 10%PVDF/PEG TFC membrane which is 1.34 compared to other membranes which correlated to morphological structure of membrane particularly.

4.1 Morphological Structure of PVDF membrane and PVDF/PEG TFC Membrane

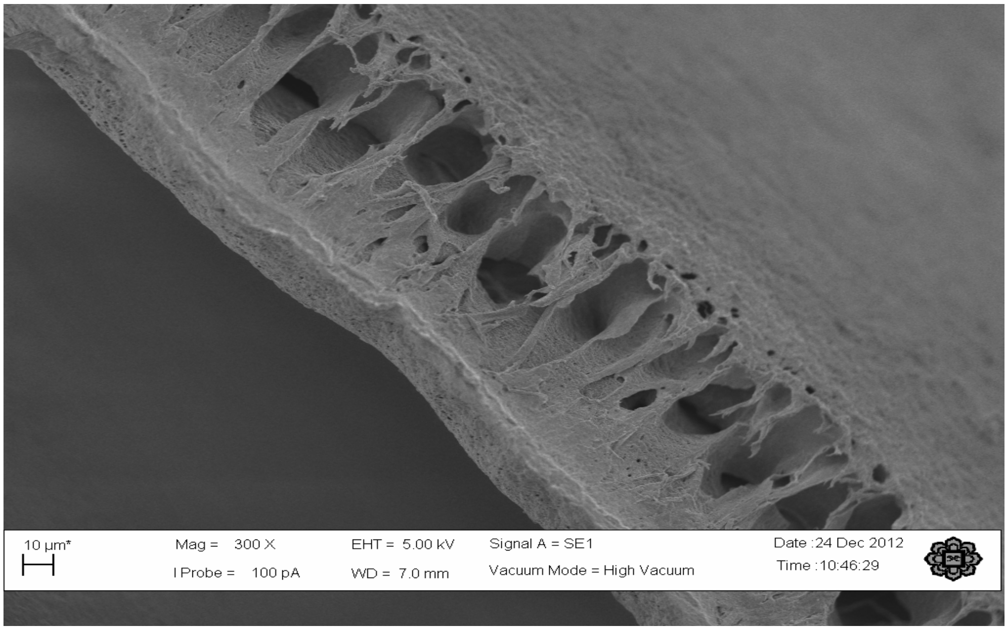


Figure 4.4 : Morphology Structure of PVDF at magnification 300X

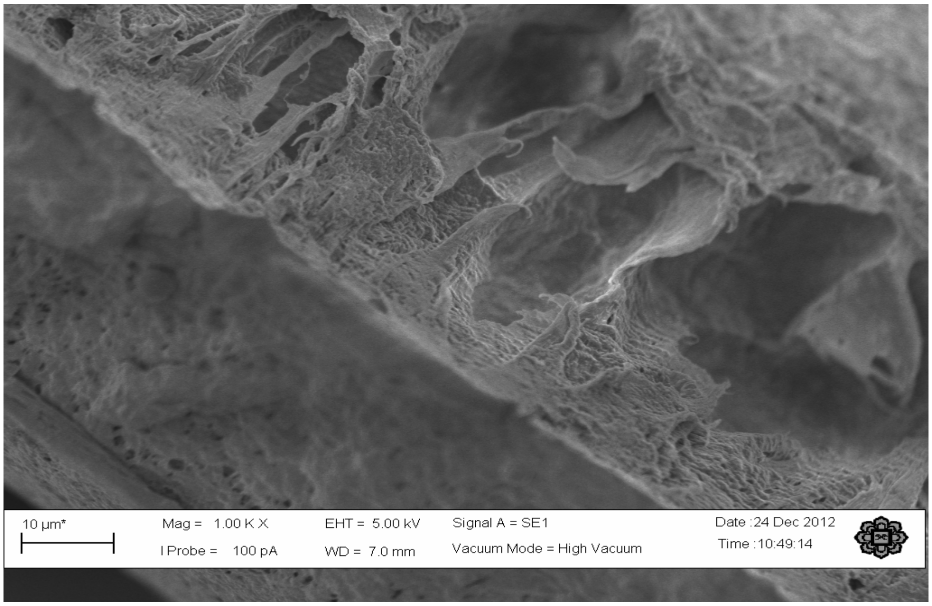


Figure 4.5: Morphology Structure of PVDF at Magnification 1.00kX

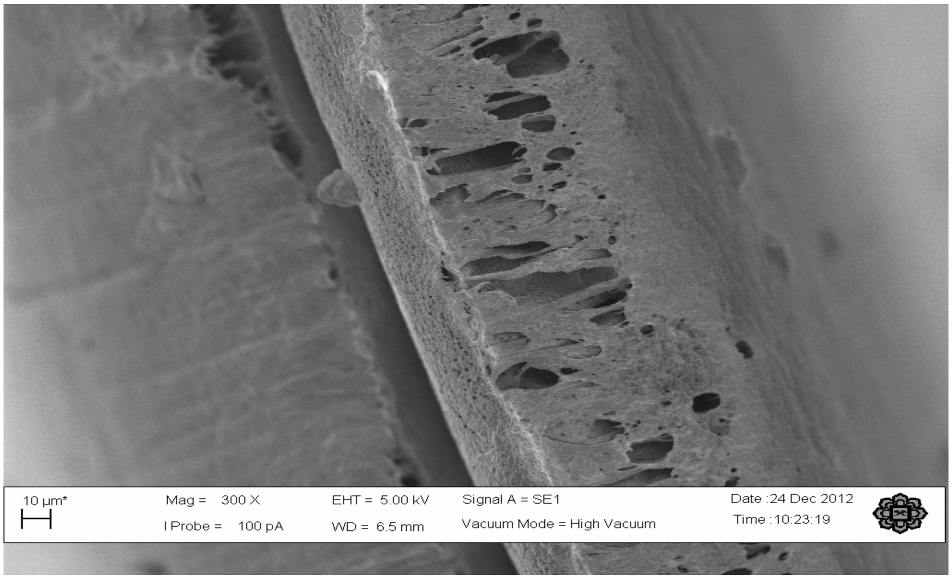


Figure 4.6: Morphology Structure of 10% PVDF/ PEG TFC Membrane at Magnification 300X

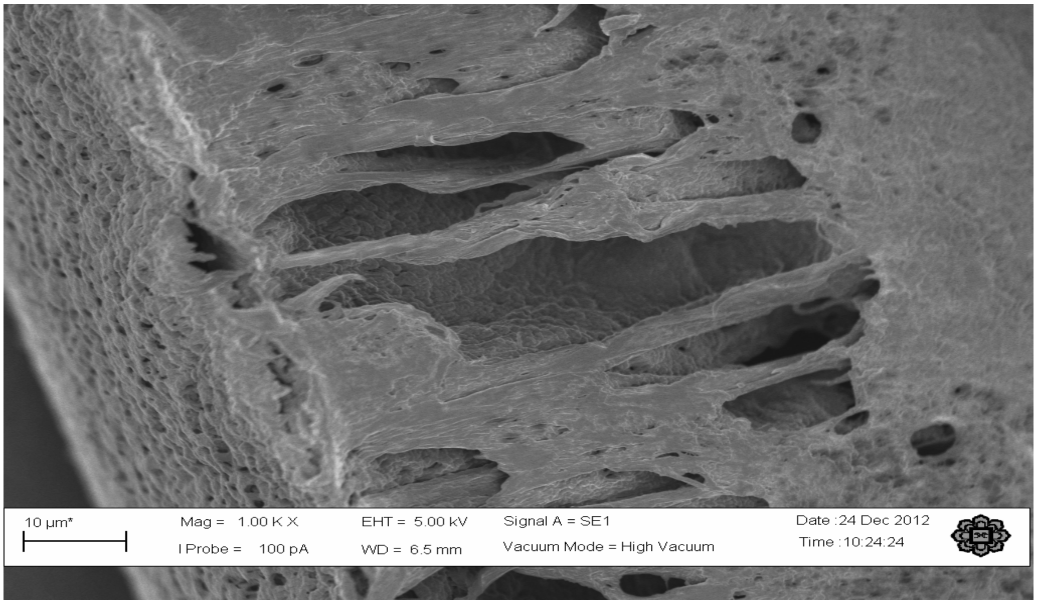


Figure 4.7: Morphology Structure of 10% PVDF/PEG TFC Membrane at magnification 1.0kX

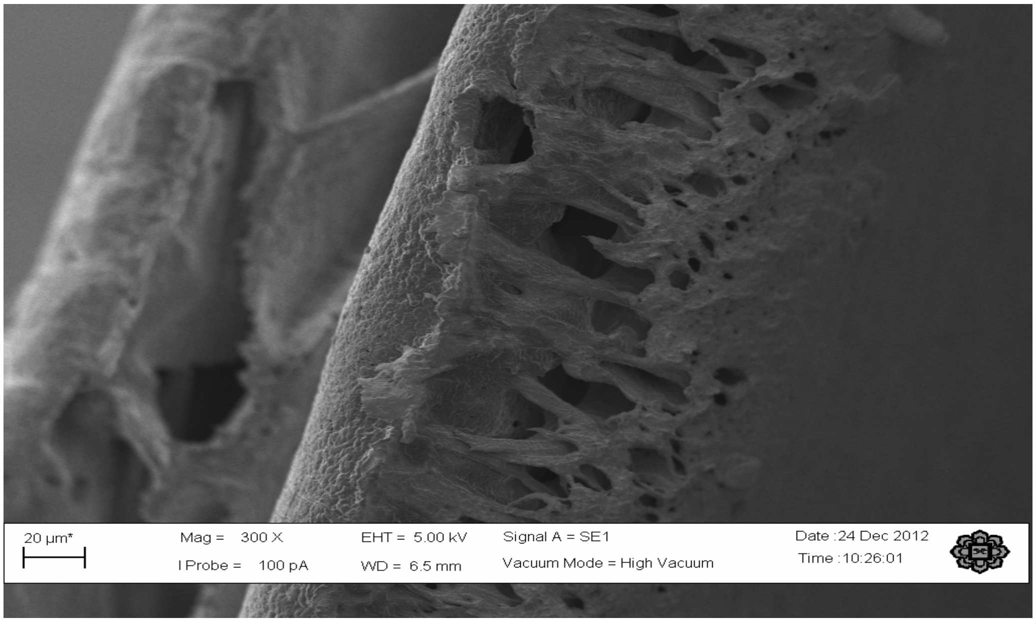


Figure 4.8: Morphology Structure of 15% PVDF/PEG TFC Membrane at magnification 300X

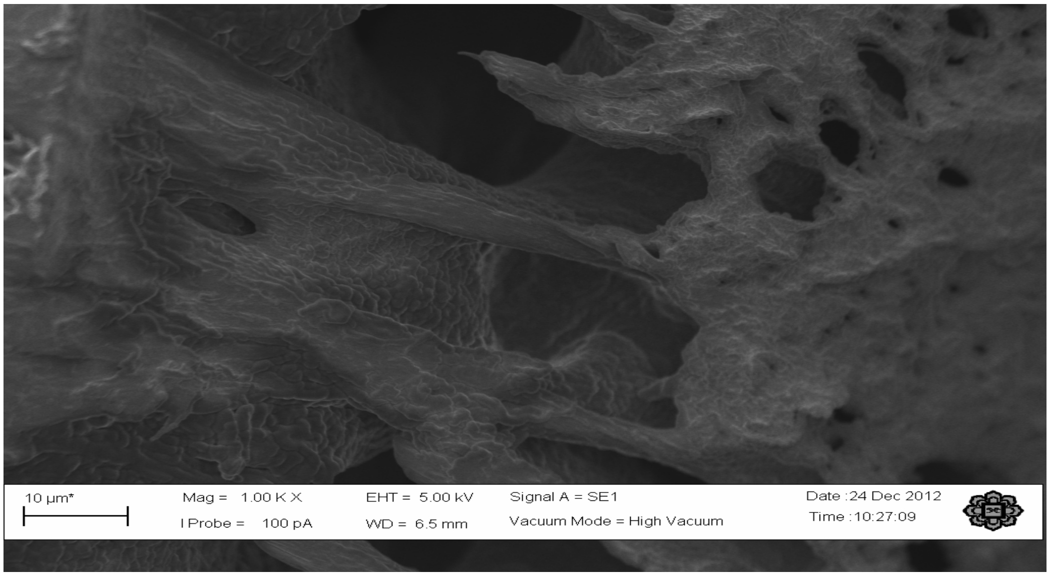


Figure 4.9: Morphology Structure of 15% PVDF/PEG TFC Membrane at Magnification 1.0kX

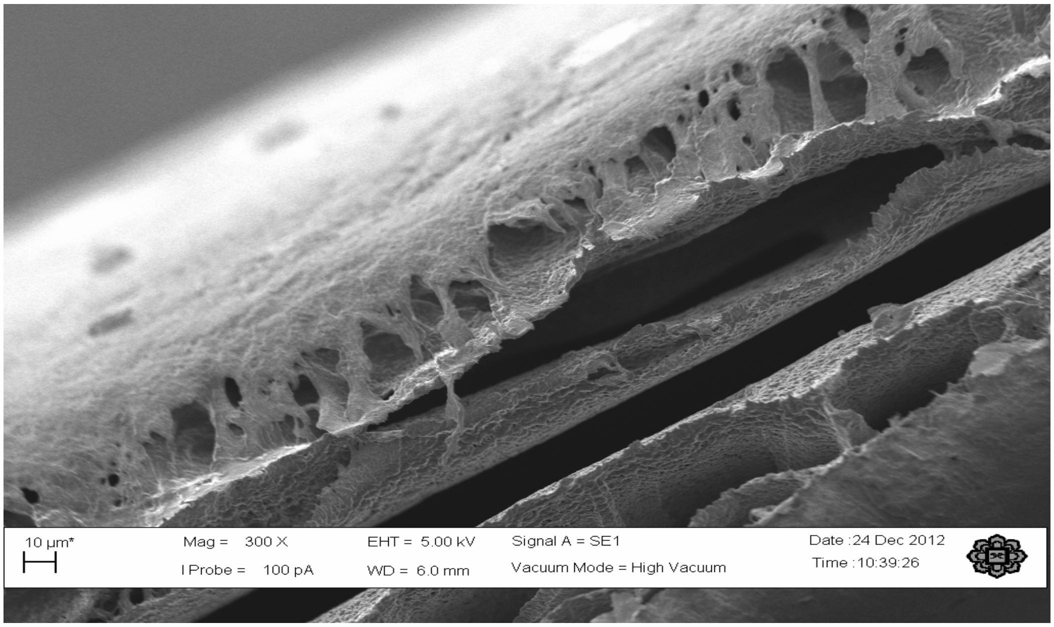


Figure 4.10: Morphology Structure of 20% PVDF/PEG TFC Membrane at Magnification 300X

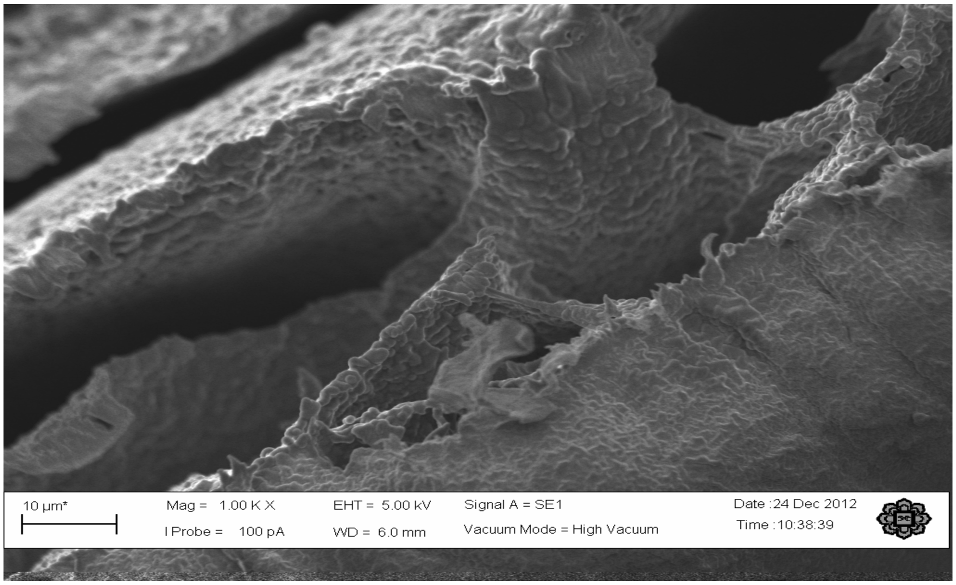


Figure 4.11: Morphology Structure of 20% PVDF/PEG TFC Membrane at Magnification 1.0kX

The morphology of PVDF/PEG TFC Membrane was investigated by Scanning Electron Microscopy (SEM), of which the results were illustrated in Figure 4.4 and Figure 4.5 for plain PVDF membrane, Figure 4.6 and Figure 4.7 for Morphology Structure of 10% PVDF/ PEG TFC Membrane, Figure 4.8 and Figure 4.9 for morphology structure of 15% PVDF/PEG TFC membrane, Figure 4.10 and Figure 4.11 for morphological structure of 20% PVDF/PEG TFC membrane accordingly. Morphology can be defined as the form and organization of a size scale above the atomic arrangement. Generally, the cross section investigation is intensely useful for characterization of the assymetric membranes.

The (SEM) examination, all the developed membranes display asymmetric structures of membrane included plain PVDF membrane and TFC membrane which made up of (PEG) selective top layer and (PVDF) supporting membrane layers, PVDF/PEG TFC membrane significantly. In term of inspection, the PVDF membrane in Figure 4.4 and Figure 4.5 indicated a large finger-like structure and overall porosity with high permeability of N_2 compared to CO_2 permeance which complied with gas permeation test result.

Figure 4.6 and Figure 4.7 revealed that smaller pore size were presented in the 10% PVDF/PEG TFC membrane with dense structure, of which the surface consist of prevalent finger-like structure and more homogenous structure compared to PVDF membrane consequently. The finger like structure permits solutes to easily diffuse from the top to bottom of the membrane specifically. Figure 4.8 and Figure 4.9 demonstrated the morphological structure of 15% PVDF/PEG TFC membrane. From the Figure 4.8, the skin layer consists of slanting finger-like structure and cracks quite often observed at the bottom layer.

The presence of macrovoid could cause membrane has low resistance to high pressure. The slanting finger-like structure was created due to the interaction between solvent and non-solvent of the prepared dope (Ngai,William, Jessica & Menachem, 2012). The membrane also has moderately small pinhole distribution and the size of the pore quite larger compared to 10% PVDF/PEG TFC membrane. Therefore, 15% PVDF/PEG turned up to quite inappropriate membrane for the preparation of high performance of thin film composite membrane for gas separation particularly.

Macrovoids and cracks highly observed on the asymmetric 20% PVDF/PEG TFC membrane which point up in Figure 4.10 and Figure 4.11 respectively. Macrovoids can be the weak points that lead to membrane collapse that must be avoided mainly for high-pressure operation of gas separation process (Lanying, Tai, Dong & Santi, 2004). Instead of that, cross sectional of 20% PVDF/PEG TFC membrane structure also consist of larger pore size and the roughly surface which contributed to lower level effectiveness of gas separation as well as the selectivity preferentially.

From the investigation, the (PEG) level in the film also affects the morphologies, as the (PEG) concentration increases, the surface smoothness decreases, and the pinhole and their size in the cross section increased. In short, the strength decreases as the level of (PEG) increases. Besides that, the film stability decrease as the (PEG) concentration level increases. (PEG) concentration level is the dominating aspect influencing the film properties (Jinghua, Peter & Stephen, 2001).

Certainly, morphological structure of PVDF/PEG TFC membranes were correlated to permeability result as stated before which presented relatively higher CO_2 permeability better than the plain PVDF membrane. After all, 10% PVDF/PEG TFC Membrane (Figure 4.6 to Figure 4.7) demonstrated the best morphological structure with smaller pore size, smoothness surface, high film stability as compared to 15% PVDF/PEG TFC Membrane (Figure 4.8 to Figure 4.9) and 20% PVDF/PEG TFC Membrane (Figure 4.10 to Figure 4.11).

4.1 Characterization of PVDF/PEG Thin Film Composite Membrane under FTIR Analysis

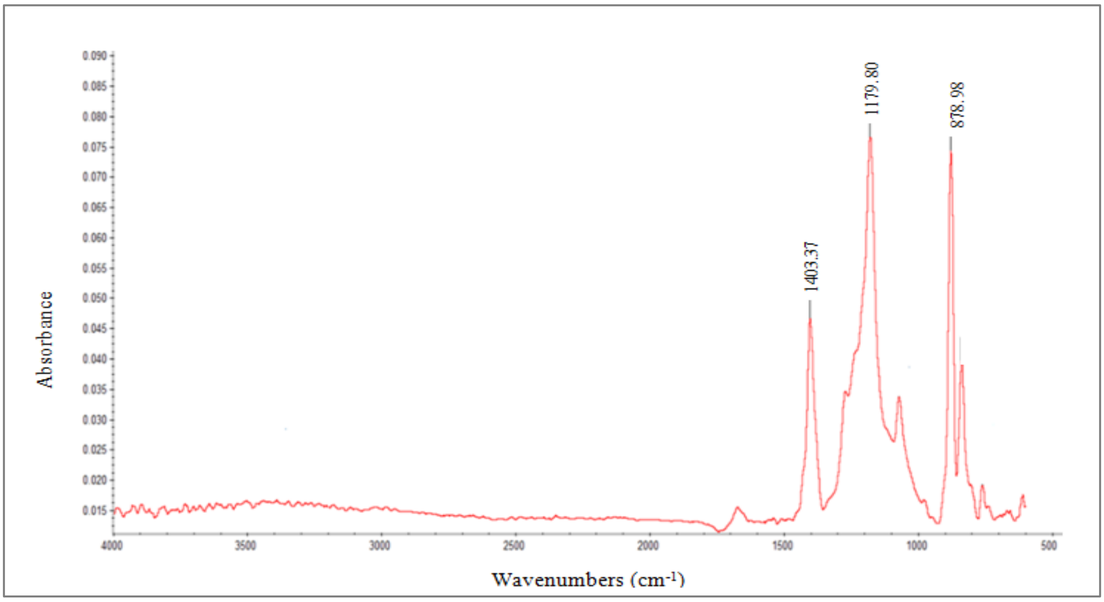


Figure 4.12 Infrared Spectrums of PVDF Membrane

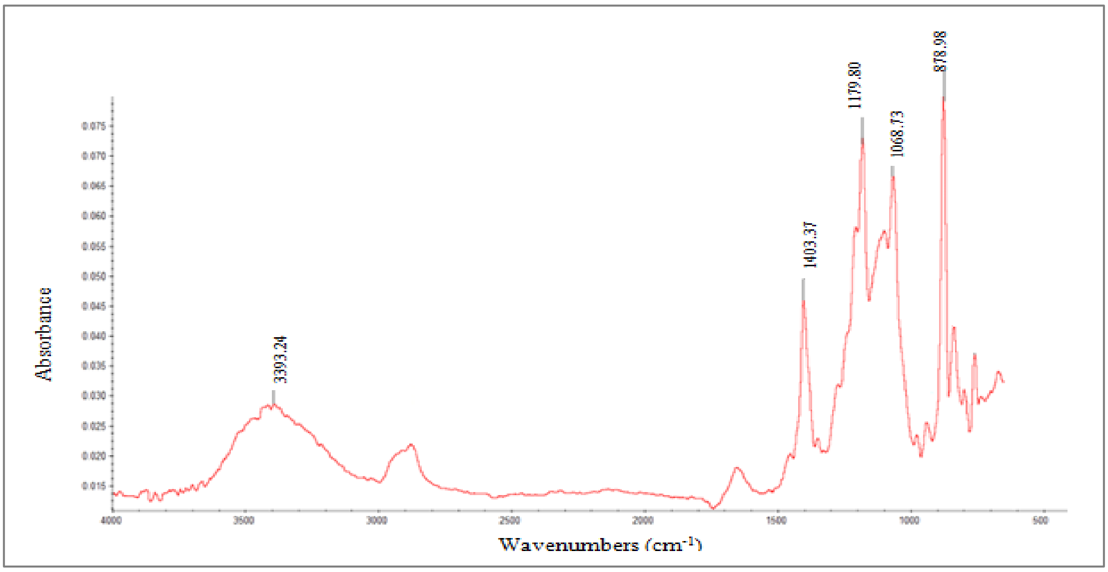


Figure 4.13 Infrared Spectrums of 10% PVDF/PEG TFC Membrane

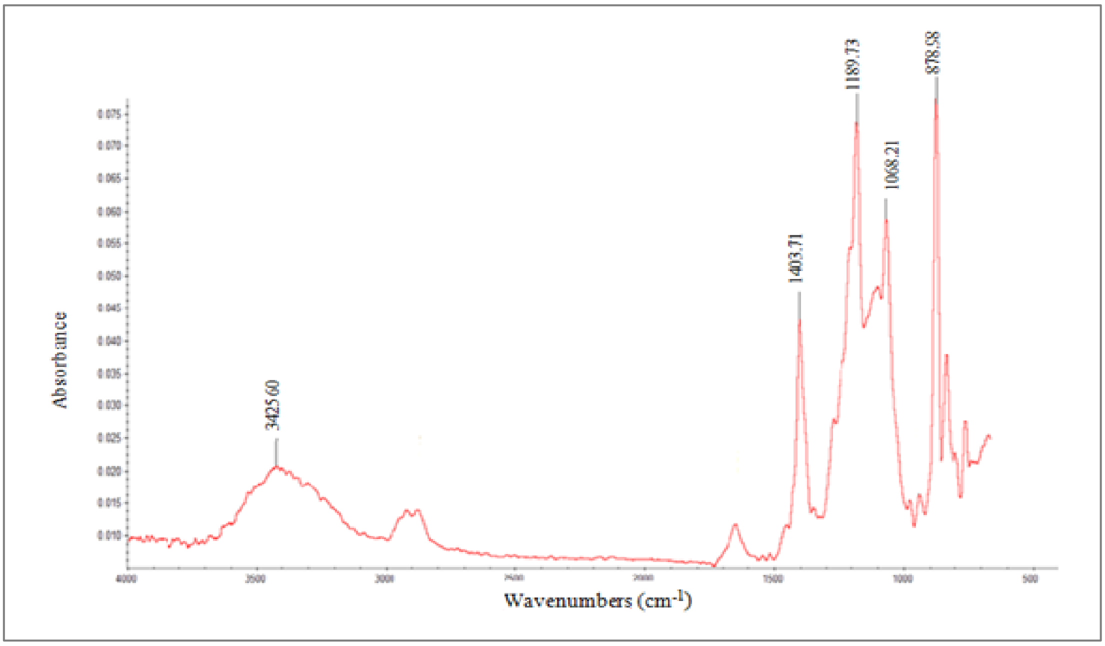


Figure 4.14 FTIR Infrared Spectrums of 15% PVDF/PEG TFC Membrane

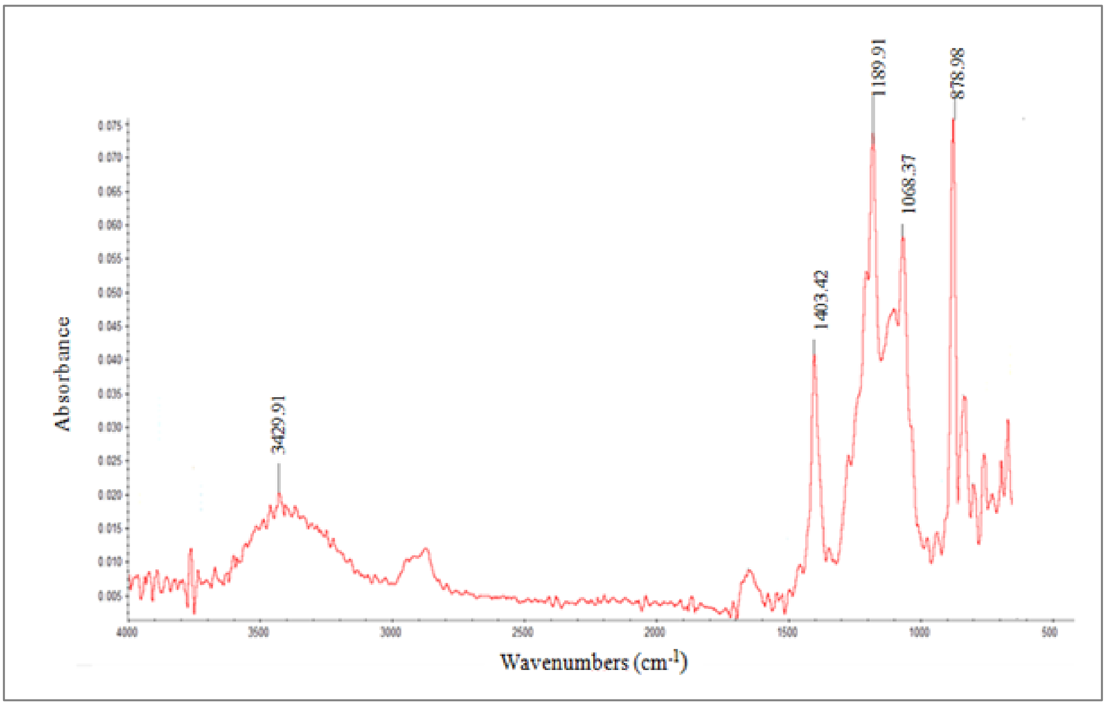


Figure 4.15 FTIR Infrared Spectrums of 20% PVDF/PEG Membrane

Fourier Transform Infrared Spectroscopy (FTIR) is a scientific device for identifying chemicals that are either organic or inorganic. It can be used to quantitate some components of an unknown mixture. It can be applied for the analysis of solids, liquids and gasses. Specifically, FTIR can be utilized to identify chemicals from polymers, coatings, drugs, spill, paints, particulates, fibers, contaminants and other certain materials. In term of characterization, FTIR is one of analytical technique for identifying functional groups of materials particularly.

Indeed, the wavelength of light absorbed is features of the chemical bond as can be seen in the annotated spectrum. The functional group of an organic and inorganic compound can be determined by interpreting the infrared absorption spectrum respectively. The FTIR spectra are usually presented as plots of intensity against wavenumbers (in cm^{-1}). Wavenumber is the reciprocal of the wavelength. In term of intensity, it is can be plotted as the percentage of light absorbance or transmittance at each wavenumber certainly. In order to identify the material being analyzed, the unknown infrared ray (IR) absorption spectrum is compared with standard spectra in computer databases from known material. Figure 4.12 shows FTIR infrared spectrum for (PVDF) membrane; Figure 4.13 shows FTIR infrared spectrum of 10% (PVDF/PEG) TFC membrane; Figure 4.14 shows FTIR infrared spectrum of 15% (PVDF/PEG) TFC membrane and Figure 4.15 shows FTIR infrared spectrum of 20% (PVDF/PEG) TFC membrane respectively.

From FTIR analysis, the characteristic IR absorption for PVDF based membrane indicated the functional group of alkane (C-H) bending, alkyl halide (C-F) stretching, and aromatic (C-H) meta bending. The peak region of alkane group were in range of 1350 - 1460 cm^{-1}, alkyl halide group in range of 1000-1400 cm^{-1} and aromatic group in range of 800 - 880 cm^{-1} (meta bend) respectively. After all, the functional group of PVDF/PEG TFC membrane also matched with the infrared spectrum of PVDF based membrane chemical bonding types which consist of alkane, alkyl halide and aromatic group. The characteristic IR absorption bands of 3393.24 cm^{-1}, 3425.60 cm^{-1} and 3429.91 cm^{-1} were observed for 10% w/v PEG, 15% w/v PEG and 20%w/v PEG respectively. These characteristic strong and broad bands appearing within range of 3200 - 3600 cm^{-1} were corresponding to O--H stretching vibrations of the hydroxyl group of PEG. Poly (ethylene glycol) PEG also show the characteristic of ether group with C-O stretching in range of 1000 - 1300 cm^{-1} whereas 1067.93 cm^{-1}, 1068.21 cm^{-1} and 1068.37 cm-^{1} were the range of peak region of 10%,15% and 20% Poly (ethylene glycol) PEG accordingly.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

Gas membrane separation is a current development and advantageous separation technology mainly in investment, energy consumption and environmental issue. Ideal gas separation membrane should demonstrate high gas permeability, excellent capability for gas selectivity, good heat and chemical stability instead of an outstanding forming and processing properties. After conducting this research study, it can be concluded that the development of thin film composite (TFC) membrane as the current alternative in order enhancing the CO_2 and N_2 capture from the flue gas emission from industrial gas separation processing unit preferentially . Development of PVDF/PEG asymmetric TFC membrane with the variation of (PEG) content which acts as the selective layer (PVDF) based membrane significantly to recognize the most effective membrane structure with highly excellent membrane performance for gas separation specifically. The selection of PEG as the top layer changed the PVDF based membrane structures and properties. In short, the better membrane performance creates the most ideal permeation rate and higher selectivity for gas separation.

In term of membrane performance, 10% PVDF/PEG TFC membrane show the highest selectivity compared to 15% w/v, 20% w/v (PEG) content and (PVDF) membrane due to the large distribution of smallest pore size, high film stability and smoothness of the membrane surface. The CO_2/N_2 selectivity increased with lower level (PEG) contents. The permeability of CO_2 was higher than N_2 due to the considerable differences in the condensability of both gases. Other than that, PVDF/PEG TFC membrane with 10%w/v (PEG) content gave the best morphology compared to 15% PVDF/PEG and 20% PVDF/PEG TFC membrane. The 10% PVDF/PEG TFC membrane illustrated the best structure with various number of pore on the membrane upper surface, highly expansion of finger -like cavities characteristics, homogenous structure which developing more porous and interconnected features. Hence, this research study indicated that PVDF/PEG TFC membrane is an attractive option for gas membrane separation technology. In the future, hopefully this research study contributes to membrane development for large scale medium which specific for gas separation technology alternatively.

5.2 Recommendations

1. The solvent of polyvinylfluoridone (PVDF) should be handled properly with extra precaution because of its high volatility and easily spread to the surrounding. Instead of that, the concentration of PEG concent should be conducted for lower percentage (5% and below) and high percentage (30% and above) in order to study and compare the best performance of membrane significantly.

2. The speed of mechanical stirrer should be maintained to be constant according to it preferable rpm in order to ensure less bubble produced during the dope solution preparation process instead of facilitate the removal of bubbles perfectly.

3. PVDF asymmetric flat sheet membrane should be coated fairly to ensure any surface pinholes on the membrane surface could be fully filled.

4. Additional studies on other fabrication parameters of asymmetric membrane such as coagulation temperature, drying method and dip coating procedure must be implemented to obtain the optimize membrane performance process.

5. Onsite testing should be performed to identify influence of other parameter such as temperature and humidity in order to determine the chemical resistance of the membrane toward any outside disturbance.

6. The casting method should be improved and handling with an effective and efficient method in order to ensure dope solution is perfectly distributed to all part of casted membrane.

7. In term of PVDF/PEG TFC membrane development, the selective top layer of Poly (ethylene glycol) PEG shall be proposed with different molecular weight instead of different percentage content of PEG selection in order to observe the change of PVDF membrane structure and properties.

REFERENCES

Baker W.R., (2004). Membrane Technology and Applications. (2Ed.). Menlo Park, California: Wiley.

Cheer, N.B. and Ismail, A.F. (2002). Development of Polysulfide Asymmetric Membrane Using Pneumatically-Controlled Membrane Casting System and The Study of The Effects of Shear Rate and Forced Convection Residence Time on Gas Separation Membrane Performance. Universiti Teknologi, Malaysia.

Diffuser Membrane Material selection. Technical Bulletin, 114, 1-2. Environmental Dynamics Inc. Missouri, Columbia. Unpublished.

Drioli E., Giorno L., (Eds.). (2009). Membrane Operations. Italy : Rende (S).

Freemantle, M. (2005, October).Membrane For Gas Separation. Chemical & Engineering News, 83, 49-57.

JingHua Y.P, Shang P, Wu S.H. (2001). Effects of polyethylene glycol on morphology, thermochemical properties and water vapor permeability of cellulose acetate free films. Pharmacetical Technology, 25, 62-74.

Kahovec, J. (Ed.). (2002). Polymer membranes. Weinheim, Germany.

Lawson K.W., Hall M.S., Lloyd D.R., (1994) Compaction of microporous membranes used in membrane distillation.I.effect on gas permeability. Department of Chemical Engineering, Separation Research Program, University of Texas, USA.

Li, N.N., Fane, A.G., Winston Ho, W.S., and Matsuura, T. (2008). Advance Membrane Technology and Application:Wiley.

Mansourizadeh A., Ismail A.F. (2012). Influence of membrane morphology on characteristics of porous hydrophobic PVDF hollow fiber contactors for CO2 stripping from water. Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi, Malaysia

Membrane Module for Gas Separation Membrane retrieved on May 2012 from *technologyreport.mecadi.com*

Naylor, T.D. (1996). Polymer Membranes- Materials, Structure and Separation Performance:Thin film Composite Membranes.(Ed.). Shropshire,UK: Rapra Tehcnology LTD

Nunes, P.S., & Peinemann, K.V. (2nd, Revised and Extended Edition). (2006). Membrane Techology in the Chemical Industry. Weinheim, Germany.

N-Methyl-2-Pyrrolidone retrieved on April 4, 2012 from *www.lyondellbasell.com*

Physical Properties of Methanol and Water retrieved on April 4, 2012 from *www.infoplease.com*

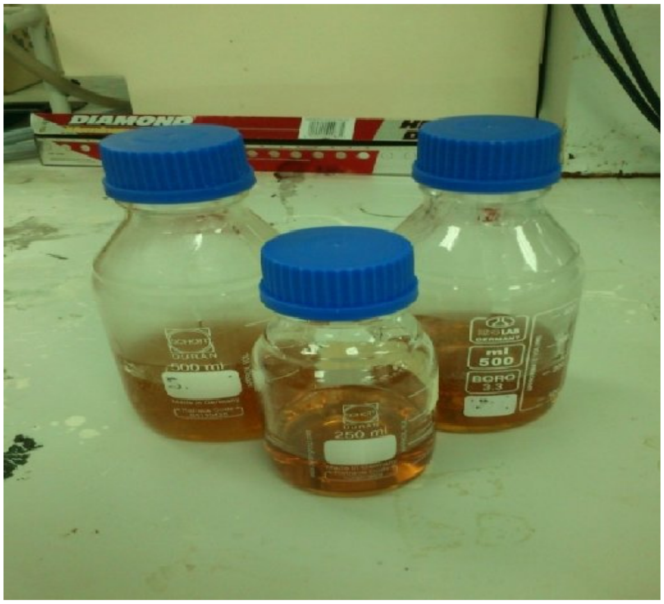
Physical Properties of Polyethylene Glycol, (PEG200) retrieved on April 2012 from *msdssearch.dow.com*

Strathmann, H., Giorno,L., Drioli, E. (2006). An introduction to membrane science and technology.

Wang, L.K., Hung, Y.T., Shammas, N.K.(2006).Advanced Physicochemical Treatment Process.(Ed.). Totowa, New Jersey: Humana Press Inc.

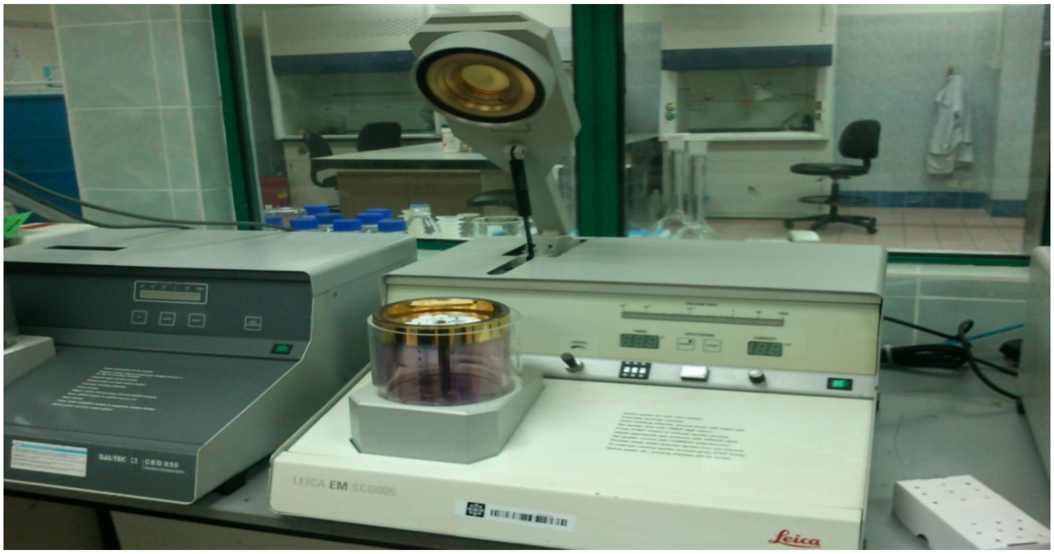
APPENDICES

Appendix A (PVDF resin and NMP solvent)

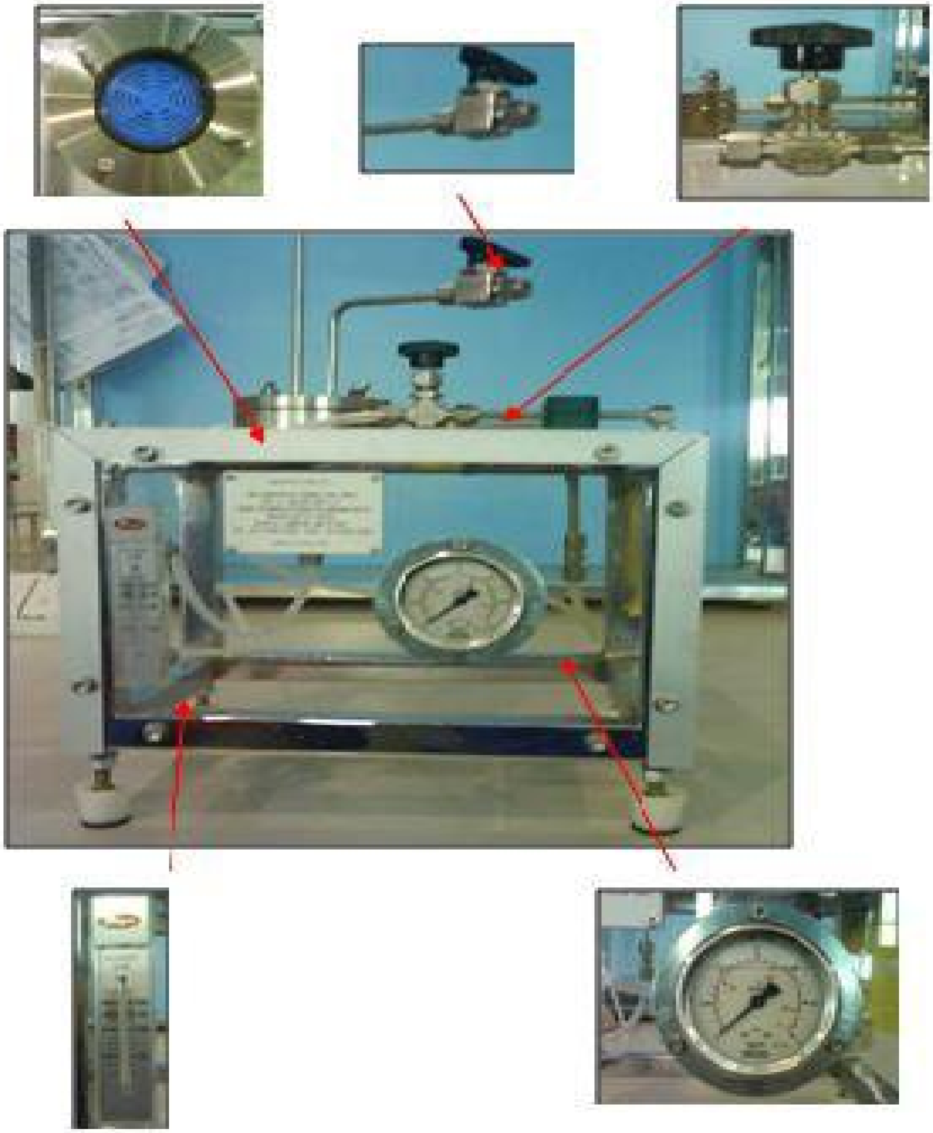


Appendix B (Dope solution of PVDF)

Appendix C (TFC Membrane)



Appendix D (Scanning Electron Microscopy, SEM)



Appendix E (Gas Permeation Test)

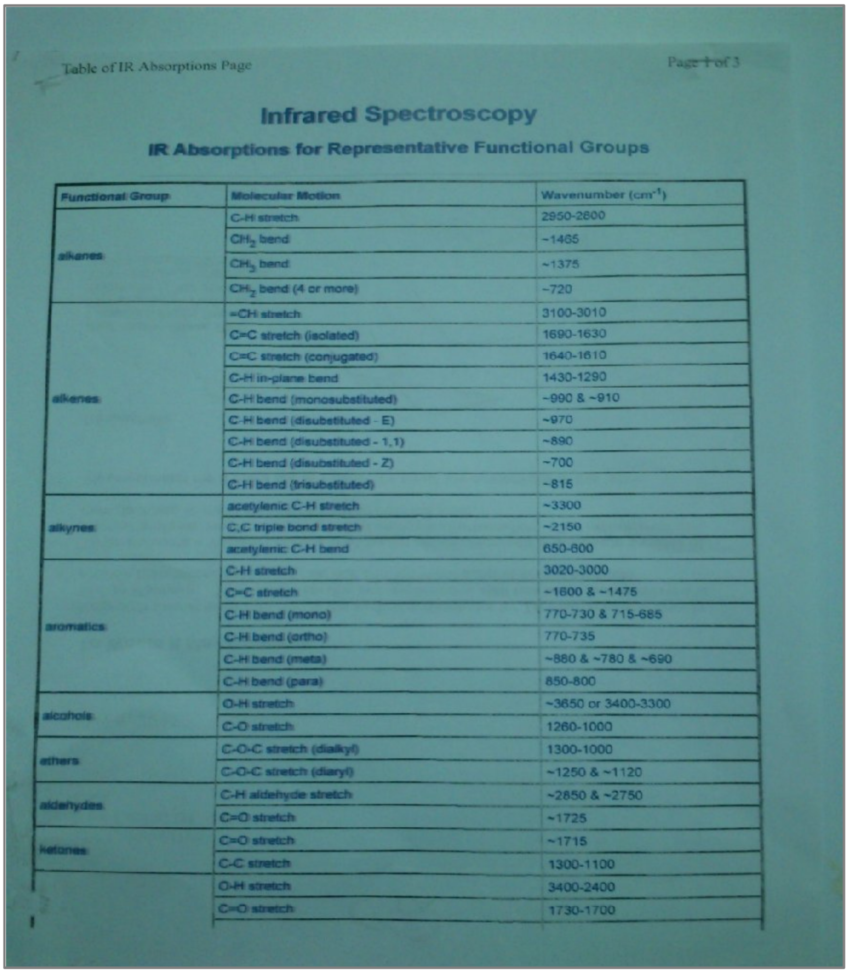


Table of IR Absorptions Page

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Infrared Spectroscopy

IR Absorptions for Representative Functional Groups

Functional Group	Molecular Motion	Wavenumber (cm^{-1})
alkanes	C-H stretch	2950-2800
	CH_2 bend	~1465
	CH_3 bend	~1375
	CH_2 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
	O-H stretch	3400-2400
	C=O stretch	1730-1700

APPENDIX F IR Absorption for Respective Functional Group for FTIR Analysis