DEVELOPMENT OF POLYVINYLIDENE FLUORIDE - POLYDIMETHYLSILOXANE (PVDF-PDMS) THIN FILM COMPOSITE (TFC) 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)

Faculty of Chemical and Natural Resources Engineering
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FEBRUARY 2013

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Gas Technology).

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Date : 25th FEBRUARY 2013

STUDENT'S DECLARATION

I declare that this thesis entitled "Development of Polyvinylidene Fluoride - Polydimethylsiloxane (PVDF - PDMS) Thin Film Composite Membrane (TFC) 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

Shaikh Abdul Nasir Bin Shaikh Ali & Arabian Binti Shaikh Hussin

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Bismillahirrahmanirrahim,

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ABSTRACT

The objectives of this research is to develop of Polyvinylidenefluoride (PVDF) – Polydimethylsiloxane (PDMS) Thin Film Composite (TFC) and study the membrane performance for gas separation of CO_2/N_2. The support PVDF membranes were prepared by dry wet phase inversion with 15 %w/v of PVDF and 82%w/v of N-methyl-2-pyrrolidone (NMP) as solvent and 3%w/v of water as non-solvent. Polydimethylsiloxane ~~(~~PDMS~~)~~ was coated on the support membrane to produce a composite membrane using a dip coating method using 10, 15, 20 ratio of PDMS/n-hexane. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) spectroscopy~~,~~ to determine chemical properties and physical of membrane. The selectivity of CO_2/N_2 gas was determined by gas permeation test. From the results, the high selectivity of the membrane behavior selected as the new membranes for gas separation membranes future. After tested by gas permeation test, the result of development PVDF-PDMS-TFC membrane gave excellent performance in separating CO_2/N_2 with higher selectivity and permeability.

PENGHASILAN POLIVINYLIDENE FLUORIDA - POLIDIMETILSILOKSAN (PVDF-PDMS) KOMPOSIT FILEM NIPIS (TFC) MEMBRAN UNTUK PENGASINGAN GAS CO_2/ N_2

ABSTRAK

Objektif kajian ini adalah untuk menghasilkan Polyvinylidene Fluoride (PVDF) - Polydimethylsiloxane (PDMS) Filem Nipis Komposit (TFC) dan mengkaji prestasi membran untuk pemisahan gas CO_2/N_2. Sokongan PVDF membran telah disediakan oleh penyongsangan fasa basah kering dengan 15% w / v PVDF dan 82% w / v N-metil-2-pyrrolidone (NMP) sebagai pelarut dan 3% w / v air sebagai bukan pelarut . Polydimethylsiloxane (PDMS) telah disalut pada membran sokongan untuk menghasilkan membran komposit menggunakan kaedah celup salutan menggunakan 10, 15, 20 nisbah PDMS / n-heksana. Pengimbas Mikroskopi Elektron (SEM) dan Fourier Spektroskopi Radiasi Infra-merah (FTIR), untuk menentukan sifat-sifat kimia dan fizikal membran. Kepilihan CO_2/N_2 gas telah ditentukan oleh ujian penyerapan gas. Daripada keputusan, kepilihan yang tinggi tingkah laku membran dipilih sebagai membran baru membran pemisahan gas masa depan. Selepas diuji dengan ujian penyerapan gas, hasil membran pembangunan PVDF-PDMS-TFC memberikan prestasi yang cemerlang dalam memisahkan CO_2/N_2 dengan pemilihan yang lebih tinggi dan kebolehtelapan.

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LIST OF ABBREVIATIONS

CH_4 - Methane gas
CO_2 - Carbon dioxide
N_2 - Nitrogen
H_2O -Water
TFC - Thin Film Composite
PVDF - Polyvinylidene Fluoride
PDMS - Polydimethylsiloxane
SEM - Scanning Electron Microscopy
FTIR - Fourier Transform Infrared Radiation
RO - Reverse Osmosis
NF - Nanofiltration
UF -Ultrafiltration
MF - Microfiltration
TMP - Trans-membrane Pressure
CA - Cellulose Acetate
PAN - Polyacrylonitrile
PP - Polypropylene
PSf - Polysulfone
PES - Polyethersulfone
PA - Polyamide
GP - Gas Permeation
NMP - N-Methyl-2-Pyrrolidone

LIST OF SYMBOLS

°C	- Degree Celcius
min	- minute
mmHg	- Milimeter Mecury
cal/g. °C	- Specific Heat
cp	- Viscosity
wt%	- Weight Percent
%	- Percentage
rpm	- Rotation per Minute
ppm	- Part per million
g/mol	- Molecular Weight
α	- Selectivity
g	- Gram
ml	- mili Litre
cm	- Centimeter
mm	- milimeter
s	- second
GPU	- Permeability
nm	- nanometer
μ m	- micrometer

CHAPTER 1

INTRODUCTION

This chapter will discuss about the researh formulation. First topic will cover up the background of study, problem statement, objectives of the research, scope of the research and the rationale and significant of doing this research.

1.1 Background of The Research

Gas separation is a process of separating various hydrocarbon components in natural gas to be used at its fullest value. It can be separated effectively by synthetic membranes, adsorption, absorption and also cryogenic distillation. This process is depend to the product or gas that we need from air we want to separate nitrogen and oxygen, so that we need to use separation method to remove oxygen from air because we want to take nitrogen as product. Nowadays, we know that the energy costs rises and impacted to the costs of industries in making process. Membrane technology for separating gases is likely to play an increasingly important role in reducing the environmental impact and costs of industrial processes. Gas separation membranes process give more benefits compare with others methods of gas separation technologies, conventional technologies such as the cryogenic distillation of air, condensation to remove condensable organic vapors from gas mixtures, and amine absorption to remove acid gases such as carbon dioxide from natural gas require a gas-to- liquid phase change in the gas mixture that is to be separated. The phase change adds a significant energy cost to the separation cost.

Membrane gas separation does not require a phase change. 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. The lack of mechanical complexity in membrane systems is another advantage. (Freeman ,2005).

1.2 Problem Statement

In industry, gas separation is important to get some gas for use. Therefore, the manufacturing and structuring membranes is a factor to the efficient separation of the gas. The study of membrane structure necessary to produce a membrane which is good for gas separation that can save time, energy, and resources used. In membrane separation, the main problem happened is the fouling of membrane that may block the pore of membrane to flow the feed. However, by using thin composite membrane it can limit the resistance of the membrane to flow which will passes more freely through the porous substructure. The fouling still happened but it was decrease.

1.3 Research Objectives

The main objectives in this research is to develop PVDF-PDMS thin film composite (TFC) membrane for CO_2/N_2 gas separation. The spesific objectives are :

i. To produce Thin Film Composite (TFC) membrane using Polyvinyldene fluoride (PVDF) as support.
ii. To study the characteristic of Thin Film Composite (TFC) membrane produced.
iii. To study the performance of Thin Film Composite (TFC) membrane produced.

1.4 Scopes of Research Proposed

In order to achieve the objectives, there are some scopes of this study defined which are :

i. Study on PVDF-PDMS Thin Film Composite (TFC) membrane using dip-coating method.

ii. Characterize on membrane structure using Scanning Electron Microscopic (SEM) and Fourier Transform Infra-Red (FTIR).
iii. Study on PVDF-PDMS Thin Film Composite (TFC) membrane based on permeance and selectivity.

1.5 Rationale And Significant

The rational of this study is to know how to designing the membrane for separating CO_2 and N_2 gas in order to design the size of pore, thickness, and also the shape of membrane.

Besides that, the defect of the membrane can be reduced and repaired after coated with PDMS. Hence it can give the beneficial to the company and reduce the cost to change the defect membrane. Other than that, with more efficient membrane produced, it will give more accurate product separated.

CHAPTER 2

LITERATURE REVIEW

2.1 Background of Membranes

Membrane term is commonly refers to a thin sheet of material, film- like structure that can separate two fluids or substances. In biological, it is a layer of tissue covering surfaces or separating or connecting regions, structures, or organs of an animal or a plant. It also known as cell membrane. In chemistry, membrane is a thin sheet of natural or synthetic material that is permeable to substances in solution.

A membrane is a layer of material which serves as a selective barrier between two phases and remains impermeable to specific particles, molecules, or substances when exposed to the action of a driving force. Some components are allowed passage by the membrane into a permeate stream, whereas others are retained by it and accumulate in the retentate stream. Membranes can be a various thickness. Their structure can be homogeneous or heterogeneous. Membranes can be classified according to their pore diameter.

For microporous membrane, it has diameter pore less than 2nm. It is the smallest pore size between the three types of membrane. For mesoporous, it has diameter pore between 2nm and 50nm. And for macroporous, it has diameter of pore over 50nm. Membranes can be neutral or charged and particles transport can be active or passive. The latter can be facilitated by pressure, concentration, chemical or electrical gradients of the membrane process. Membranes can be generally classified into synthetic membranes and biological membranes.

2.2 Membrane Module

Membrane module is housing for membranes in a suitable device. The feasibility of a membrane process depends on the design of membrane module since the active separation membrane area is directly influenced by the membrane module configuration. The cost reduction of membrane module has led to the commercialization of membrane process in the 1960s and 1970s (Baker et al.,1991). There are four types of membrane module commonly used nowadays; plate and frame, spiral wound, tubular and hollow fiber. The earliest module has been designed are plate-and-frame and tubular membrane. It is based on simple filtration technology. This both systems still available use until today, because of their relatively high cost and inefficiency, they have been substituted by hollow fiber and spiral wound membrane module.

2.2.1 Plate And Frame

It was among the earliest types of module used in a membrane systems and the design is principally based on conventional filter press. Figure 2.1 shows membrane feed spacers and product spacers are layered together between two end plates. Because of the comparatively high production cost as compared to others membrane modules and leaks caused by the numerous gasket seals in the system have limited the usage of this system to small scale application. The use of plate and frame is now normally limited to electro dialysis and pervaporation systems (Baker et al., 1991).

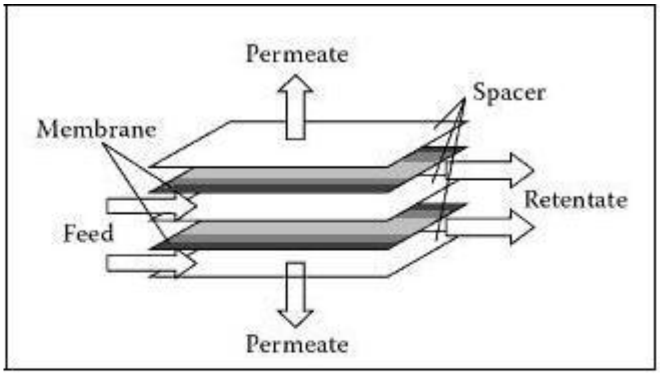


Figure 2.1 : Plate And Frame Module

2.2.2 Tubular

This type of modules is usually made by casting a membrane onto the inside of a pre-formed tube, which is referred to as the substrate tube. These are generally made from non-woven fabrics such as polyester or polypropylene. The range of diameter tubes is from 5-25mm, with 12.5mm in regular usage. In this type of module, there are two mainly types of housing system which known to be the supported and tubes housing system.

Basically, in supported housing system the tubes of membrane are supported by perforated or porous stainless steel tubes. A bundle of tubes of these membranes is mounted into a vessel that collects permeation and caps are fitted to the end to give different flow pattern of shown in figure 2.2. Exhibiting high mechanical strength, so that this type of module can be used at high pressure up to 60 bar of separation process like reverse osmosis. In the unsupported housing design, the membrane is supported only by substrate tube and a cartridge is constructed by potting the ends of a bundle of tubes in an epoxy resin. These types of designs propose lower capital cost than the supported tube module but, it has a reduced tolerance to pH, pressure, and temperature (Baker et al., 1991).

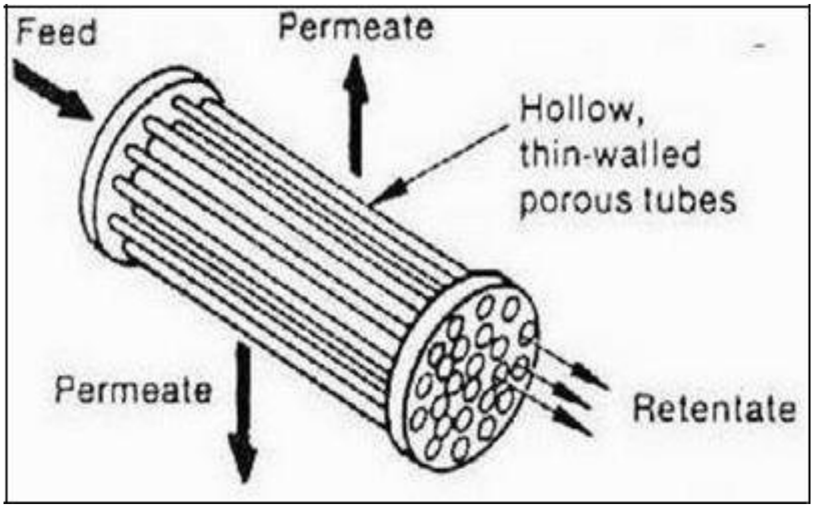


Figure 2.2 : Tubular Membrane Module

2.2.3 Hollow Fiber

There are two basic configurations for hollow- fiber membrane module. In this module, a loop of fiber or a closed bundle is contained in a pressure vessel. In this system, it was pressurized from the shell side and permeate passes through the fiber wall and exits via the open fiber ends. This design will allow large fiber membrane areas to be contained in an economical system. Since the fiber wall supports a considerable hydrostatics pressure. These fibers commonly have a small diameter around 100µ m of inside diameter and ~200µm of outside diameter as shown in figure 2.3 (Baker et al., 1991).

The second basic design for hollow fiber module is more common. In this case, the fibers are laid out parallel to each other in bundles and the open ends are then cast into two resin blocks which are bonded into shrouds to form a cartridge. It sort to minimize the pressure drops in the inside of the fibers, the fibers often have larger diameters than fine fibers used in closed loop system. Membrane in these configurations are available for reverse osmosis (RO), ultra-filtration (UF) and microfiltration (MF) applications such as seawater desalination, water clarification, fruit clarification, electrophoretic paint recovery and oil waste water treatment (Scott et al., 1996).

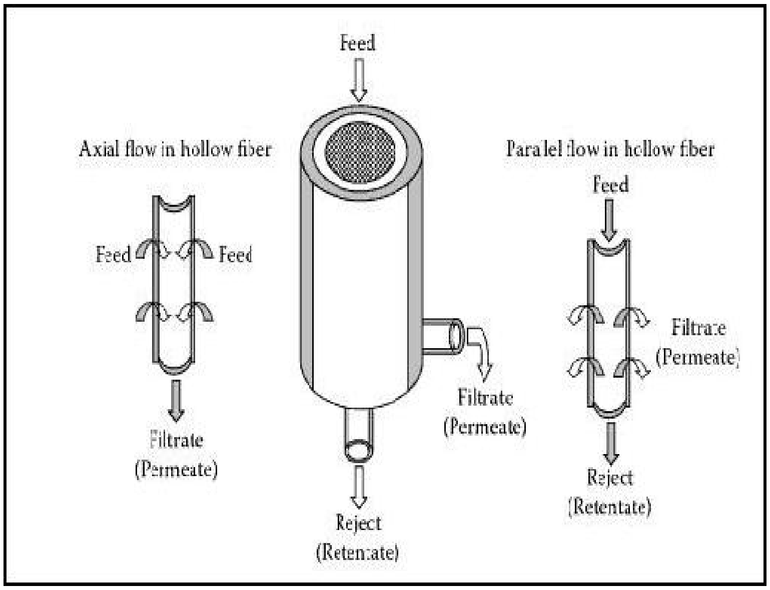


Figure 2.3 : Hollow Fiber Membrane Module

2.2.4 Spiral Wound

This type of module consist of membrane envelopes and feed spacers that wound around a perforated central collection tube as shown in figure 2.4. Feed solution passes through axially and down the module across the membrane envelope. A portion of the feed solution permeates into the membrane envelope, where it spirals toward the center and exits through the collection tube (Scott et al., 1996). These modules were designed in an effort to pack as much membrane surface as possible into a given volume (Senthilmurugan et al., 2005). Small scale spiral wound modules consist of a single membrane leaf wrapped around the collection tube.

In the large membrane area module, using single membrane leaf might generate large pressure drop due to the longer path taken by the permeate to reach the central collection tube. Multiple short leaves have been utilized to keep the pressure in the module in a manageable level (Van der Meer and van Dijk, 1997).

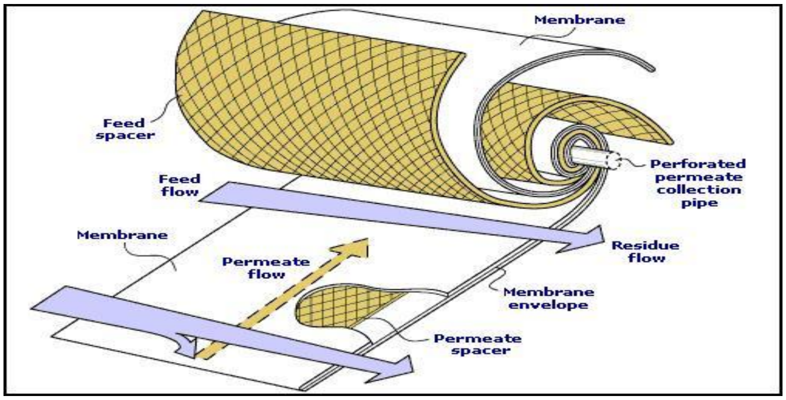


Figure 2.4 : Spiral Wound Membrane Module

2.3 Membrane Material

In produce membrane, we must select the suitable materials to let the membrane more efficient and can separate completely. There are several criteria that we should select in producing membrane. The membrane material may refers to the material or substance from which the membrane it is made. Usually, the material of membrane is manufactured from a synthetic polymer, although other forms, ceramic and metallic membranes may be available. Now, almost all membranes manufactured for drinking water production are made of polymeric material, since the cost of this material less expensive than other material to construct membrane.

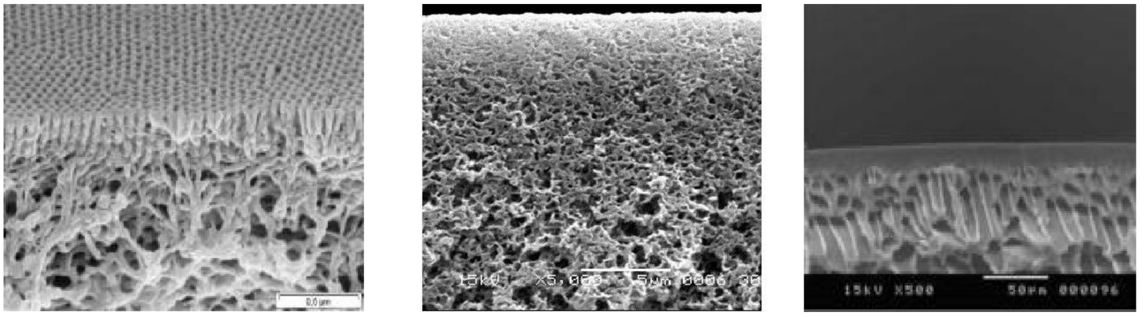
The material properties of the membrane may significantly impact the design and operation of the filtration system. For example, membranes constructed of polymers that react with oxidants commonly used in drinking water treatment should not be used with chlorinated feed water. Mechanical strength is another consideration, since a membrane with greater strength can withstand larger trans- membrane pressure (TMP) levels allowing for greater operational flexibility and the use of higher pressures with pressure-based direct integrity testing. Similarly, a membrane with bi-directional strength may allow cleaning operations or integrity testing to be performed from either the feed or the filtrate side of the membrane. Material properties influence the exclusion characteristic of a membrane as well. A membrane with a particular surface charge may achieve enhanced removal of particulate or microbial contaminants of the opposite surface charge due to electrostatic attraction. In addition, a membrane can be characterized as being hydrophilic such water attracting or hydrophobic such water repelling. These terms describe the ease with which membranes can be wetted, as well as the propensity of the material to resist fouling to some degree.

Micro-Filtration (MF) and Ultra-Filtration (UF) membranes may be constructed from a wide variety of materials, including cellulose acetate (CA), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polypropylene (PP), polysulfone (PS), polyethersulfone (PES), or other polymers. Each of these materials has different properties with respect to surface charge, degree of hydrophobicity, pH and oxidant tolerance, strength, and flexibility.

Nano-Filtration (NF) and Reverse-Osmosis (RO) membranes are generally manufactured from cellulose acetate or polyamide materials and there are various advantages and disadvantages associated with each. While cellulose membranes are susceptible to biodegradation and must be operated within a relatively narrow pH range of about 4 to 8, they do have some resistance to continuous low- level oxidant exposure. In general, for example, chlorine doses of 0.5 mg/L or less may control biodegradation as well as biological fouling without damaging the membrane. Polyamide (PA) membranes, by contrast, can be used under a wide range of pH conditions and are not subject to biodegradation. Although Polyamide (PA) membranes have very limited tolerance for the presence of strong oxidants, they are compatible with weaker oxidants such as chloramines. Polyamide (PA) membranes require significantly less pressure to operate and have become the predominant material used for Nano-filtration (NF) and Reverse Osmosis (RO) applications.

2.4 Structure of Membrane

A characteristic that influences the performance of all membranes is the trans-wall symmetry, a quality that describes the level of uniformity throughout the cross-section of the membrane. There are three types of construction that are commonly used in the production of membranes: symmetric, asymmetric (including both skinned and graded density variations), and composite as figure shown in Figure 2.5 :



(a) **(b)** **(c)**

Figure 2.5 : Membrane Structure : (a) Symmetric Membrane; (b) Asymmetric Membrane; (c) Composite Membrane

Symmetric membranes are constructed of a single material (homogeneous), while composite membranes use different materials (heterogeneous). Asymmetric membranes may be either homogeneous or heterogeneous. In a symmetric membrane, the membrane is uniform in density or pore structure throughout the cross-section, while in an asymmetric membrane there is a change in the density of the membrane material across the cross sectional area. Some asymmetric membranes have a graded construction, in which the porous structure gradually decreases in density from the feed to the filtrate side of the membrane. In other asymmetric membranes, there may be a distinct transition between the dense filtration layer and the support structure. The denser skinned layer is exposed to the feed water and acts as the primary filtration barrier, while the thicker and more porous understructure serves primarily as mechanical support. Some hollow fibers may be manufactured as single- or double- skinned membranes, with the double skin providing filtration at both the outer and inner walls of the fibers. Like the asymmetric skinned membranes, composite membranes also have a thin, dense layer that serves as the filtration barrier. However, in composite membranes the skin is a different material than the porous substructure onto which it is cast. This surface layer is designed to be thin so as to limit the resistance of the membrane to the flow of water, which passes more freely through the porous substructure. Nano-Filtration (NF) and Reverse Osmosis (RO) membrane construction is typically either asymmetric or composite, while most Micro-Filtration (MF) and Ultra-Filtration (UF) membranes are either symmetric or asymmetric.

2.5 Process And Application of Membrane

Some of the membrane processes such as reverse osmosis (RO), ultra-filtration (UF) and micro-filtration (MF) or electro dialysis are today state-of-the-art and utilized on a large industrial scale with a significant technical and commercial impact. Other processes such as membrane contactors, membrane emulsifiers or catalytic membrane reactors are still the subject of intensive research and development effort.

However, all membranes processes have one feature in common, such they can perform the separation of certain molecular mixtures effectively, energy efficiently, and also economically. Even more diversified than the membrane structures and membrane processes are their applications. Presently the application of membranes is concentrated on four main areas, there are separation of molecular and particulate mixtures, the controlled release of active agents, membrane reactors and artificial organs, and energy storage and conversion systems. In these applications a large variety of processes and membrane structures are used which are tailor- made for the specific application as tabulated in task 2.1.

Table 2.1 : Application of Membranes

Separation of Molecular And Particulate Mixtures	**Controlled Release of Active Agents**	**Membrane Reactors And Artificial Organs**	**Energy Conversion And Energy Production Systems**
Micro-Filtration and Ultra-Filtration	Therapeutic drug delivery systems	Catalytic membrane reactors	Fuel cell separators
Reverse Osmosis	Pesticide depots	Bioreactors	Battery separators
Dialysis and Electro dialysis	Fertelizer delivery system	Diagnostic devices and sensors	Electrochemical synthesis

Separation of Molecular And Particulate Mixtures	**Controlled Release of Active Agents**	**Membrane Reactors And Artificial Organs**	**Energy Conversion And Energy Production Systems**
Gas separation and pervaporation	Air conditioning systems	Bio-hybrid and artificial organs	Pressure retarded osmosis
Membrane distillation and postreaction	Packing material and protective coatings	Integrated membrane system	Reversed electro dialysis

The applied driving forces to achieve a certain mass transport in membrane processes are gradients in the electrochemical potential of individual components induced by concentration gradients causing a diffusion of molecules or an electrical potential gradient resulting in a migration of ions and hydrostatic pressure differences causing a convective flux (Strathmann, 2006).

Membranes have many uses in the industry to let the process run completely. As cited K . Scott and R. Hughes; the main uses of membrane in the industry are, first as the filtration of micron and submicron size suspended solid (and dispersed solid) from liquid and gases containing dissolved solid. Second, membranes also use to remove macromolecules and colloids from liquids containing ionic species. Third is to separate mixtures of miscible liquids. Fourth, the selective separation gases and vapors from gas and streams. Fifth, the selective transport of ionic species only. Lastly, the virtually complete removal all material, suspended and dissolved, from water.

2.6 Membrane Fouling

Membrane fouling happened when solute or particles deposit onto a membrane surface or into membrane pores in a way that may disturb the membrane's performance. It is a major obstacle to the widespread use of this technology. It may cause flux and affect the quality of the water or permeate produced. Some of fouling may require a chemical cleaning method to remove the cake thickness on the membrane surface or just replacing the membrane. This increases the operating costs of a treatment plant. There are various types of foulants such colloidal (clays,flocs), biological (bacteria, fungi), organic (oils, polyelectrolytes, humics) and scaling (mineral precipitates).

Fouling of membrane can be divided into reversible and irreversible fouling based on the attachment strength of particles to the membrane surface. For the reversible fouling can be removed by a strong shear force of backwashing. Formation of a strong matrix of fouling layer with the solute during a continuous filtration process will result in reversible fouling being transformed into an irreversible fouling layer.

2.7 Advantages of Membranes

The advantages of membrane are compactness and light in weight, low labour intensity, modular design permitting easy expansion or operation at partial capacity, low maintenance because of no moving parts, low energy requirements and lastly low cost especially for small sizes. (Bernardo et. al, 2009).

2.8 Disadvantages of Membranes

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 (Zuo.et.al,2010).

2.9 Membrane Gas Separation

2.9.1 History

Systematic studies of membrane phenomena traced by the philosopher scientist in eighteenth century. In 1748, Abbe Nolet coined the word 'osmosis' describing the permeation of water through a diaphragm. Membranes are not quit use and had no industrial or commercial uses around nineteenth to earlier of twentieth centuries. On that time, membranes only use for laboratory tools to develop an experiment and theories test. As example, Traube and Pfeffer made the measurement of solution osmotic pressure. It was used by van't Hoff in 1887 to develop his limit law, which explains the behavior of ideal dilute solutions. At the same time, Maxwell and others used the concept of a perfectly selective semi-permeable membrane in developing the kinetic theory of gases.

In earlier investigation of membrane, it was investigated with every type of diaphragm available to them such as bladders of pigs, cattle or fish and sausage casings made of animal gut. Later, they preferred collodion (nitrocellulose) membranes because this things could be made reproducibly. In 1907 Bechhold has devised a technique to produce of graded pore size by a bubble test. Early 1930s, microporous collodion available commercially. Around next 20 years this microfiltration membrane technology was expended to other polymer, cellulose acetate. Membranes found their significant application at the end of World War II. The drinking water supplies in Germany and Europe had broken down and need to test for safety. From that, US Army was sponsored researcher to develop filters and exploited by the Milipore Corporation later. By 1960, the technology and science of membranes was developed but at that time, it still use in only a few laboratory and small, specialized industrial applications.

Membrane filtration not widely used and no significant membrane industry existed and the sale of membrane is slow because it is too expensive, too slow, too unselective and too unreliable. So, the industries prohibited their widespread use as a separation process. But this problems found their solution to each these problems during last 30 years and membrane-based separation process are now common place.

In early 1960s, membrane separation from a laboratory was transformed to an industrial process. These membranes consist of ultrathin, selective surface film on a much thicker but much more permeable microporous support, which provides the mechanical strength. The flux of Loeb-Sourirajan reverse osmosis was 10 times higher than that of any membrane and it is potentially for doing method of desalting water. At the same time, the medical separation process also developed independently. In 1945 in The Netherlands, W.J Kolf has demonstrated the artificial kidney using the system of membrane separation, but it is just for a small scale only. It was need about 20 years to refine the technology for the large scale and was completed by early 1960s.

Since then, the membrane most use in artificial organ and become a major life-saving procedure. In medical applications, membranes also important thing for controlling drug delivery systems and a key figure in this area was Alex Zaffaroni, who founded Alza, one of company dedicated for developing this product in 1966. The membrane techniques that developed by Alza and their competitors become widely used to improve the efficiency and safety of drug deliver y for pharmaceutical industry.

From 1960 to 1980, there were very big changes in the status of membrane technology. Building on the original Loeb-Sourirajan technique, other membrane formation processes, including interfacial polymerization and multilayer composite casting and coating, were developed for making high-performance membranes. From this process, it can produces the thin membranes with selective layers as thin as 0.1 µm or less by a number of companies. Method of packaging membranes into large membrane-area-spiral-wound, hollow-fine- fiber, capillary, and plate-and-frame modules were also developed, and advances were made in improving membrane stability. Micro-filtration, ultrafiltration, reverse osmosis and electrolysis were established processes with large plants installed worldwide by 1980.

From the development of membranes in 1980s, it was emergence of industrial membrane gas separation processes. Monsato Prism, in 1980, was the first major developed membrane for hydrogen separation. A few years after, Dow was producing systems to separate nitrogen from air, while Cynara and Separex were producing systems to separate carbon dioxide from natural gas. Gas separation technology is evolving and expanding rapidly by the year. The final development of the 1980s, first commercial pervaporation systems for dehydration of alcohol was introduced. About 100 and more of ethanol and isopropanol pervaporation dehydration plants have now been installed. Other pervaporation applications are at the early commercial stage.

2.9.2 Application of Membrane Gas

The are many application that used membrane for gas separation. It commonly widely used in petrochemical applications such for hydrogen separation. In industries of petrochemical, the hydrogen need to separate from hydrocarbon to get pure hydrocarbon before it will send to the process plant. Other than that, membrane gas separation also used in ammonia plant to separate hydrogen/nitrogen gas.

2.9.3 Market of Membrane Gas

The use of membranes in separation processes is growing slow but it is still steady grow up. As cited Baker in 2002, he estimated that the market scale of membrane gas separation technology in year 2020 will increase to be five times of that of year 2000.

It is expected that membrane gas separation will become more important role in reducing the environmental impact and costs of industrial processes, particularly now, although energy cost is volatile, the global hydrocarbon reservoirs are destined to reduce dramatically during this century. There are many opportunities to increasing the markets for membrane gas separation. In curtain case, the membrane materials, membrane configuration, and preparation routes are insufficient to fully develop these new fields. A broad range of materials was investigated and were achieved with different improvement by the time in this field. Nowadays, many of the research work is being to find new materials and to development of new membrane structures that exhibit both higher selectivity and permeability to specific gases.

2.9.4 Mechanism of Membrane Gas Absorption

Separation of mixture is possible either using porous or non-porous membranes. Separation in porous membrane is through the different in Knudsen flows of the components in the pores which are of the size less than the mean free paths of the molecules. Generally low separation factors are achieved and only one commercial application is known, the enrichment of uranium hexafluoride using porous ceramic membranes. Separation of gases through non-porous membranes depends on the difference in permeabilities of the constituent gases. Gas permeation (GP) is the only means by which membranes can be used to separate gas mixtures without a change in phase. Separation of different gases is achieved by virtue of differences in molecular size and gas solubility in the membrane. Gases of smaller molecular size have larger diffusion coefficient and in a convection free environment in the pores of a membrane can be suitably separated by virtue of the different mobilities.

The solubility of gaseous components in the membrane will combine with diffusion to determine the permeability and selectivity of separation. This is particularly true of asymmetric membranes which have a thin dense skin layer which controls performance. The selectivity of these membranes is represented by the ratio of permeability of any two components in the membrane. This factor is a specific characteristic of a membrane and generally veries inversely with gas permeability. This therefore means that to achieve a high selectivity requires the membrane to operate with a low permeability. A major problem with asymmetric membranes was found to be their susceptibility to faults and pins holding which caused a drastic fall off in selectivity. This problem was solved by coating the membrane skin with a thin layer of silicon polymer, which exhibits high permeability and low selectivity, which effectively sealed the faults.

Membranes for gas permeation are either one or two types, elastonomer such polydimethylsilicone and polymethylpentene, or glassy polymer such polyimide or polysulphone. Elastonomers generally show rather low selectivities for some separations whereas glassy polymers exhibit higher selectivity but lower permeability. The latter membranes exhibit high permeability compared to homogeneous membranes, but are accompanied by lower selectivity.

2.9.5 N_2 And CO_2 Gas Separation Process

CO_2 has a stronger electrostatic quadrupole than N_2, leading to a more intense interaction of CO_2 with the zeolite material, which translates into a preferential adsorption of CO_2 in CO_2/N_2 mixtures. Thus, it can be expected that surface diffusion of CO_2 would make a significant contribution to its permeation, while at the same time adsorbed CO_2 would reduce the N_2 permeation flux through the membrane; both factors would lead to selective CO_2/N_2 separations (Kusakabe et al., 1997).

2.10 Thin Film Composite (TFC) Membrane

2.10.1 TFC Membrane

TFC membrane is an asymmetric membrane which is comprised of a fabric, a porous support layer commonly made of polymer, and a dense ultra thin salt rejection barrier layer. The porous support layer is made by the phase inversion technique, while the thin layer is made by interfacial polymerization (polycondensation). Many routes were described to form the ultrathin barrier layer in the composite membranes.

These techniques includes; casting an ultrathin dense layer separately and then cover the microporous support layer with the thin dense layer (lamination), interfacial polymerization, dip-coating a polymer solution onto the microporous layer and then dry the coated layer and using a gaseous phase monomer plasma to deposit the barrier film directly on the microporous support layer (plasma polymerization). Among those methods, interfacial polymerization is the most widely used technique and polyamide TFC membranes are industrially produced by this method (Takeshi et al., 2010).

2.10.2 Technology Development In TFC Membrane

It was also found that the water flux of TFC-RO membranes could be doubled without affecting the salt rejection by incorporating zeolite nano-particles in the thin layer of the TFC-RO membranes. To prevent the microbial fouling, a new type of anti-fouling membranes was developed by introducing TiO 2 nano-particles to TFC membranes in order to reduce the loss of permeability. Water permeability of TFC membranes could be increased using an oxygen plasma treatment. The reason behind that is the introduction of carboxylic group which increases the hydrophilicity of the treated membrane. On the other hand, the chlorine resistance of the TFC membrane can be enhanced using an argon plasma treatment which causes the cross- linking to take place at the nitrogen sites on the membrane surface (Takeshi et al, 2010).

2.10.3 Application of TFC Membrane

Thin film composite membranes are used in water purification, as a chemical reaction buffer (batteries and fuel cells), and in industrial gas separations.

2.10.4 Advantages of TFC Membrane

A filtration membrane's performance is rated by selectivity, chemical resistance, operational pressure differential and the pure water flow rate per unit area. Due to the emphasis on flow rate, a membrane is manufactured as thinly as possible. These thin layers introduce defects that may affect selectivity, so system design usually trades off the desired flow rate against both selectivity and operational pressure. In applications other than filtration, parameters such as mechanical strength, temperature stability, and electrical conductivity may dominate.

2.10.5 Disadvantages of TFC Membrane

Thin film composite membrane also have problem in curtain process or system. The disadvantage of TFC membrane is limited tolerance to chlorine and lack of membranes with high pressure normalized flux.

2.10.6 Structure And Material of TFC Membrane

As is suggested by the name, TFC membranes are composed of multiple layers. Membranes designed for desalination use an active thin- film layer of polyimide layered with polysulfone as a porous support layer. Other materials, usually zeolites, are also used in the manufacture of TFC membranes.

CHAPTER 3

METHODOLOGY

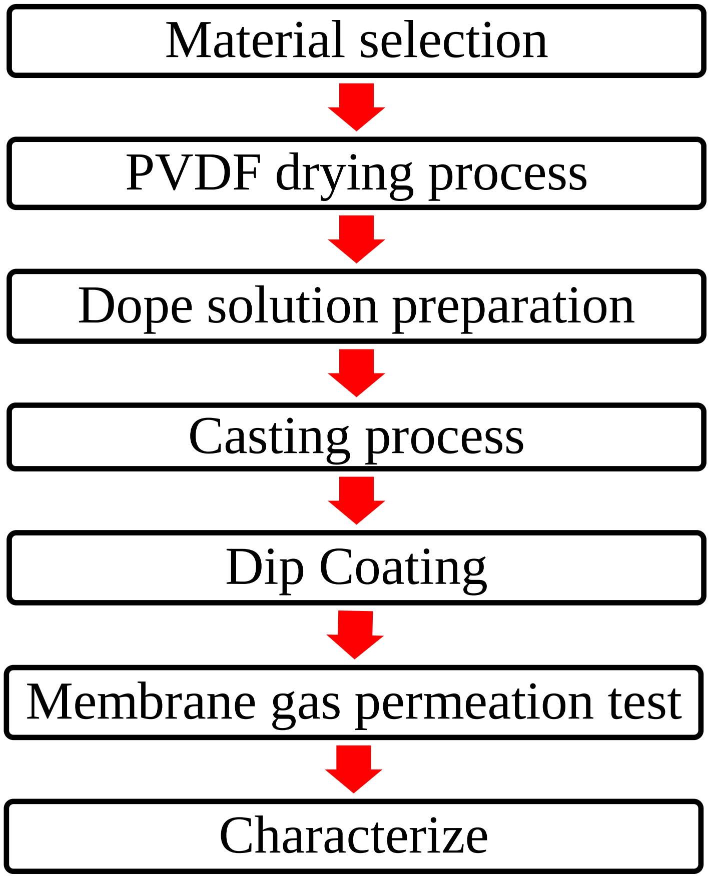


Figure 3.1 : General Process Flow Method

3.1 Preparation of Polyvinylidine Fluoride (PVDF) Microporous Membrane

In the process of making membrane, polymer of Polyvinylidene fluoride (PVDF) will produce as a support membrane.

3.1.1 Materials

Material that will use for this method based on their properties. In this process, they need microporous hydrophobic membrane as a medium for mass transfer between two phases. Polyvinylidenefluoride (PVDF) is one of the good material mainly used for the preparation of microporous hydrophobic membrane because it have a good solubility in many common organic solvents.

3.1.1.1 Polymer

Polyvinylidenefluoride (PVDF) in a solid obtained from the supplier as a raw material for producing PVDF support membrane.

Table 3.1 : Properties of PVDF

Melting Point	166-170°C
Density	1.78 g/mL at 25 °C
Vapor Pressure	15 mm Hg (32 °C)
Refractive Index	n20/D 1.42
Solubility	Some polar solvents such as organic esters and amines:
Form	Powder
Stability	Stable. Incompatible with strong oxidizing agents
EPA Substance Registry	Silica
System	Ethene, 1,1-difluoro-, homopolymer(24937-79-9)
CAS-No	24937-79-9
Molecular Weight	0
Molecular Formula	(C2H2F2)n

3.1.1.2 Solvent

N-Methylpyrrolidone (NMP) obtained from supplier as a solvent to produce solution of PVDF polymer.

Table 3.2 : Properties of NMP

Molecular Weight	99.1 g/mol
Density - liquid (**20°C)**	1.03 g/ml
Boiling Point (760 mmHg)	204.3 °C
Freezing Point (760 mmHg)	-23.6 °C
Viscosity (20°C)	1.7 cp
Heat of Vaporization (100°)	122 cal/g
Specific Heat – liquid (0°C)	0.401 cal/g.°C
CAS-No	872-50-4
Molecular Formula	C_5HgNO
Molecular Weight	99.13 $gmol^{-1}$
Melting Point	-24˚C

3.1.1.3 Non-Solvent

Deionized water will use as non-solvent in making dope solution. Water is act to mix well the dilution of NMP and PVDF.

3.1.2 Dope Solution Process

Before start the process, polymer of PVDF in solid will drying in oven with temperature of 50˚C within 15minutes to remove the humid and water on the solid. 15wt% of PVDF polymer will dissolve in 82 wt% N-Methylpyrrolidone (NMP) using mechanical stirrer with speed 200 rpm and temperature of 60˚C for 24 hours in a 1000 mL four-necked round-bottomed vessel. The heat supplied by using heating mantle and thermometer used to make sure the temperature constant. When solution mixed well, 3 wt% of deionized water was drop inside solution using dropper to prevent solidification of solution. The dope solution produced and degas. Then it will be kept stagnant for 30 minutes to remove bubbles inside solution by using ultrasonic water bath with frequency 6.

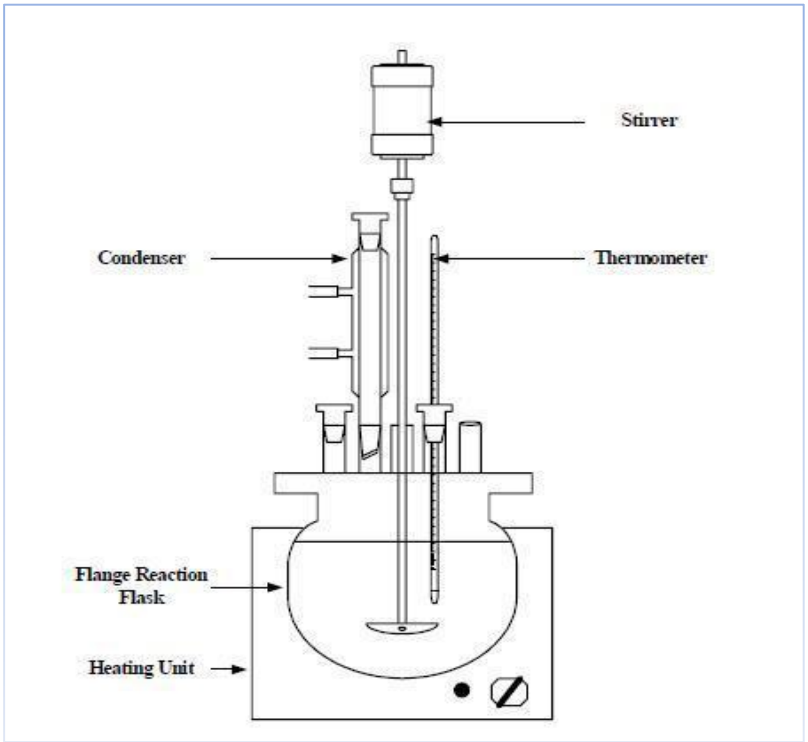


Figure 3.2 : Dope Solution Preparation Vessel

3.2 Casting Process

In this process, dope produced will be cast to get shape and the thickness flat-sheet membrane. Solution or dope will cast on a flat glass plate by using glass rod. At the end of the glass rod, it will be wrapped with tape of a circumference. After 15s, the casted dope solution will be immersed in deionized water with ambient temperature. Within a few minutes, solidification will be observed and membrane will remove from coagulation bath after 10 minutes. Then membrane will soak using deionized water after taking out from coagulation bath. Lastly, membrane will dry at ambient temperature for 2 hours to remove humidity and water from membrane.

3.3 Preparation of Polydimethyl siloxane (PDMS) Coating

In this process, polymer of Polydimethylsiloxane (PDMS) will be act as a coating for support membrane, Polyvinylidenefluoride (PVDF), by using dip coating method.

3.3.1 Material

Polydimethylsiloxane (PDMS) will use as a coating based on their chemical and physical properties that can protect the support membrane and give more selectivity to the separation.

3.3.1.1 Polymer

Polydimethylsiloxane (PDMS) in a liquid obtained from the supplier as a polymer for coat the membrane.

Table 3.3 : Properties of PDMS

Melting Point	-35˚C
Boilling Point	155 – 220 ˚C
Density	0.971
Vapor Pressure	5 mmHg (20˚C)
Refractive Index	1.4035
Flash Point	63˚C
Water Solubility	Insoluble
Molecular Weight	94.187
Molecular Formula	C_5H_6Si
CAS-No	9016-00-6

3.3.1.2 Solvent

N-Hexane obtained from the supplier will be used as a solvent to produce the PDMS solution.

Table 3.4 : Properties of n-Hexane

Molecular Formula	C_6H_{14}
Molecular Weight	86.10 g/mol
Density	0.66 g/cm^3
Boiling Point	68.95 °C
Melting Point	-93.5 °C

3.3.1.3 Non-Solvent

Deionized water will use as non-solvent in coating solution to make the solution of PDMS and n-hexane mix well.

Table 3.5 : Properties of Water

Molecular Formula	C_6H_{14}
Molecular Weight	86.10 g/mol
Density	1000 kg/m^3
Boiling Point	99.98 °C
Melting Point	0 °C

3.3.2 Dip-Coating Method

Liquid Polydimethylsiloxane (PDMS) with different weight percent (10%,15%, and 20%) will be dissolved in a n- hexane solvent using magnetic stirrer at ambient temperature till well. The solution produced will be store in a stock bottle to prevent it evaporate to the ambient. The solution of PDMS with different percentage will be drop on the layer of PVDF membrane surface by using dropper. The coated membrane will vulcanize under room temperature for 2 min to let the excess solvent of n-hexane evaporate. Then let it cure in an oven under temperature 60°C for 90 minutes.

3.4 Membrane Characterization

In this study, membrane will be characterize by using two devices, Fourier Transform Infrared Radiation (FTIR) and Scanning Electron Microscopy (SEM). FTIR can identify the unknown materials in the membrane. It also can determine the quality or consistency of a sample and the amount of components in a mixture. Other than that, it also can detect the functional group of membrane produced. SEM can reveal the structure of texture, chemical composition, crystalline structure and orientation of materials in the membrane. It also can analyze the morphology of surface, cross-section, pore diameter and pore size distribution of membrane.

3.5 Membrane Permeability and Selectivity

From the result will get from the experiment, the membrane permeability and selectivity can be determine by using the equation 3.5-1 and 3.5-2 below :

$$P = \frac{Vl}{At\,\Delta p}\ [(cm^3\ (STP)cm)/cm^2 cmHg] \qquad \textbf{Equation 3.5-1}$$

$$\frac{P}{I} = \frac{V}{At\,\Delta p}\ [(\frac{cm^3(STP)}{cm^2 cmHg}] \qquad \textbf{Equation 3.5-2}$$

I = Thickness of the membrane (cm)

A = The effectiveness membrane area in cm^2

V = The volume (cm^3) displaced in time t(s)

Δp = The transmembrane pressure (cmHg)

The membrane permeability can be determined by using the equation 3.5.1. From the derivation of that equation it will form the membrane permeance equation, 3.5.2. The membrane permeance equation will use to calculate the permeance of membrane for different gas flow, Corbon Dioxide (CO_2) and Nitrogen (N_2), and will put into the selectivity equation 3.5-3 :

$$\alpha = \frac{\frac{P}{l}\{CO_2\}}{\frac{P}{l}\{N_2\}}$$ **Equation 3.5-3**

3.6 Gas Permeation Test

The set up for the single gas permeation experiments using the liquid membrane is shown in Figure 3.3 .

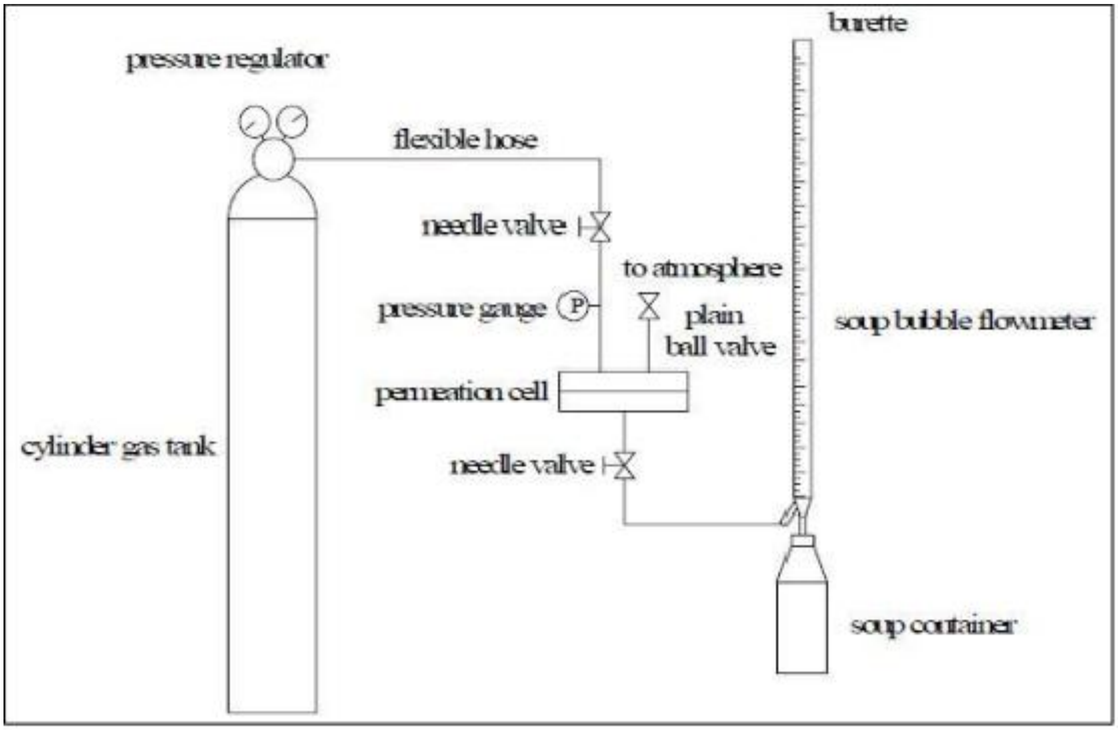


Figure 3.3 : Experimental Set-up For Single Gas Permeation Test

The apparatus consisted of a membrane module which was made according to ASTM D1434 standard. The configuration of this module is illustrated in Figure 3.4.

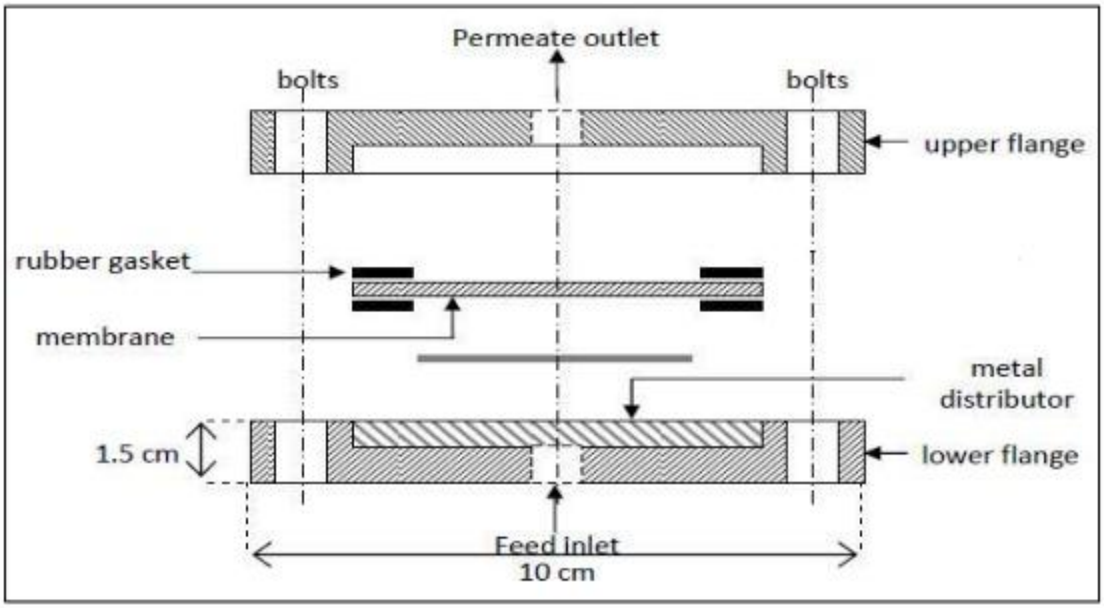


Figure 3.4 : Schematic of Membrane Module Test

A stainless steel disk was placed in the bottom section to provide mechanical support for the membrane. The membrane was positioned on top of the sintered disk and sealed by O-rings.

The gas permeation tests were carried out using pure N_2 and CO_2 as test gases at room temperature with pressure differences of 0.5,1.0, and 1.5 bar. The gases were obtained from local companies with purities higher than 99%. The downstream pressure was atmospheric throughout the experiments. The permeation tests always began with

N_2 and ended with CO_2 and the gas flow rates of each gas were measured by a soap bubble flow meter. The movement of gas passing the membrane will be observed for the distance of 10cm burette. Permeability of gases through each membrane was measured at least four times; the average of all measurements was then reported as the overall permeability.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Membrane Morphology by Using Scanning Electron Microscopic (SEM)

Scanning Electron Microscopic (SEM) was used to obtain for each membrane cross-section images of the membrane and images of its skin layer. The cross-section images provided information on the membrane structure. With SEM it is also possible to observe the membrane skin layer.

In this study, membranes will be observed to see the structure of membrane that generally affects the performance of membrane. The parameters for the membrane structure that was considered are such porosity, roughness, pore size, pore shape and pore size distribution (Y. Wyart et. al, 2008). The views of membrane with various percentages of PDMS are illustrated in image as shown in Figure 4.1 to Figure 4.8.

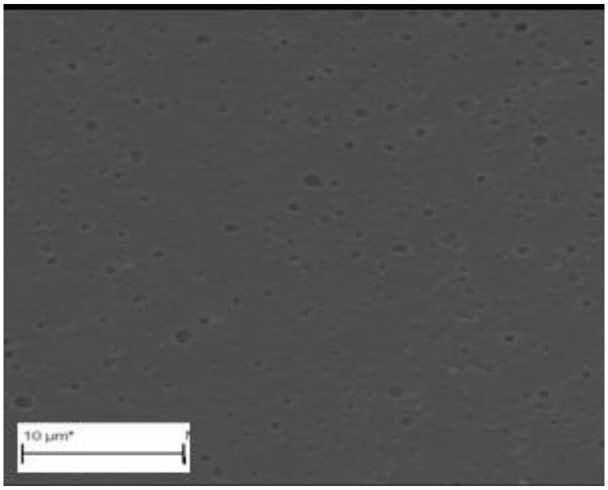


Figure 4.1 : The Surface Image of PVDF Membrane coated with 0% of PDMS at Magnification 1.5 K X

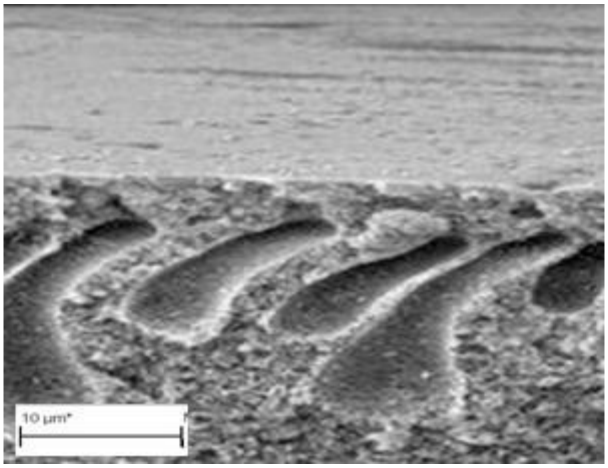


Figure 4.2 : The Cross-Section Image of PVDF Membrane coated with 0% of PDMS at Magnification 1.0 K X

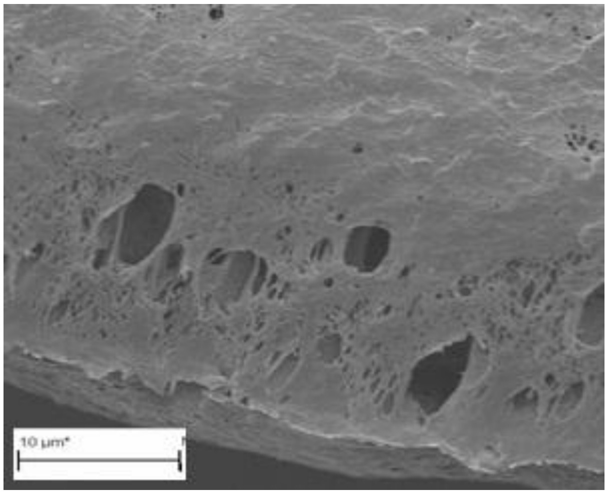


Figure 4.3 : The Cross-Section Image of PVDF Membrane coated with 10% of PDMS at Magnification 1.0 K X

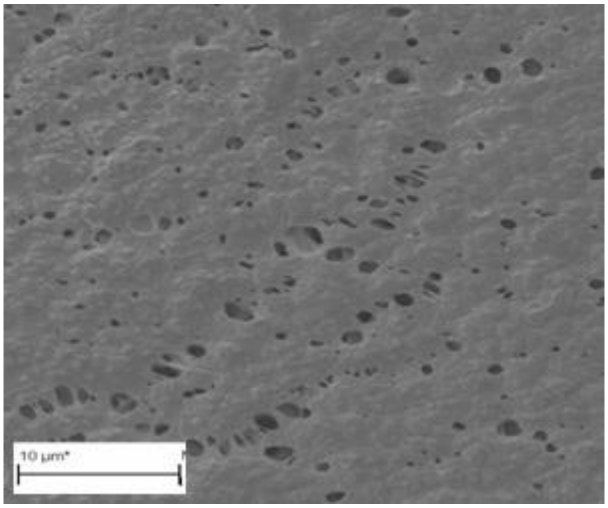


Figure 4.4 : The Surface Image of PVDF Membrane coated with 10% of PDMS at Magnification 1.5 K X

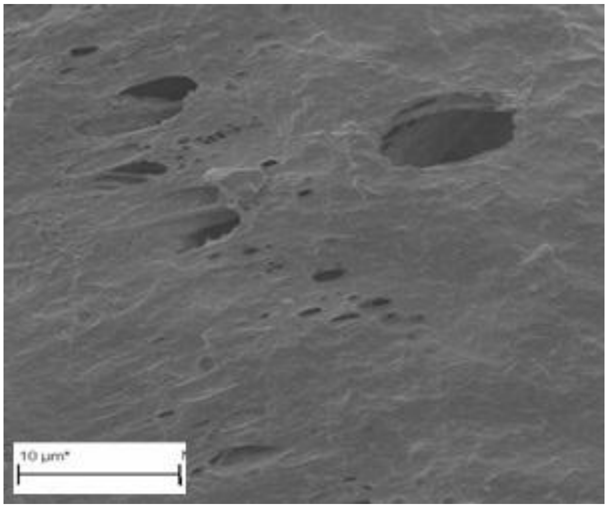


Figure 4.5 : The Cross-Section Image of PVDF Membrane coated with 15% of PDMS at Magnification 1.0 K X

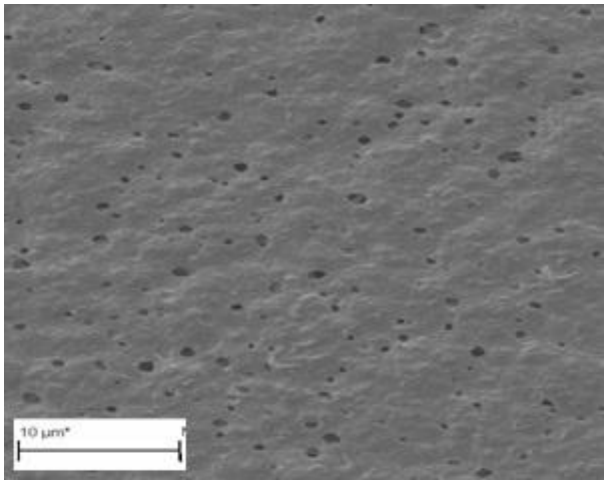


Figure 4.6 : The Surface Image of PVDF Membrane coated with 15% of PDMS at Magnification 1.5 K X

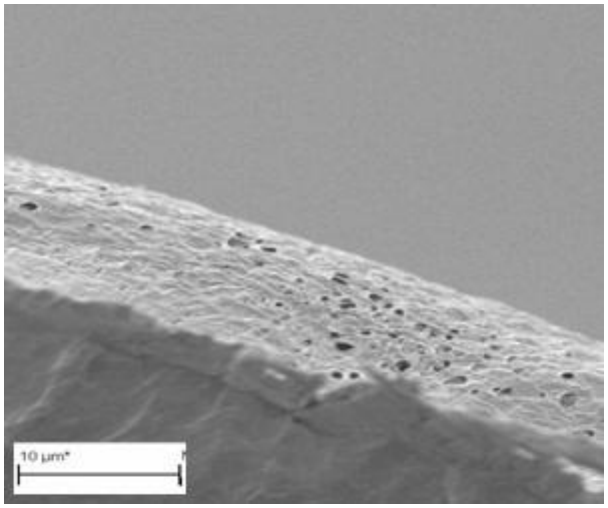


Figure 4.7 : The Cross-Section Image of PVDF Membrane coated with 20% of PDMS at Magnification 1.0 K X

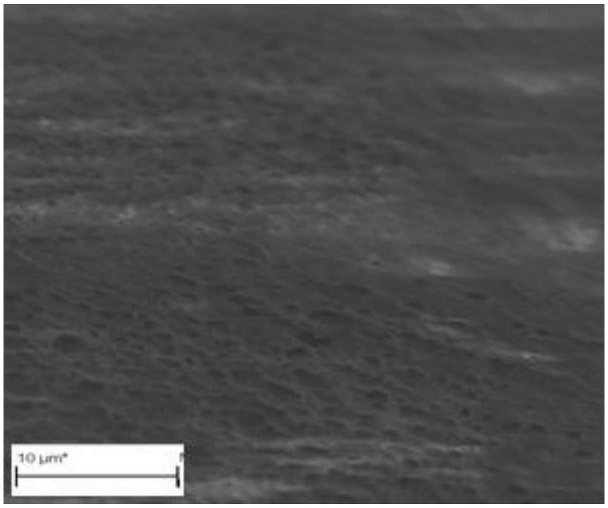


Figure 4.8 : The Surface Image of PVDF Membrane coated with 20% of PDMS at Magnification 1.5 K X

Figure above shows the view of the structure of cross-section and surface layer for the membrane produced. The view of the structure characterized for the cross-section at magnification of 1.00 K X and 1.5 K X for the surface area. Figure 4.1 till Figure 4.8 represented the view for membrane coated with 0%, 10%, 15% and 20% of PDMS respectively.

Figure 4.1 and 4.2 above illustrated views of the surface area and cross-section of the uncoated PVDF membrane. From the view on cross-section, the finger-like pore formed inside the membrane can be defective the membrane with pin-holes. As observed, there many of large pores on the surface of the membrane formed and it may cause the performance of membrane becomes low.

The view of PVDF membrane that coated with PDMS illustrated in Figure 4.3 till 4.8. The structure of membranes shows the change by increasing the concentration of PDMS. As can see, the pore size on cross-section view of the membrane with 10% PDMS is larger than the membrane with 20% PDMS. The increasing of the PDMS concentration formed the smallest size of pore. From the view of surface layer, it shows the decreasing of the porosity by increasing the concentration of PDMS on membrane. The highest concentration of PDMS has the lowest porosity on the membrane surface compare with the other membranes because with presence of PDMS as a coating layer, it is capable to repair the defect such a pin-hole on the surface of the membrane (Cho et. al, 2006).

The changes of the structure in membrane produced were observed. It shows the change in surface morphology for the non-coating membrane and coated membrane. With a coating of PDMS onto the membrane as showed in figure 4.3 to Figure 4.8 above, the high performance and high selectivity of membrane will be on PVDF membrane coated with 20% of PDMS.

4.2 Performance Membrane For Different Percent of PDMS Coated

In this study, the performance of the membrane is refer on permeability and selectivity of the membrane produced. To get these values, permeation test must be done to get the permeation rate. The permeation rate is based on formula 3.5-1, 3.5-2, and 3.5-3.

For this test, membrane performed by using permeation cell with effective permeation area of 24.63 cm^2 (Diameter = 5.6 cm). The tests were carried out with different gas (CO_2 and N_2) and different pressure (0.5 bar, 1.0 bar and 1.5 bar). From four times reading taken, the average can be calculated to get the more accurate values.

Table 4.1 : The Distribution of Time Taken For Carbon Dioxide (N_2) Gas

Sample	**Pressure (bar)**		
	0.5	**1**	**1.5**
	Time (s)		
20% of PDMS	4.53	2.05	1.84
	5.19	2.04	1.74
	4.44	1.97	1.84
	4.44	2.01	1.93
Average (s)	**4.65**	**2.02**	**1.85**
15% of PDMS	4.57	1.96	1.9
	4.68	2.02	1.76
	4.4	1.93	1.78
	4.22	1.97	1.79
Average (s)	**4.46**	**1.92**	**1.8**
10% of PDMS	4.01	1.87	1.73
	4.41	1.89	1.79
	4.3	1.84	1.8
	4.34	1.78	1.8
Average (s)	**4.26**	**1.85**	**1.78**
0% of PDMS	3.42	1.65	1.46
	3.38	1.69	1.48
	3.34	1.59	1.54
	3.46	1.62	1.49
Average (s)	**3.4**	**1.65**	**1.49**

Table 4.2 : The Distribution of Time Taken For Nitrogen (CO_2) Gas

Sample	**Pressure (bar)**		
	0.5	**1**	**1.5**
	Time (s)		
20% of PDMS	4.08	2.46	2.59
	4.03	2.38	2.59
	3.97	2.48	2.55
	3.98	2.50	2.64
Average (s)	**4.02**	**2.44**	**2.6**
15% of PDMS	3.72	2.32	2.25
	3.99	2.22	2.31
	3.98	2.27	2.23
	3.94	2.34	2.33
Average (s)	**3.91**	**2.28**	**2.28**
10% of PDMS	2.83	1.78	1.64
	2.92	1.67	1.7
	2.9	1.83	1.72
	3.01	1.80	1.78
Average (s)	**2.92**	**1.76**	**1.71**
0% of PDMS	2.63	1.66	1.65
	2.57	1.75	1.71
	2.61	1.72	1.64
	2.59	1.68	1.68
Average (s)	**2.6**	**1.71**	**1.67**

Results from Table 4.1 and 4.2 above calculated to get the values of permeability and selectivity of the membrane as shown in Table 4.3 below :

Table 4.3 : The Calculation Results of Permeability and Selectivity of Membrane

Membrane	**Pressure**	**Permeability**		**Selectivity**
		N_2	**CO_2**	
0%	37.5	6368.745	8328.358	0.764706
	75.01	6560.862	6330.656	1.036364
	112.51	4843.805	4321.718	1.120805
10%	37.5	5083.036	7415.661	0.685446
	75.01	5851.58	6150.808	0.951351
	112.51	4054.645	4220.625	0.960674
15%	37.5	4855.097	5538.039	0.876682
	75.01	5638.241	4747.992	1.1875
	112.51	4009.594	3165.469	1.266667
20%	37.5	4656.716	5386.5	0.864516
	75.01	5359.12	4436.648	1.207921
	112.51	3901.226	2775.873	1.405405

The characteristic of the membrane is based on the permeance and the selectivity. From Table 4.3, the permeance graph is determined by plotting the permeance value of gas versus various pressure (0.5 bar, 1.0 bar and 1.5 bar) as shown in Figure 4.9 and Figure 4.10 respectively for the N_2 and CO_2 gas permeance. It presented the trend of gas permeance for the N_2 and CO_2 with various pressure and percentage of PDMS on the membrane. While the graph of CO_2/N_2 selectivity presented in Table 4.11. The trend of permeance graph for N_2 gas shown that the permeance increase at 0.5 to 1.0 bar and decrease at 1.0 to 1.5 bar. It is because of the fouling or crystalline happened on membrane pore. Diffusivity parameter increases because of the growth of lamellar micro-crystallites in perpendicular to machine direction (Mousavi et. al, 2010).

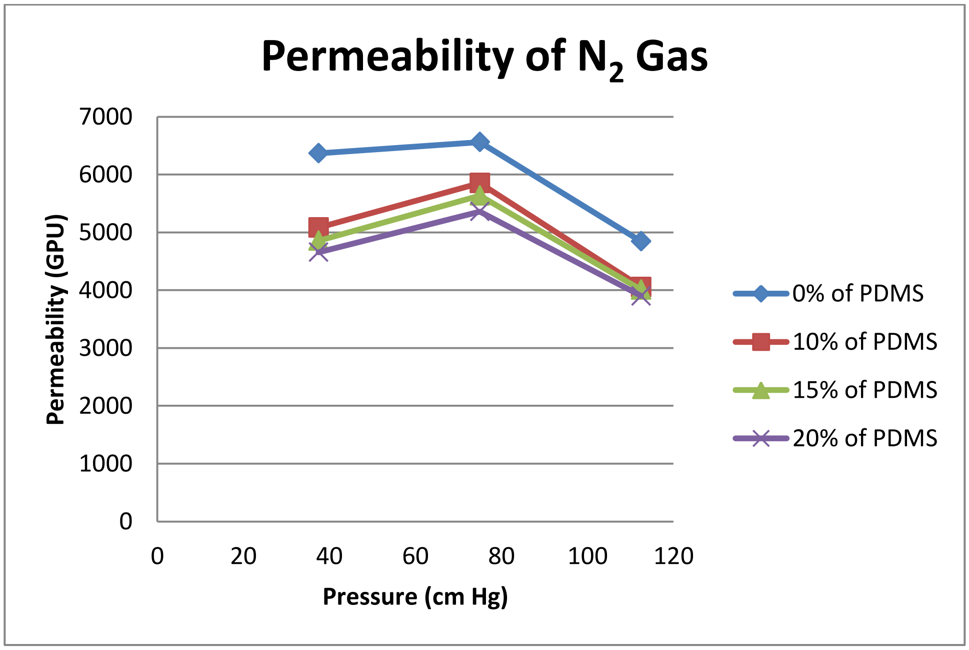


Figure 4.9 : N_2 Permeance With Different Feed Pressure for The Various Percentage of PDMS on Membrane

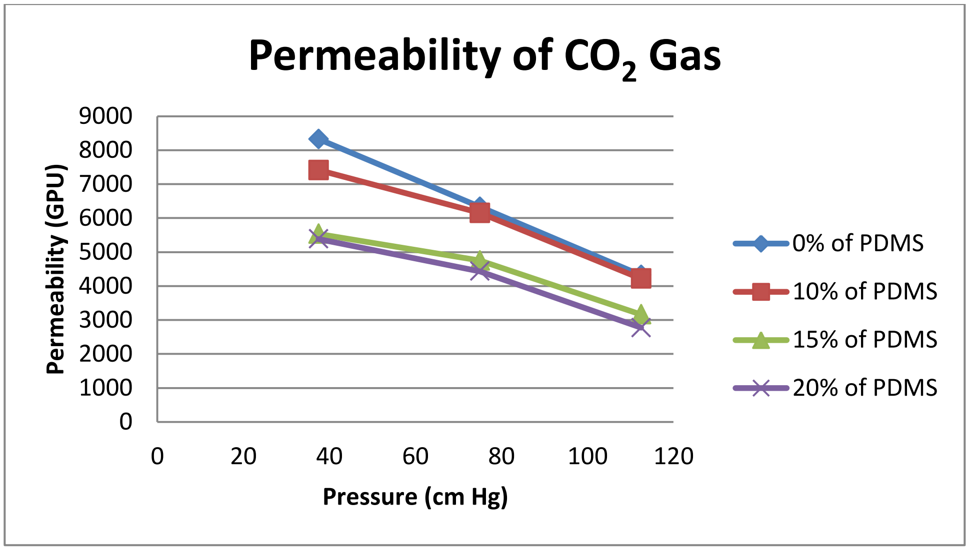


Figure 4.10 : CO_2 Permeance With Different Feed Pressure for The Various Percentage of PDMS on Membrane

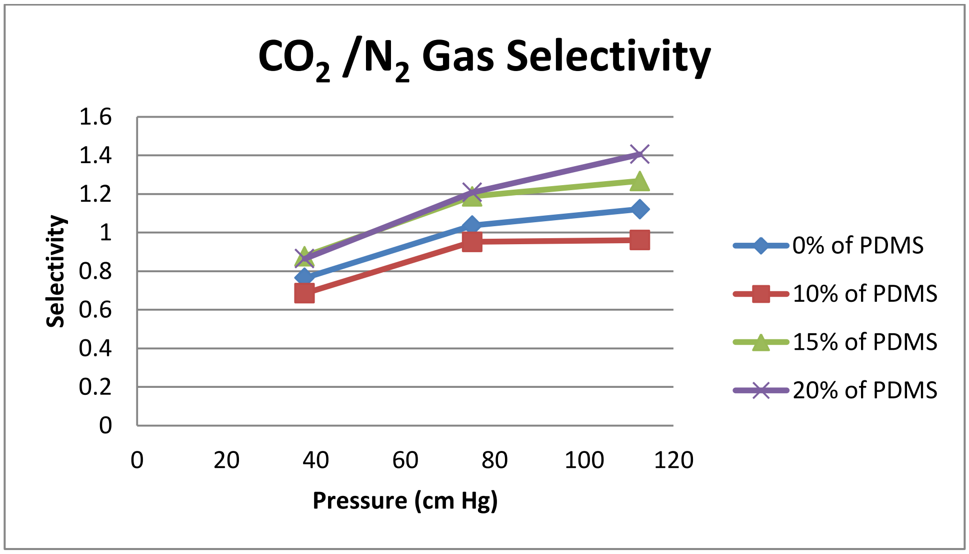


Figure 4.11 : CO_2 / N_2 Selectivity With Different Feed Pressure for The Various Percentage of PDMS on Membrane

Based on Figure 4.9, it shows a graph permeance to gas N_2. From the graph, it shown that the membranes coated with 20% PDMS has a lowest permeance value than 0%, 10%, and 15%. At the same time. graph in Figure 4.10 also shows the same trend as the graph in Figure 4.9. From the results obtained, the membranes coated with high concentration of PDMS give lower permeance. The decreasing of permeability shows the membrane is increase in solubility, which mean the gas is easily passing through the membrane. It occurs because the micro pores of the membrane are covered with PDMS to close the pin-holes and for any defect on membrane, so the movement path of the gas molecules to pass through the membrane becomes slow (Cho et. al, 2006). Similarly to CO_2 gas, permeance values of membrane coating with 20% of PDMS is lowest than the membrane coated with 0%,10% and 15% of PDMS. The range of the permeance value for N_2 (4000 GPU – 7000 GPU) gas is lower than CO_2 (5000 GPU – 9000 GPU) due to the size of the N_2 atom is smaller than CO_2. So that, the N_2 gas molecules easily passing through the membrane pore compare with the CO_2 gas. Knudsen diffusion predicts a selectivity of less than unity. Molecular sieving relies on size exclusion to separate gas mixtures. Pores within the membrane are of a carefully controlled size relative to the kinetic (sieving) diameter of the gas molecule. This allows diffusion of smaller gases at a much faster rate than larger gas molecules. In this case, the selectivity is greater than unity, as N_2 has a smaller kinetic diameter than CO_2 (Scholes et. al, 2008).

From permeance values, the selectivity of the membrane obtained. From the graph of selectivity in Figure 4.11, it shows the value of selectivity is different. Selectivity values for 0% PDMS membrane is very low compared to the membrane which is coated with 20% PDMS. It’s mean the selectivity is directly proportional to the

PDMS concentration on the membrane while the permeance of membrane is inversely proportional with the concentration of PDMS. A highly permeable membrane tends to have low selectivity, and visa versa (Scholes et. al, 2008).

4.3 Result of FTIR Analysis

In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. Figure 4.4 showed the FTIR absorbance peak for membrane coated with 10% of PDMS. While figure 4.5 and 4.6 below showed the FTIR absorbance peak for the membrane coated with 15% and 20% of PDMS respectively.

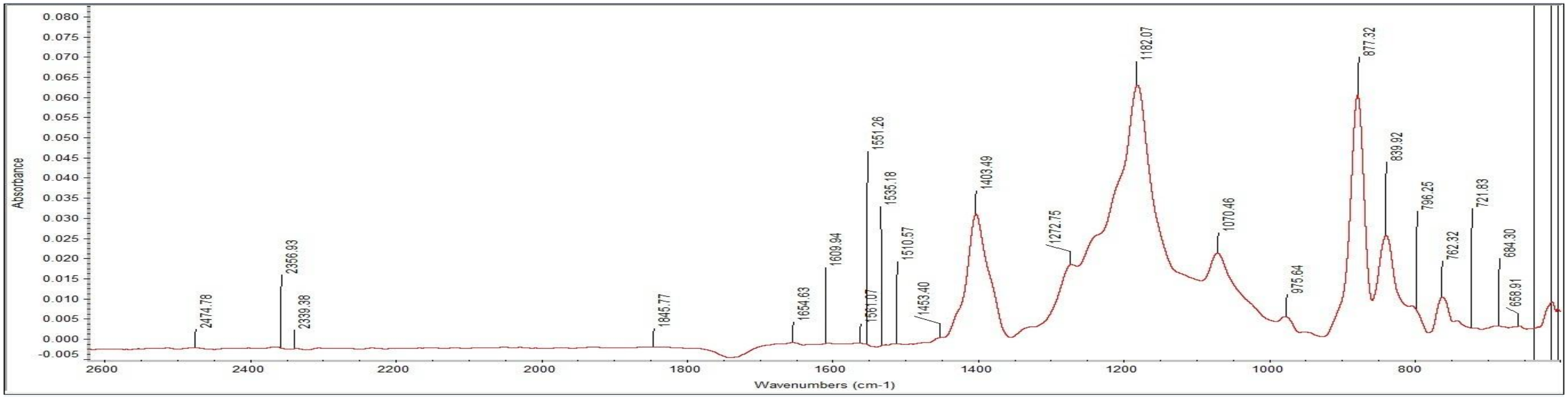


Figure 4.12 : FTIR Absorbance Peak For Membrane Coated With 10% of PDMS

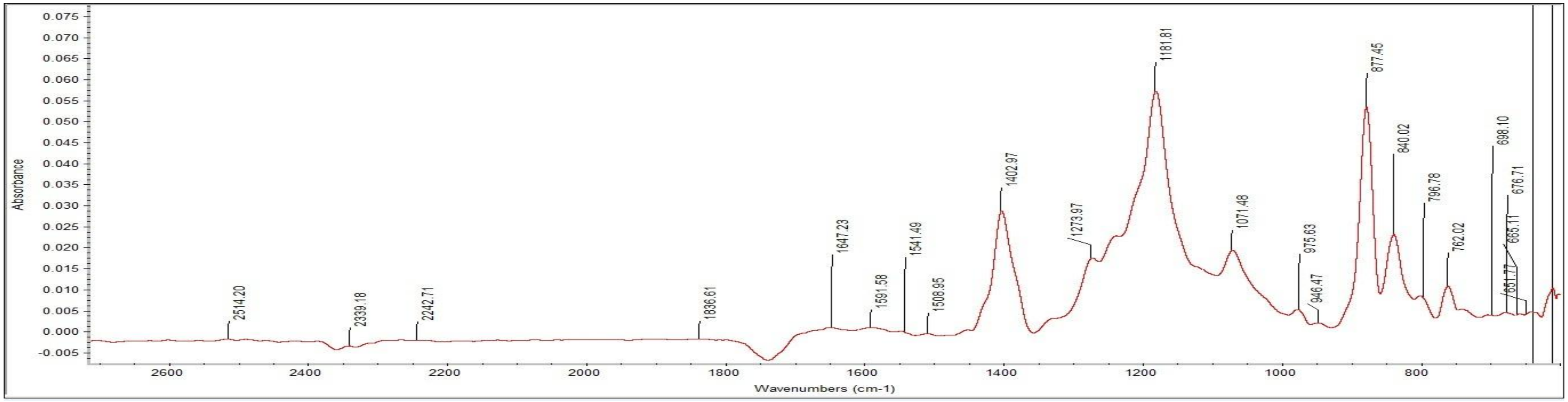


Figure 4.13 : FTIR Absorbance Peak For Membrane Coated With 15% of PDMS

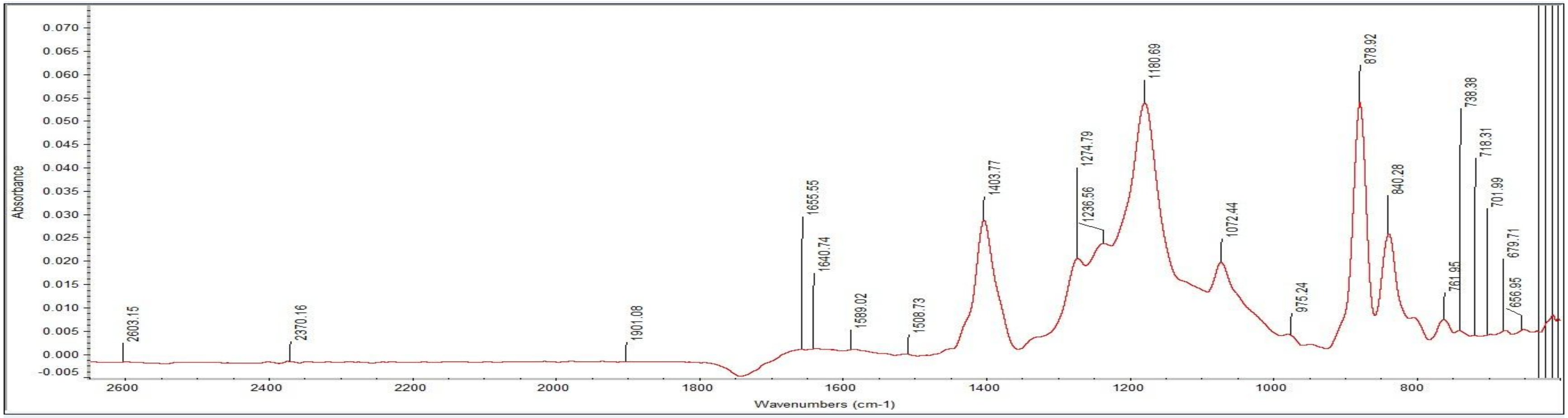


Figure 4.14 : FTIR Absorbance Peak for Membrane Coated With 20% of PDMS

Figure 4.12 to Figure 4.14 shows the FTIR results of the membrane coated with PDMS at different percentages (10%, 15% and 20%). By using FTIR, the component of PVDF and PDMS can determined whether exists in membranes. The spectrum indicates the functional groups that presence in the sample, which are siloxane group (Si-O) stretching vibration between 1000-1100 cm^{-1}, while PVDF is between 1000 cm^{-1} to 1400 cm^{-1}. In that range, the obvious peak and highest peak is treated as components for PVDF and PDMS. In Figure 4.12, the PVDF components identified exists in the range of 1000 cm^{-1} to 1400 cm^{-1} on the highest peak of 1182.07 cm^{-1}. While the highest peak for PDMS in the range of 1000 cm^{-1} to 1100 cm^{-1} identified exists at the highest peak of 1070.46 cm^{-1}. In Figure 4.13, the PVDF components identified existed at the peak of 1181.81 cm^{-1}, while the PDMS components were identified in existence at the peak of 1071.48 cm^{-1}. For Figure 4.14, the PVDF component was identified exists at the peak of 1180.69 cm^{-1}, while the PDMS components were identified at the peak of 1072.44 cm^{-1}.

Indeed, PVDF and PDMS components are really present in the membranes. PDMS wavelength values in Figure 4.12, Figure 4.13 and Figure 4.14 increased. This is because the percentage of the PDMS membrane is also increased for three samples. While it showed the decreasing wavelength value of PVDF in these figures because while conducting the dip-coating, the presence of PDMS component in membrane will reduced the value of PVDF during the reactions occur.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The use of membrane in separation gas is become most important and widely used nowadays. Based on the results of this study, a number of conclusions were drawn. The difference in concentration of coating layer on PVDF support membrane really can affect the performance of the membrane. PVDF membrane show the high selectivity when the concentration of PDMS coating solution increases. The high selectivity membrane will be used for their best performance. By using SEM, the membrane pore showed change in size with the percent concentration of PDMS coating the membrane. The pore size on membrane reduced with the increasing percent concentration of PDMS solution. It shown that the PDMS repaired the defect on membrane and close the pin-holes the defect the membrane performance. Other than that, permeability of membrane decrease with percent of concentration PDMS coating solution. It show that the fouling on membrane is decrease when the percent of PDMS coating solution increase.

5.2 Recommendations

From the experiment done, the recommendation that can be improved for future work :

1. The conventional method for casting can be change with other method because this method can affect the thickness of membrane with different pressure applied on dope solution while running the casting.

2. The temperature of water bath while doing casting process must be control by puting the temperature controller to make sure the temperature is not to hot to avoid the membrane layer wrinkled and curled because of the heat.

3. The buble flowmeter can be replaced with the burrete to take the reading time of moving gas in while doing permeation test to get more accurate result for calculation of permeability and selectivity.

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APPENDICES

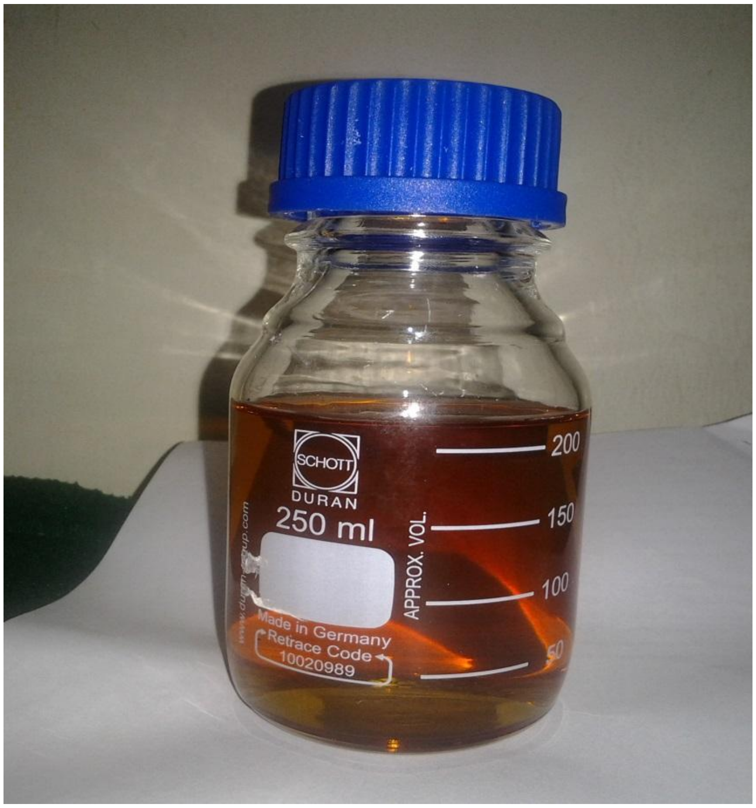

Figure A.1 Dope Solution

Figure A.2 Membrane Casting Process

Figure A.3 Removing Bubbles In Ultrasonic Water bath

Figure A.4 Dip-Coating Process

Figure A.5 Fourier Transform Infrared Radiation (FTIR)

Figure A.6 Scanning Electron Microscopic (SEM)

Figure A.7 Samples Coated With Layer of Gold For SEM

Figure A.8 Gas Permeation Test

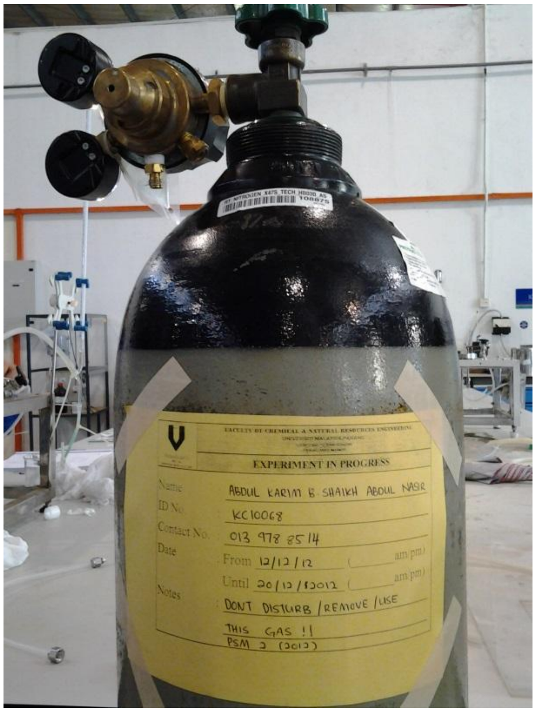

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Figure A.9 Nitrogen Gas Cylinder

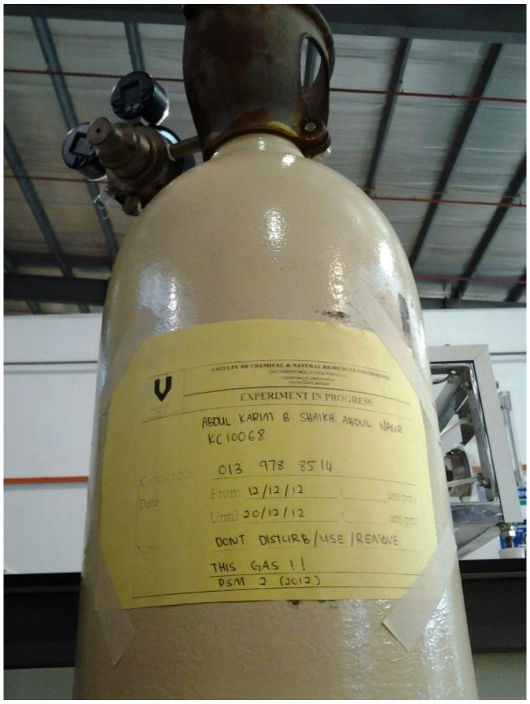

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Figure A.10 Carbon Dioxide Gas Cylinder