PERFORMANCE OF POLY(VINYL ALCOHOL) ASYMMETRIC MEMBRANE INCORPORATED WITH GRAPHENE OXIDE FOR PERVAPORATION DEHYDRATION OF ETHANOL AQUEOUS SOLUTION

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by

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LIST OF SYMBOLS

Symbol	**Description**	**Unit**
A	Membrane active area	m2
wt%	Mass fraction in percentage	%
T	Temperature	℃
P	Pressure	mm Hg
t	Time	hr or min
W_d	Dry weight prior emission	g
W_s	Swollen weight after immersion	g
J	Total permeate flux	$g/m^2.h$
J_w	Water permeate flux	$g/m^2.h$
α	Separation factor	-
PSI	Pervaporation separation index	$g/m^2.h$

LIST OF ABBREVIATIONS

PVA	Poly(vinyl alcohol)
PVDF	Polyvinylidene fluoride
GO	Graphene oxide
MMM	Mixed matrix membrane
SEM	Scanning electron microscopy
TEM	Transmission electron microscope
DMF	N,N-dimethylformamide
DMSO	N,N-dimethylsulfoxide
DMAc	N,N-dimethylacetamide
PBO	Polybenzoxazole
PBOZ	Polybenzoxazinone
PBI	Polybenzimidazole
2D	2-dimensional
AAO	Anodic aluminium oxide
EDA	Ethane diamine
PSI	Pervaporation separation index
hr	Hour (Unit for time)
min	Minute (Unit for time)
g	Gram (Unit for mass)
mg	Milligram (Unit for mass)
ml	Milliliter (Unit for volume)
cm	Centimeter (Unit for length)
nm	Nanometer (Unit for length)

w	Water
e	Ethanol
p	Permeate
f	Feed

PRESTASI MEMBRAN ASSIMETRI POLI(VINIL ALKOHOL) YANG DIGABUNGKAN GRAPHENE OKSIDA UNTUK PROSES PENYEJATTELAPAN DEHIDRASI LARUTAN AKUES ETANOL

ABSTRAK

Menggunakan kaedah penyongsangan fasa dan penuangan larutan, membrane polivinil alkohol/polyvinylidene fluorida (PVA/PVDF) yang digabungkan dengan graphene oksida (GO) telah disediakan dan dibandingkan dengan membran PVA/PVDF yang tulen. Membran yang terhasil telah dicirikan dengan menggunakan pengimbasan elektron mikroskopi (SEM), ujian tegangan mekanikal, dan ujian darjah pengembangan. Prestasi membran tersebut telah dikaji terhadap proses penyejattelapan dalam dehidrasi 95wt% larutan akueus etanol. Hasil kajian menunjukkan bahawa darjah pengampulan GO ke dalam membran PVA/PVDF meningkatkan jumlah fluks yang meresap dengan 296.6 g/m^2.h berbanding 257.5 g/m^2.h yang dicapai oleh membran PVA/PVDF tulen. Kajian lanjut mengenai sampel telapan telah menunjukkan bahawa sampel yang menelap melalui GO-PVA/PVDF membran telah mencapai faktor pemisahan yang lebih tinggi iaitu 557.6, lebih kurang dua kali ganda yang diperolehi oleh membran PVA/PVDF tulen dengan 249.5 sahaja. Oleh itu, keputusan ini membawa kepada indeks pemisahan penyejattelapan (PSI) yang lebih tinggi dicapai oleh membrane GO-PVA/PVDF berbanding membran PVA/PVDF tulen dengan masing masing 159,925 g/m^2.h dan 59,690 g/m^2.h. Kesimpulannya, keputusan ini memanifestasi penggabungan GO ke dalam membran dalam mencapai keseimbangan diantara jumlah penelapan fluks dan factor pemisahan, sekali gus meningkatkan prestasi membran terhadap proses penyejattelapan.

PERFORMANCE OF POLY (VINYL ALCOHOL) ASYMMETRIC MEMBRANE INCORPORATED WITH GRAPHENE OXIDE FOR PERVAPORATION DEHYDRATION OF ETHANOL AQUEOUS SOLUTION

ABSTRACT

Using phase inversion and solution casting method, polyvinyl alcohol/polyvinylidene fluoride (PVA/PVDF) incorporated with graphene oxide (GO) membrane was prepared and compared with pure PVA/PVDF membranes. The resultant membranes were characterized by using scanning electron microscopy (SEM), mechanical tensile test, and degree of swelling. The resultant membranes performance were studied on the pervaporation of dehydration of 95wt% ethanol aqueous solution. The results showed that the incorporation of GO sheets onto the PVA/PVDF membrane increased the total permeate flux with 296.6 g/m^2.h as compared to 257.5 g/m^2.h achieved by pure PVA/PVDF membrane. Further characterization on the permeate samples showed that the permeate through GO-PVA/PVDF membrane exhibited higher separation factor of 557.6, approximate doubled the value obtained by pure PVA/PVDF membrane with 249.5 only. Thus, this lead to higher pervaporation separation index obtained by GO-PVA/PVDF membrane as compared pure PVA/PVDF membrane with 159,925 g/m^2.h and 59,690 g/m^2.h respectively. In conclusion, the incorporation of GO sheets onto the membrane capable to overcome the trade-off between the total permeation flux and separation factor, thus enhance the overall performance of the pervaporation process.

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

1.1.1 History of Pervaporation Process and Its Application

Distillation column is the most virtual operation unit which most of the plant use it to separate the component from a mixture. It is the most common liquid-liquid separation unit and carried out either in batch or continuous process. Distillation column operate based on the relative volatility and difference in boiling points of the component in the mixture. The feed of the mixture is heat up to a temperature where the light key may vaporize, leaving less volatile component as liquid and produce as bottom product. However, conventional distillation have a difficulty in separating close boiling point and azeotropic mixture (Peng et al., 2007). Traditional azeotropic distillation and extractive distillation are two techniques carrying out this separation. These techniques have many problems such as process complexity, large equipment investment, and high energy consumption.

The vision of a green and sustainable future has spurred the interests around the world in advancing the current separation technologies to conserve energy, as well as to achieve waste minimization and zero discharge. Process integration and recovery of valuable products from waste streams are considered of paramount importance to accomplish this vision. In this regard, membrane technologies may serve as promising alternatives over conventional separation processes in the industries. Membrane-based separation processes are emerging and advanced separation technologies that maybe widely applied in water, energy, food, chemical and healthcare sectors (Baker, 2012).

On the other hand, pervaporation provides an alternative solution to solve those problems. The pervaporation process can be traced to the 1910s when Kober defined the term of ‘per-vaporation’ from the abbreviation of ‘permeation’ and ‘evaporation’ after observing the selective permeation of water through the collodion and parchment membrane (Farber, 1935). Pervaporation is a membrane-based separation technology, provides competitive advantages over conventional separation techniques such as distillation and absorption processes in separating azeotropic mixtures, thermally sensitive compounds and organic–organic mixtures, as well as in removing dilute organic compounds from wastewater. Pervaporation which come from the combination of permeation and vaporization, is a method to separate a mixtures of liquid by partial vaporization through selective porous membrane.

In pervaporation, liquid feed works at relatively low pressure, low temperature, low energy consumption and low operating cost in running the process (Rachipudi et al., 2013). The separation of liquid mixture include the phase change where liquid mixture enter the feed and permeate as vapor through the partially vacuum condition at the bottom part of the membrane as shown in Figure 1.1. The significant gradient of high partial vapor pressure at the feed to the low partial pressure at permeate act as the driving force of the desired component to permeate across through the non-porous membrane, and let the component to evaporate after passing through the membrane (Qiu et al., 2010).

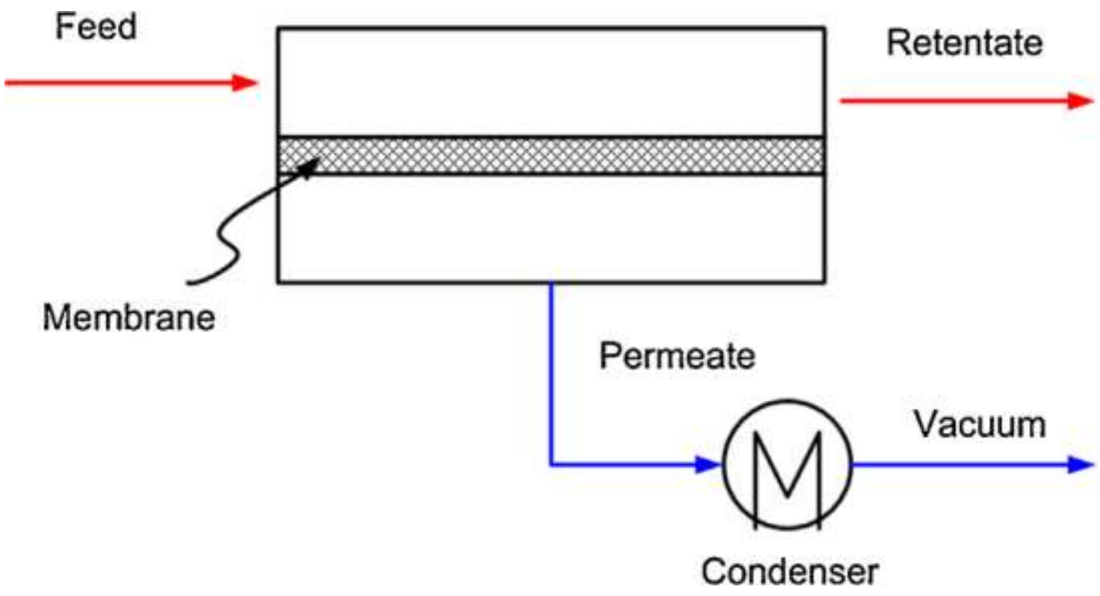

Figure 1.2: Schematic of pervaporation apparatus

1.1.2 Type of membrane used in pervaporation process

In determining the performance of the pervaporation, the selection of the membrane plays an important role. Polymer membrane prepared by phase inversion technique often used for the organic component recovery and can be classify as hydrophilic and hydrophobic. Hydrophilic membrane has the strong affinity towards water which preferentially to absorb water molecules from the major organic component. On the other hand, hydrophobic membrane plays the role of absorbing the organic molecules. The hydrophobic characteristic is also known as water repellent, prohibiting the permeability of water while the hydrophilic characteristics or water loving property encourages water spreading across the membrane.

For the separation of water-ethanol mixture, both type of membrane are suitable to be used depending on the feed concentration. The desired component to be permeated by the membrane should not be greater than 10wt. % of the component in the mixture.

Unfortunately, most of the polymeric membrane would lead to the significant degree of swelling in aqueous solution, which reduce the permeability as well as mechanical strength declined (Sajjan et al., 2013).

At the beginning of 20th century, graphene has become intensive study due to its excellent physical, mechanical and chemical properties. Graphene has found out to be the most attractive material because its nanometer size was about 10,000 times smaller than a human hair. Incorporation of these nano-size particles in known polymer membrane has come out to be successful technology, which improve the membrane properties. This include improvement in both membrane forming properties of a polymer and physical-chemical stability of inorganic (Penkova et al., 2009).

1.2 Problem Statement

Pervaporation is found to become an alternative pathway in solving the close boiling point and azeotrope mixture in performance of distillation column. The selection of the correct membrane becomes an important part to achieve high performances of the process.

PVA has proved to be an ideal material for membranes used in separating organic mixtures because of its polar, hydrophilic and good membrane-forming properties (Pandey et al., 2003). However, pure PVA membrane is susceptible to swell. Because of its hydrophilic nature, PVA need to be modified to reduce its swelling in water for aqueous based system applications. Therefore, various types of fillers are usually added to enhance the performance of the membrane while increasing the mechanical strength.

Recently, two-dimensional carbon-based materials such as graphene and its derivative GO, have brought new opportunities for fabricating mixed matrix membrane. GO has an excellent mechanical strength (Lee et al., 2008), high electrical conductivity (Jung et al., 2008), superior thermal conductivity (Balandin et al., 2008) and other fantastic properties, thus attracting considerable attention in various fields of research. Because GO membranes can be produced inexpensively on a large scale, they have great potential in various application including in the development of PVA membrane as additives. Besides, the PVDF support layer also was study as it has been recorded to contribute to the high performance of the membrane by liable providing porous support to GO-PVA plugging (Zhan et al., 2010).

Through all the research, the common problem for the pervaporation is the trade-off in between the total flux and separation factor, since GO has an excellent properties as mentioned above. It is postulated that when GO is adding into the PVA polymer matrix to produce mixed matrix membrane supported by PVDF would contribute to the enhancement in both the total permeation flux and separation factor. This is the reason why this project focused on the fabrication and characterization of the GO-PVA/PVDF mixed matrix membrane for dehydration of ethanol solution via pervaporation.

1.3 Research objectives

The objectives of this study is:

I. To synthesize of the PVA/PVDF and GO-PVA/PVDF mixed matrix membranes.

II. To characterize of the resultant mixed matrix membranes via degree of swelling, tensile test and scanning electron microscope.

III. To study the performance of the resultant mixed matrix membranes for pervaporation dehydration of the ethanol-water mixture.

CHAPTER 2

LITERATURE REVIEW

2.1 Fundamentals of the pervaporation process.

A fundamental understanding of the mass transfer phenomena is vital for researchers to identify the preferred membrane materials and design the desired membrane structure and configuration. A summary of the main concepts and terminology applied to pervaporation has been published by Böddeker (Böddeker, 1990). The permeation of a component through a pervaporation membrane can be explained from both thermodynamic and kinetic perspectives. Thermodynamically, it involves the solubility of the component into the membrane material, while kinetically it engages the diffusion of the penetrant across the membrane. The coupled transport among different penetrants also affects each individual permeation. In addition, these penetrants may swell up the membrane, change its microscopic structure and significantly enhance diffusion rates as compared with those through a dry membrane (Mulder and Smolders, 1984).

On the contrary, the diffusion selectivity is greatly dependent on the size and shape of the permeating components, the mobility of polymer chains and the interstitial space among them, the interactions among the permeating components as well as between the components and the membrane material (Mulder, 2012). As a result, the pervaporation membranes can be tailored into either an organic-selective (organics preferentially permeate through the membranes) or a water-selective (water preferentially permeates through the membranes) by means of material selection and morphological engineering during the membrane fabrication process.

The performance of a pervaporation membrane is generally evaluated according to its productivity and capability to separate the components from the feed mixture. This performance can be expressed by total permeation flux and separation factor through an experiment.

2.2 Transport model across membranes.

A proper understanding of the membrane separation mechanism may provide direct information on the research and development of an appropriate membrane. The solution-diffusion model is accepted by the majority of membrane researchers (Feng and Huang, 1997) as the mass transport model in pervaporation. According to this mechanism, pervaporation consists of three consecutive steps:

(i) Sorption of the permeant from the feed liquid to the membrane.

(ii) Diffusion of the permeant in the membrane.

(iii) Desorption of the permeant to the vapor phase on the downstream side of the membrane.

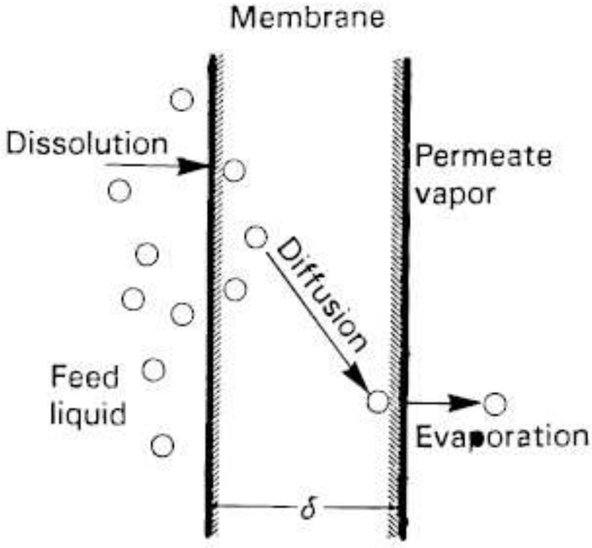

Figure 2.1: Diagram of solution-diffusion transport model (Feng and Huang, 1997)

In general, solubility and diffusivity are concentration dependent. Both of these contribute to the selectivity measure of the membrane. A number of mathematical equations for mass transport have been formulated on the basis of Fick’s diffusion equation using different empirical expressions of concentration dependence of solubility and/or diffusivity. However, those equations cannot be taken for granted unless they are used within the experimentally established range for which the relationships expressed for diffusion and thermodynamic equilibrium are applicable.

2.3 Recent membrane development in pervaporation

Early development of pervaporation membranes is mainly for dehydration of organic solvents. It was mainly using hydrophilic polymers such as PVA, cellulose, chitosan, alginate, etc. that would enhance the solubility selectivity of water toward the membrane through hydrogen bonding interactions (Bolto et al., 2009). However, these membranes are susceptible to swell, thus crosslinking processes are generally employed to stabilize the membranes.

Also in recent years, research on pervaporation membranes for solvent dehydration applications has shifted toward the exploration of new chemically and thermally stable materials to dehydrate aggressive solvents at elevated operating temperatures. In this regards, polymer with stiff and rigid chains have been considered as the promising candidate in this application. The glassy characteristic of these polymers could improve the diffusivity selectivity of the membranes during the dehydration process as the water molecule is smaller than most of the organic molecules (Jiang et al., 2009).

Meanwhile, the perfluoropolymer-based membranes have been studied by several research groups for dehydration of butanol, isopropanol, ethanol, N,N-dimethylformamide (DMF), N,N-dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMAc) and hydrogen peroxide (H_2O_2). Despite of their intrinsic hydrophobicity, the size exclusion mechanism has been proposed for these amorphous perfluoropolymer membranes as the dominant separation mechanism in dehydration applications (Smuleac et al., 2010).

On the other hand, aromatic polymers such as polybenzoxazole (PBO), polybenzoxazinone (PBOZ) and polybenzimidazole (PBI) have also been reported to show a great potential in solvent dehydration because of their excellent chemical and thermal resistance. Both PBO and PBOZ membranes were synthesized through the thermal rearrangement process from their respective precursors and were found to be applicable in dehydration of alcohols (Ong et al., 2012). Meanwhile, PBI-based pervaporation membranes were pioneered by Chung and co-workers (Wang et al., 2010). They have fabricated PBI membranes in the forms of flatsheet and hollow fiber configurations for dehydration of various solvents such as alcohols, glycols and acetone. In addition, PBI was employed as a filler to improve the performance of Matrimid (a soluble thermoplastic polyimide) membranes through polymer blending (Chung et al., 2006).

It is interesting to note that since the pioneering work on graphene from Geim and co-workers (Novoselov et al., 2004), it has attracted a great attention in various research fields because of its unique mechanical, electrical and thermal properties (Rao et al., 2009). Its oxidized form, graphene oxide (GO), is even more attractive to researchers owing to its abundant oxygen-containing groups (Dreyer et al., 2010), which provides a good dispersion of its particles in water and an ability of chemically modifying it. Therefore, a variety of GO applications have been explored such as biosensing, photocatalysis, electronics and optoelectronics and others. However, graphene/GO based membranes for separation applications are a relatively new topic, especially for their applications in pervaporation.

2.4 GO sheets in PVA membrane

Recent advances in the synthesis and characterization of graphene based 2D nanomaterials have brought new ideas for the design and fabrication of membranes with special structures as well as increased permeability, selectivity and resistance to fouling. As an important derivative and intermediate of graphene, graphene oxide (GO) does not only have a lot of characters of graphene, but an improvement to graphene because of the abundant oxygenic functional groups existed on the surface of graphene oxide. GO can be considered to be the oxidized form of graphene and was first reported in 1859 (Brodie, 1859). The preparation method was then improved by Hummers (Humers and Offeman, 1958) and Staudenmaier (Tian et al., 2014). The conventional method for preparing GO is that natural graphite flakes are oxidized by using strong oxidants such as $KMnO_4$, $KClO_3$, or $NaNO_2$ in the presence of a strong acid, such as concentrated sulfuric acid or nitric acid. GO sheets possess exceptionally good mechanical properties and flexibility. Hydrogen bonding interactions between GO nanosheets enable the films to be highly stable in water once dried (Paul, 2012).

A lot of works have been carried out to obtain high performance membranes by combining GO and common polymeric materials. Besides, membranes made with pure GO were also reported, which exhibited a lot of special properties for separation due to their 2D channels, hydrophilic surface as well as the defects on GO sheets. Among the special properties of GO membranes, the priority permeability for water attracted a lot of interests. It was found that GO sheets consist of hydroxyl, epoxy, and other hydrophilic functional groups on their openings and edges. Combined with the layered structure formed by GO laminates, these hydrophilic functional groups made GO membranes even completely impermeable to liquids, vapors, and gases, including helium (as the smallest particle), but allow unimpeded permeation of water. Similar GO membranes could be fabricated for the dehydration of organic solvents due to the high selectivity of water.

The vacuum self-assembly method was used to fabricate GO composite membrane for pervaporation dehydration of butanol (Chen et al., 2015). The GO sheets were prepared using the modified Hummers method and underwent centrifugal pre-treatment to remove large size GO sheets, thus improving separation properties. By using anodic aluminium oxide (AAO) macro porous membrane as a substrate, the composite membrane showed a high separation performance for the butanol aqueous solution. The separation factor of 230 and permeate flux of 3100 g/m^{2}h were reported when 10% of water in butanol solution was used as feed solution at 50°C. However, there was no direct comparison between a pure AAO membrane and AAO membrane with GO sheets as filler. Furthermore, the GO membrane was claimed to show good stability even after long period but the test was only carried out for 1800 min, which is considered short. Due to that, the ability of the composite membrane to be used for long period which is the drawback of vacuum self-assembly technique, still remained questionable.

Understanding the advantage of pressure-assisted self-assembly technique, numerous study were done to utilize this technique to incorporate GO sheets into pervaporation membrane. In fact, this technique has been tested to fabricate freestanding GO for the dehydration of alcohol recently (Tang et al., 2014) The unique part about this research is that the GO thin films were not supported by any support layer such as polysulfone, owing the description free-standing. Based on the literature, the optimum ultrafiltration pressure was at 5 bar, at which the film showed the most organized packing. In terms of pervaporation performance, a separation factor of 227 was achieved when 85wt% ethanol aqueous solution was used at 24°C.

On top of that, there was also another article that utilized pressure driven filtration to deposit GO sheets on porous Al_2O_3 tube (Li et al., 2014). As compared to the previous article, porous alumina tubes were used as a support layer to increase the stability of the membrane. Since the alumina surface was negatively charged, the GO sheets must first be treated with ethane diamine (EDA) to reverse the surface charge to enhance the interaction between both layers. It was reported that the separation for larger organic molecules such as isopropanol and ethyl acetate was better as compared to the separation of smaller molecules such as ethanol.

2.5 Phase Inversion and Solution Casting

There are many methods to prepare the membrane for the lab-scale research of pervaporation. The most widely used to form the polymer based membrane is called phase inversion. Membranes for phase inversion can be synthesized from any polymer-solvent mixture that forms a homogeneous solution under certain conditions of temperature and composition, but separates into two phases when these conditions are changed. For example, phase inversion can be induced by evaporation of a volatile solvent from a homogeneous polymer solution, or by cooling a casting solution which is homogeneous only at elevated temperatures. There are numerous processes for the fabrication of integrally skinned asymmetric membranes from a homogeneous dope such as PVDF.

The three main processes are:

(i) Dry phase inversion

(ii) Wet phase inversion

(iii) Dry/wet inversion

Referring to Figure 2.2, the difference between the dry and wet inversion is whether the outlet of the spinneret or casting knife is submerged directly in a non-solvent coagulant. (Nasir et al., 2013)

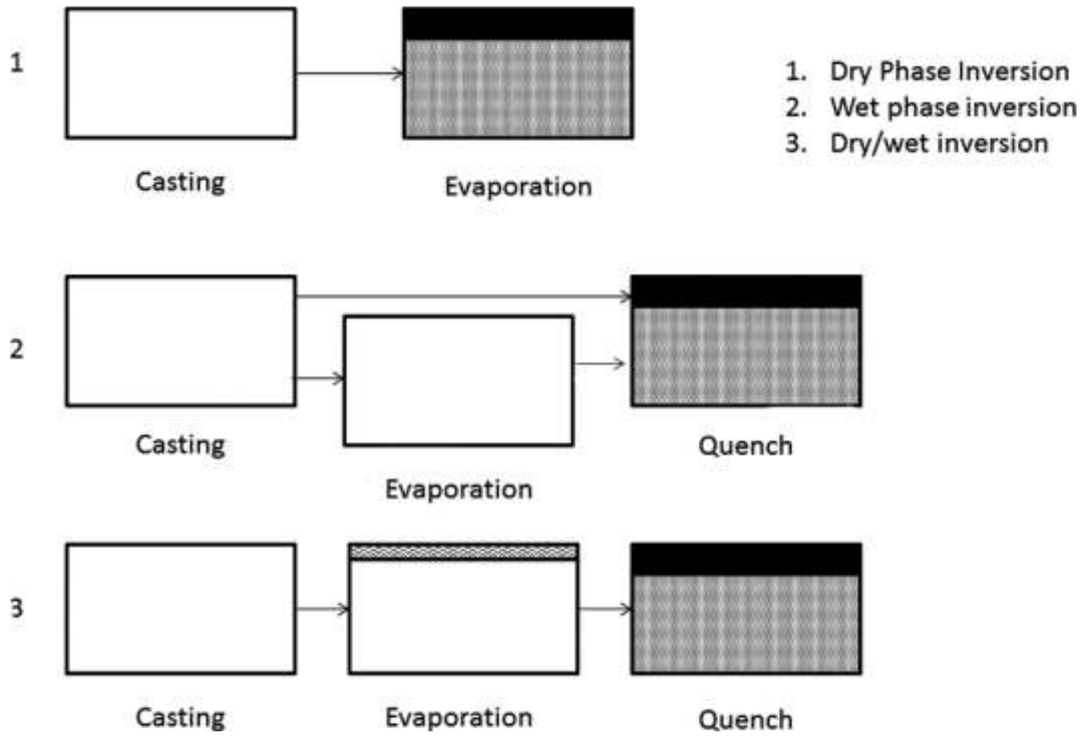

Figure 2.2: Type of phase inversion method (Nasir et al., 2013)

Moving on to the next step of producing the dense layer of the membrane, solution casting method becoming the most popular method. Solution casting method is appropriate for small-scale preparation of membrane samples. The polymer solution is spread on a flat glass plate with a casting knife. This knife consists of a steel blade placed on two runners. The thin film forms the membrane that has been left after the solvent evaporation (Baker, 2000). This method is simple in operation and cheap and the final membrane is crystalline and isotropic.

Mahajan et al. (Mahajan et al., 2002) tried to solve the problem of void creation between polymer and molecular sieve phase in conventional solution-casting methods for the formation of MMMs and developed the membrane in two steps under high temperature. Other studies were carried out for making casting solutions for MMM fabrication. These solutions were prepared by adding first a molecular sieve to the solvent to obtain a slurry, then a polymer powder was mixed into this slurry.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The materials and chemicals used to conduct the experiments are shown below.

Table 3.1: List of the materials and chemicals with their specification and supplier

Material	Specification	Supplier
PVDF	MW ~180,000 by GPC	Sigma Aldrich
DMF	99.8% purity	Sigma Aldrich
PVA	96% hydrolyzed	Acros Organics
GO powder	4-10% edge oxidised 15-20 sheets	Sigma Aldrich
Ethanol	96% purity	Fisher Scientific (M) Sdn Bhd
Deionized water	N/A	Obtained in the lab
Distilled water	N/A	Obtained in the lab

3.2 Membrane Preparation

In this study, the membrane was prepared through phase inversion method. There were 2 type of membrane to be prepared. The first membrane is the pure PVA supported by PVDF layer (PVA/PVDF) while second membrane is the PVA incorporated with GO supported by PVDF layer (GO-PVA/PVDF). The schematic diagram of the membrane preparation is shown in Figure 3.1.

3.2.1 Preparation of PVDF layer

The PVDF solution was prepared by dissolving 15g of PVDF powder into 85g of DMF solution to form 15wt% PVDF solution. The solution was then stirred vigorously using a hot plate stirrer for an overnight at the 80^{O}C to ensure the formation of homogenous PVDF solution.

After formed a homogenous solution, it was filtered and the solution was casted onto a glass plate which was covered by non-woven cloth, and quickly immersed into a water bath for 15 minutes. It was then allowed to dry at room temperature. The completely dried membrane was subsequently peeled off into 47 mm square.

3.2.2 Preparation of pure PVA membrane

The PVA membrane was prepared by using solvent casting technique. The PVA solution was prepared by dissolving 5g of PVA pellets into 95g of water. In order to facilitate the dissolution, the solution was kept at 90 °C under constant stirring to form a homogeneous solution for at least 6 hours.

Then the PVA solution were casted by spreading 5ml of the solution onto a petri dish covered with the previous prepared PVDF layer. The casted solution was allowed to dry under ambient condition for 72 hours. The membrane was then peeled off and stored in an enclosed bag.

3.2.3 Preparation of GO-PVA membrane

The homogenous PVA solution prepared from Section 3.2.2 was used for the following step. GO powder was added according to the desired mass ratio. In order to produce PVA solution with 0.01wt. % of GO, 2mg of GO powder was added into 19.98g of PVA solution. The mixture was then sonicated using a tip sonicator (UP200S ultrasonic processor by Heilscher Ultrasound Technology) for 10 minutes until a homogenous solution was formed. Later, the solution was capped or covered with parafilm and stirred overnight using a magnetic stirrer. Upon stirring, the solution was then sonicated again for 5 minutes prior to solution casting. Finally, the GO-PVA solution were casted into the PVDF layer using the same technique as Section 3.2.2.

The overall of the schematic of the membrane preparation used in this project is summarized in Figure 3.1.

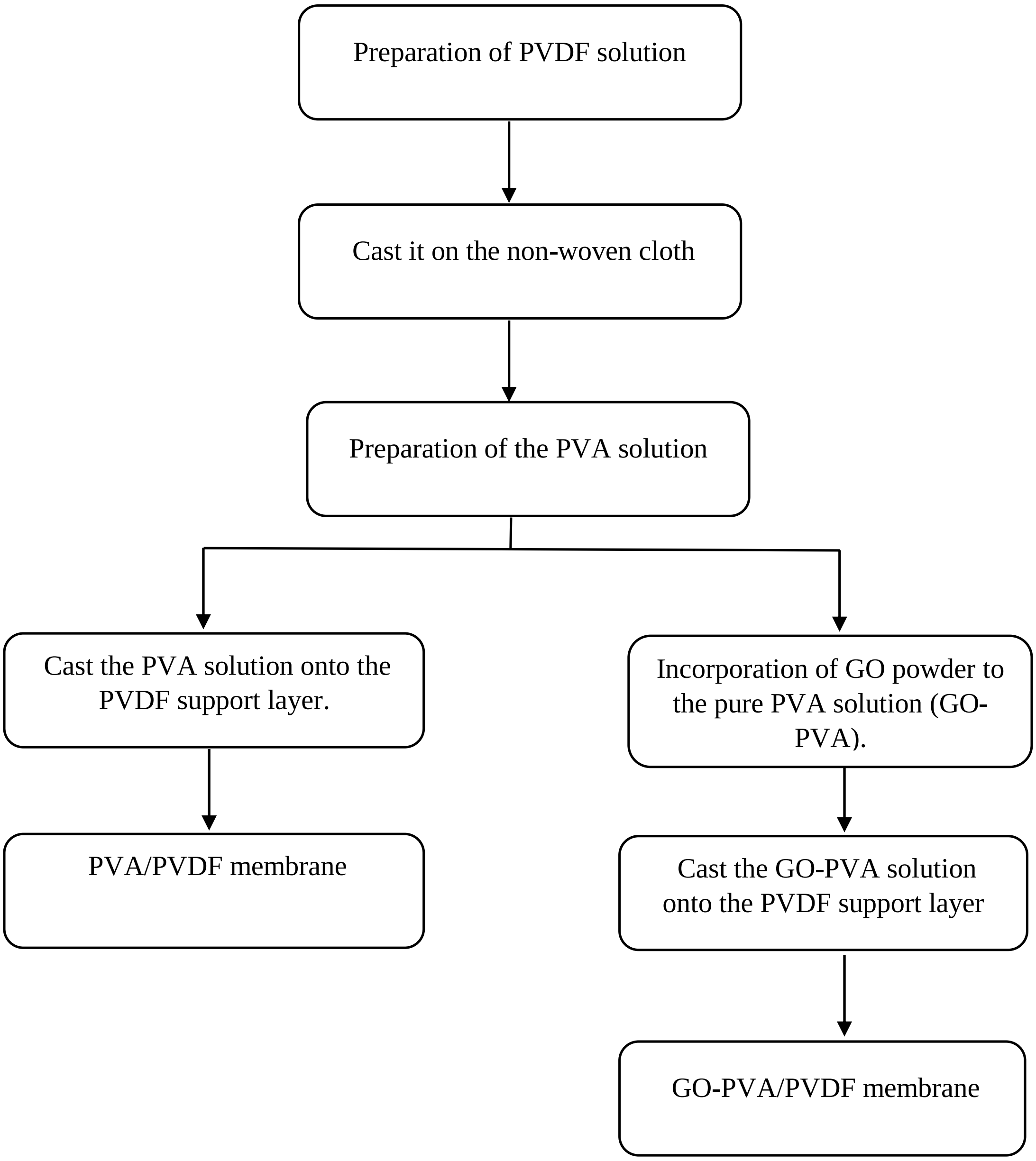

Figure 3.1: The schematic diagram of the membranes preparation

3.3 Membrane Characterization

Before the membranes could undergo the pervaporation process, some characterization need to be to study it properties. The characterizations were done by using scanning electron microscopy (SEM), degree of swelling test and tensile test.

3.3.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a method to study for the surface morphology of the membrane. The membranes were vacuum dried and coated with a conductive layer of sputed gold. The surface morphology of the membranes were visualized using a Variable Pressure Field Emission Scanning Electron Microscope (VPFESEM) at School of Materials and Mineral Resources Engineering, USM.

3.3.2 Tensile Test

The membranes were cut into dumbbell shape as shown in Figure 3.2 with gauge length of 12 mm. The test was carried out using mounted universal testing machine with stretching speed is set at constant rate of 50 mm/min. 6 samples of both GO-PVA/PVDF and PVA/PVDF membranes were tested and the data were recorded.

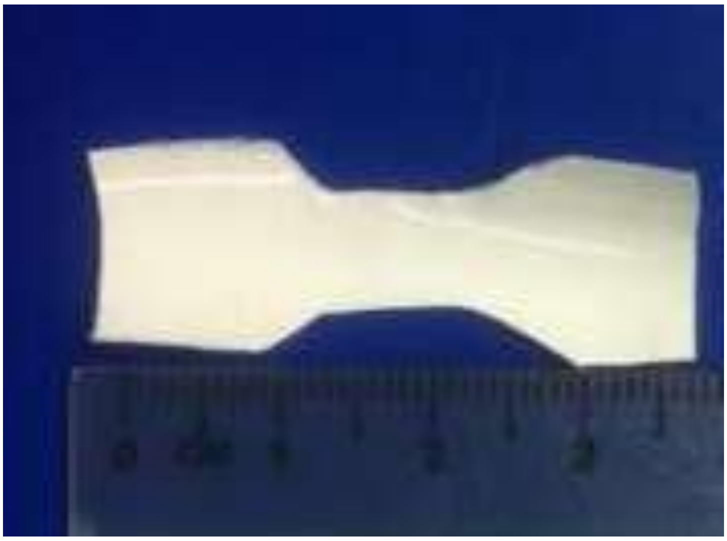

Figure 3.2: Samples of dumbbell shape of cut membranes.

3.3.3 Degree of Swelling

If the membrane is hydrophilic, swelling could happen due to the interaction between the membrane and contacting liquid. Thus, the degree of swelling could be tested by comparing the weight of dry membrane and swollen membrane. Firstly, the prepared membranes were cut into same dimension and were weighted using an electronic balance. The membranes were than immersed into 3 different solutions which are pure water, pure ethanol and 95wt% ethanol solution for 48 hours to enable the membrane sample to reach equilibrium. After that, the membrane were removed from the solutions and carefully weighted to record the swollen weight. The degree of swelling of each of the membranes were calculated by:

$$Degree\ of\ swelling, S = \frac{W_s - W_d}{W_d}\ x\ 100\% \qquad (3.1)$$

Where W_d = Dry weight of the membrane (g)

W_s = Swollen weight of the membrane (g)

3.4 Pervaporation Process

The feed solution consists of 10wt.% of deionized water and 90wt.% of ethanol solvent. The process conditions such as 30℃ and 5 mmHg downstream pressure of the pervaporation study were kept constant throughout the experiment. 250 ml of the feed solution was fed into the feed tank and place onto the magnetic stirrer. Feed mixture was circulated using perisaltic pump from feed tank to the permeation cell, and the retentate from permeation cell was recycled to the feed tank by perisaltic pump. The driving force of the separation was created using vacuum pump in order to generate the difference of the pressure between the top and the bottom sides of the membrane. The permeate that passes through the membrane was collected through cold trap immersed in the liquid nitrogen. Downstream pressure was kept at 5 mmHg by vacuum pump. The system was stabilized for 4 hours before the collection of samples.

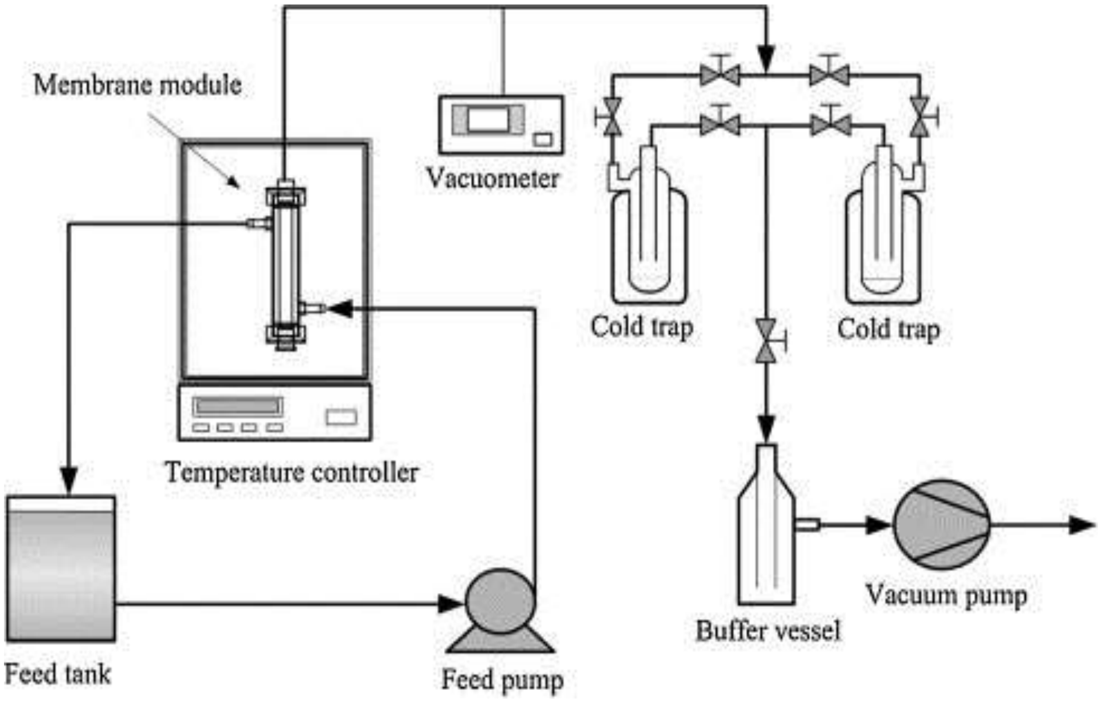

Figure 3.3: The schematic of pervaporation apparatus

3.4.1 Flux, separating factor and pervaporation separation index

The water content of the permeate was determined by using Karl Fischer Moisture Titrator (MKS-500).

During the analysis, about 3 μg sample was taken from the collected permeate by using a syringe, weighed, then injected into the titration medium. The injection process have to be done quickly to prevent any moisture of surrounding enter the moisture titrator and affecting the result. Each sample was analyzed thrice to reduce the tolerance of the analysis and get the average value.

On the other hand, the total permeation flux of the membrane could be calculated by using the equations below:

$$J = \frac{w_p}{A.t} \tag{3.2}$$

where:

J = flux (g/m^2 h)

W_p = permeate weight (g)

A = cross sectional membrane area (m^2)

t = permeation time (hr)

The mass of water permeate was obtained from the percentage of permeate water content from the overall permeate. Meanwhile, the cross sectional area of the membrane was calculated from the membrane where it effective area was around 8.6 cm^2 and the time taken for the pervaporation experiment was 4 hours.

The separation factor can be calculated using equations below.

$$\alpha = \frac{Y_i/Y_j}{X_i/X_j} \tag{3.3}$$

where

α = separation factor

Y_i = weight fraction of component i in the permeate

Y_j = weight fraction of component j in the permeate

X_i = weight fraction of component i in the feed

X_j = weight fraction of component j in the feed

Another parameter is pervaporation separation index (PSI). PSI was used to determine the overall performance of the membrane and it can be calculated as below:

$$PSI = J_w \cdot \alpha \tag{3.4}$$

where:

PSI = pervaporation separation index ($g/m^2.h$)

A = separation factor

Jw = flux of water through the membrane ($g/m^2.h$)