

**FABRICATION AND CHARACTERIZATION OF
POLYVINYL ALCOHOL ASYMMETRIC MEMBRANE
SUPPORTED BY POLYVINYLIDENE FLUORIDE FOR
DEHYDRATION OF ETHANOL VIA PERVAPORATION**

TAN CHEE YEANG

UNIVERSITI SAINS MALAYSIA

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DEHYDRATION OF ETHANOL VIA PERVAPORATION**

by

TAN CHEE YEANG

**Thesis submitted in partial fulfilment of the requirement
for the degree of Bachelor of Chemical Engineering**

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LIST OF SYMBOLS

Symbol	Description	Unit
A	Membrane active area	m ²
c	Mass fraction	-
wt. %	Mass fraction in percentage	%
T	Temperature	mm Hg
t	Time	hr or min
W _d	Dry weight prior immersion	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
Q	Mass of permeate	g

LIST OF ABBREVIATIONS

BP	Bucky paper
CNT	Carbon nanotubes
DMF	Dimethylformamide
PAA	Poly (acrylic acid)
PAN	Polyacrylonitrile
PVA	Poly(vinyl alcohol)
PVDF	Polyvinylidene Fluoride
MWCNT	Multiwalls Carbon nanotubes
PSI	Pervaporation separation index
MMM	Mixed matrix membrane
MOF	Metal-organic frameworks
SEM	Scanning electron microscope
SILM	Supported ionic liquid membrane
TBT	Tetrabutyl titanate
w	Water
e	Ethanol
p	Permeate
f	Feed

PENGHASILAN DAN PENCIRIAN MEMBRAN ASIMETRI POLI(VINIL ALKOHOL) DITANGGUNG OLEH POLYVINYLIDENE FLUORIDA UNTUK PROSES DEHIDRASI BAGI ETHANOL MELALUI PENYAHHDIRATAN

ABSTRAK

Membran asimetri poli(vinil alcohol)-tiub nano karbon dinding berlapis/polyvinylidene fluorida/fabrik tanpa tenun (PVA-MWCNT/PVDF/Non-woven) telah dihasilkan untuk proses dehidrasi bagi larutan ethanol (95 wt. %) dan air (5 wt. %) pada 30 °C melalui penyahhidratan. Tiub nano karbon dinding berlapis yang telah difungsikan dengan kumpulan karboksil (-COOH) telah ditambah ke dalam membran poli(vinil alkohol) sebagai pengisi nano untuk meningkatkan kebolehlarutan dan daya resap antara molekul air dan membran. Lapisan berliang polyvinylidene fluorida telah digunakan sebagai lapisan sokongan bagi membran poli(vinil alkohol) untuk meningkatkan kekuatan mekanik membran. Polimer poli(vinil alkohol) telah ditetapkan di dalam berliang lapisan polyvinylidene fluorida untuk meningkatkan keutuhan struktur membrane melalui proses penurasan. Keputusan ujian tegangan menunjukkan bahawa kekuatan mekanik membran PVA-MWCNT/PVDF/Non-woven telah ditingkatkan. Regang tegangan membran PVA-MWCNT/PVDF/Non-woven telah dikurangkan sebanyak 14 % manakala tegangan tarik ultimat telah ditingkatkan sebanyak 18 %. Apabila membran PVA-MWCNT/PVDF/Non-woven diuji dengan larutan ethanol (95 wt. %) dan air (5 wt. %) dalam ujian pengampulan, sebanyak 15 % kekurangan dalam darjah pengampulan telah dicatat. Dari segi proses penyahhidratan pula, Tiub nano karbon dinding berlapis telah meningkatkan kadar pemisahan sebanyak 4 kali ganda. Namun begitu, fluks telap bagi

membran PVA-MWCNT/PVDF/Non-woven merupakan 10 % bagi membran PVA/PVDF/Non-woven sahaja.

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ABSTRACT

The asymmetric PVA-MWCNT/PVDF/Non-woven membrane is fabricated for dehydration of 95 wt. % aqueous ethanol solution at 30 °C via pervaporation. The functionalized MWCNT containing carboxyl groups (-COOH) functional groups are incorporated in the PVA membrane as hydrophilic nanofillers to enhance the permeate flux and separation factor by increasing the solubility and diffusivity between water molecules and the pervaporation membrane. Besides, the porous PVDF layer is employed as the support layer for the PVA membrane, to increase the mechanical strength of pervaporation membrane. To further enhance the structural integrity of the membrane, the PVA polymer is immobilized into the porous sites of PVDF porous layer via vacuum filtration process. The results obtained from mechanical tensile test showed that the effectiveness of these modifications in improving the mechanical strength. In the presence of functionalized MWCNT, the strain before break of asymmetric PVA-MWCNT/PVDF/Non-woven membrane had reduced approximately 14 % from the values recorded for the asymmetric PVA/PVDF/Non-woven membrane while 18 % increase in tensile stress is observed. For swelling test, 15 % decrease in terms of swelling degree is observed when the asymmetric PVA-MWCNT/PVDF/Non-woven membrane is tested with 95 wt. % aqueous ethanol solution. Besides that, the presence of functionalized MWCNT as filler enhanced the separation factor by 4 folds during

dehydration of 95 wt. % aqueous ethanol solution at 30 °C via pervaporation. However, the total flux obtained for the asymmetric PVA-MWCNT/PVDF/Non-woven membrane is only 10 % of the value obtained for the asymmetric PVA/PVDF/Non-woven membrane.

CHAPTER 1: INTRODUCTION

1. Introduction

1.1. Research background

Pervaporation is one of the membrane technologies which famous for its energy intensiveness and cost effectiveness. During the pervaporation, the minor components from the feed solution liquid is allowed to transfer across the membrane, it eventually being removed as permeate in vapor state at downstream side. Usually, a vacuum pump is connected at the permeate side to drive the operation (Neel, 1991). Among the pervaporation applications, the dehydration of aqueous organic solvent is highly focused and developed due to its economical significant. It is crucial to know that the effectiveness of pervaporation is usually achieved by removing the minor components from its majorities counterparts using an effective selective membrane (Shao and Huang, 2007). Thus, the researches usually focus on improving the performances of pervaporation membrane. A good pervaporation membrane is ideally showing high permeability, selectivity and stability. The trade-off between total permeate flux and separation factor is a common challenge to be resolved (Kariduraganavar et al., 2009).

The hydrophobic and hydrophilic properties of membrane materials, and the intermolecular interactions between membrane materials or between membrane materials and permeate, usually contributes to the effectiveness of pervaporation membrane. Thus, the membrane performance can be engineered by manipulating these interactions by adjusting the ratio of suitable membrane material. Polymeric membranes are the conventional pervaporation membrane. Polymeric membranes exhibit weak mechanical

strength and required modifications like surface functionalization treatment. As an example of polymeric membrane, poly(vinyl alcohol) (PVA) membrane is largely applied in the dehydration of aqueous organic solvent due to its excellent water perm-selective properties, high-abrasion resistance, elongation, tensile strength and flexibility (Chapman et al., 2008). Later, composite membrane is introduced. Asymmetric membrane which consists of a thin layer homogenous membrane coated on a porous layer is one of the examples. The porous supports are usually fabricated from polymeric substance via phase inversion process (Jian et al., 1996, Ong and Tan, 2015). The polyvinylidene fluoride (PVDF) is usually used as porous support for a homogenous layer to form asymmetric composite membrane. Besides that, mixed matrix membranes (MMMs) emerged as another species of composite membrane. Initially, suitable inorganic fillers such as carbon black, carbon nanotubes (CNTs), titanium dioxide, zeolites, metal-organic frameworks (MOFs) and etc. are dispersed into the polymeric membrane. For example both the permeation flux and separation factor of pervaporation membrane shows improvement with the addition of CNTs (Kim et al., 2007). The tendency of CNTs to aggregate has lowered the dispersion efficiency of CNTs into polymer matrix. Various modification treatments like functionalization by chemical agents are introduced to solve this problem. Continuous innovation and improvement on pervaporation membrane often leads to the production of novel membrane which shows more possibilities on membrane fabrication. The symmetric bucky paper supported ionic liquid membrane (BP-SILM) that exhibits high pervaporation performance and good membrane stability (Ong and Tan, 2015) is a good example of novel membrane.

1.2. Problem statement

The researches in pervaporation technology usually focus on the modification of membrane to produce membranes with high permeability, selectivity and structural stability. The trade-off between total permeate flux and separation factor is a common phenomenon that limits the performance of pervaporation operation. Various membrane material, membrane structure and fabrication method has been introduced as innovative approaches to improve the performance of pervaporation membrane.

The lack of mechanical strength and stability are the major drawback for the conventional polymeric membrane. There was an issue with the broken PVA membrane during pervaporation in the tranesterification of soybean oil with methanol (Guerreiro et al., 2006). In order to overcome this weakness, various forms of composite membranes including asymmetric membrane and mixed matrix membrane are introduced. However, the composite structure might lose integrity when the phases in the composite do not swell or expand in a coordinated manner.

In this study, MWCNT with carboxyl groups (-COOH) functional groups are incorporated in the PVA polymer membrane as effective hydrophilic nanofillers to break the trade-off between permeation flux and separation factor. The PVDF porous membrane is employed as the supported layer for the PVA membrane to produce an asymmetric composite membrane with better mechanical strength. To further enhance the integrity of the composite membrane, a vacuum filtration process is implemented to immobilize the PVA polymer into the porous site of the PVDF support layer. The

fabricated membrane is then characterized and tested with pervaporation operation for dehydration of 95 wt. % aqueous ethanol solution at 30 °C.

1.3. Research objectives

The main objectives of this study are:

- i. To fabricate asymmetric porous polyvinylidene difluoride layer supported polyvinyl alcohol membrane.
- ii. To characterize the fabricated membrane via swelling test, tensile test and scanning electron microscope.
- iii. To dehydrate ethanol water mixture by pervaporation using the fabricated membrane.

CHAPTER 2: LITERATURE REVIEW

2. Literature Review

2.1. Pervaporation

Over the past several decades, industry has been focused on continuous improvement and innovation on their production methods in order to remain competitive among competitor around the world. Under this background, membrane technologies have developed as additional well-established separation processes as it offers several advantages over the traditional separation methods. These advantages include the high selectivity, low energy consumption, moderate cost to performance ratio and compact and modular design (Lipnizki et al., 1999). Pervaporation is a liquid separation process involving membrane as selective barrier. When the feed mixture contacts with the membrane at one side, components are absorbed by the membranes and diffuse through the membrane. Later, this portion of solution evaporates as permeate in vapour state from the other side of the membrane. The driving force for the mass transport is the vapour pressure difference between feed solution and permeate vapour which can be maintained by applying vacuum or gas purge at permeate side. The difference in sorption and diffusion properties between components give rises to the separation of liquid (Neel, 1991).

2.1.1. Pervaporation Mass Transfer model

To give a clearer insight on the process, pervaporation can be described by the classical solution-dilution mechanism of transport. The mass transport across the selective membrane involves three successive steps. (1) Sorption of permeate from bulk feed solution to the surface of membrane at upstream side. (2) Diffusion of permeate across the membrane. (3) Desorption of permeate to vapor phase at the downstream side of membrane (Feng and Huang, 1997, R.D. Noble, 1995).

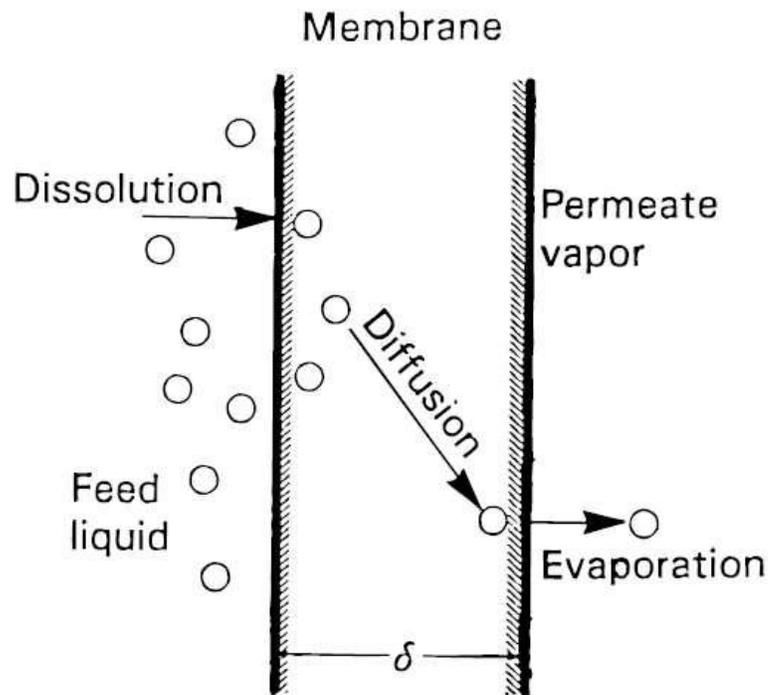


Figure 2.1: Schematic diagram of the solution-diffusion model

2.1.2. Application of pervaporation

Generally, pervaporation uses the most selective membranes to remove the minor components (usually less than 10 wt. %) to enhance the separation while reduce energy consumption. Thus, it is recognized as the most cost-effective liquid separation technology which offers incomparable advantages when dealing with heat-sensitive, close-boiling, and azeotropic mixtures. Its mild operating conditions, no emission to the environment, and no involvement of additional species into the feed streams give extra merits over the conventional technology (Shao and Huang, 2007).

As a matter of fact, pervaporation process can be applied in few areas namely dehydration of organic solvents, removal of dilute organic compounds from aqueous streams, organic-organic mixtures separations and pervaporation-based hybrid process including pervaporation-reaction hybrid process and pervaporation-distillation hybrid process (Smitha et al., 2004, Lipnizki et al., 1999, Marbelia et al., 2016). Hybrid processes exist in the sense that pervaporation alone might not able to achieve the product specifications required by market and the environmental standard (Lipnizki and Field, 1999). Therefore, the hybrid process integrates the benefits offered by conventional methods (better separation factor) and pervaporation (energy intensive and cost saving). For example, introducing a pervaporation unit before distillation column can effectively reduce the operating energy needed by prior splitting an azeotrope mixture (Nagy et al., 2015).

As the dehydration of organic solvents like alcohol, ether, ester and acid which likely to form azeotrope with water is largely represents the application of the pervaporation (Shao and Huang, 2007). Thus, technology in this area is well developed.

A scenario called synergic effect is contributing to the development in this area too. It is a phenomenon in which the smaller water molecule can be dissolved and transported easily across hydrophilic membranes. Comparatively, bigger organic molecules diffuse hardly across the organophilic membrane (Koros and Kamaruddin, 1995).

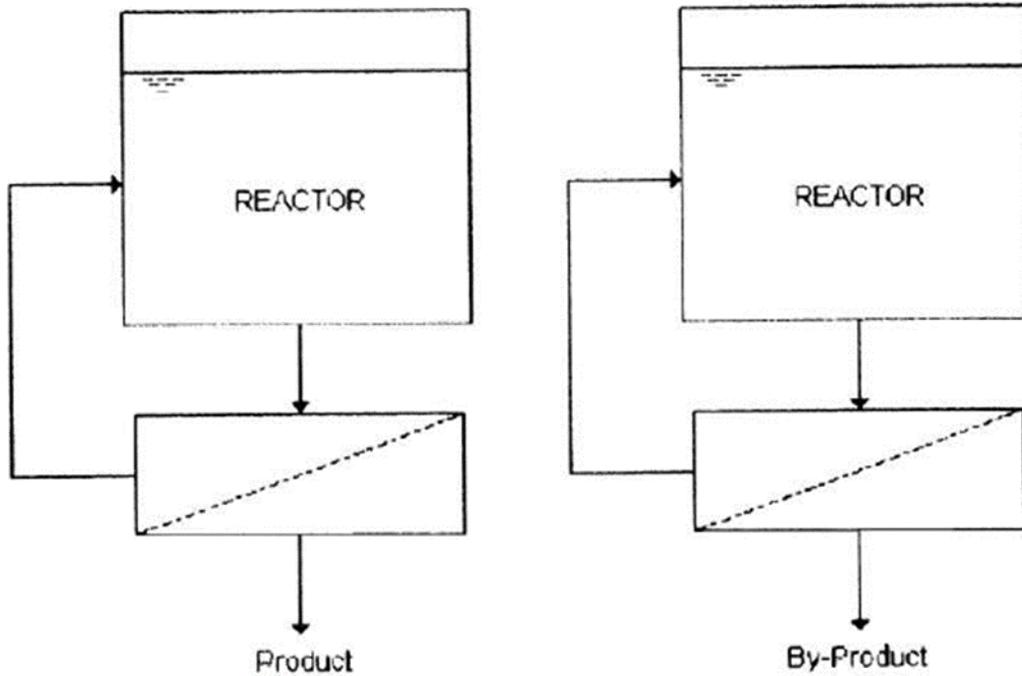


Figure 2.2: Schematic diagram of pervaporation-reaction hybrid process

2.2. Pervaporation Membrane

Various types of pervaporation membranes have been fabricated and studied by innovative researchers from time to time to improve the performances of pervaporation separation. Among all, the key focuses in the development of pervaporation membrane are to improve the permeability, selectivity and stability of membrane. A trade-off between total permeate flux and separation factor is a common issue to be resolved (Kariduraganavar et al., 2009). Thus, a lot of innovative on the membrane material, membrane structure, fabrication method and modification method have been proposed to produce pervaporation membrane with better mechanical strength and structural stability at various operation conditions.

2.2.1. Fundamental properties of the pervaporation membrane

Generally, the membrane materials can be categorized into two groups which are hydrophilic and hydrophobic. Hydrophilic membranes usually tend to absorb water, whereas hydrophobic membranes are water-repellent which usually prefer the absorption of organic particles (Chapman et al., 2008). Ideally, high-selective sorption and high-selective diffusion are preferred in pervaporation membrane. These characteristics are dependent on the inter- and intra-molecular structure of membrane materials (Chapman et al., 2008). In the case of dehydration of organic solvent, the pervaporation membrane is preferentially to have high-sorption capability for selective permeation of water. This can be achieved by choosing membrane materials that interact with water by dipole-dipole actions, ion-dipole actions and/or hydrogen bonding (Semenova et al., 1997). In short, the properties of every membrane's components and its intermolecular interaction contribute

fundamentally to the performance of pervaporation membrane. The ratio of hydrophilic to hydrophobic moieties can be manipulated to produce membrane with desired separation factor, permeability and other properties (Chapman et al., 2008).

2.2.2. Polymeric membrane

Traditionally, polymeric membranes are largely applied in pervaporation technology. In earlier dehydration research, naturally occurring polymers like cellulose, and its derivatives are used. Subsequently, synthetic polymers including poly (acrylic acid) (PAA), poly (vinyl alcohol) (PVA), polyacrylonitrile (PAN), and nylon 6 are investigated too.

2.2.3. Composite membrane

Later, numbers of composite membranes are introduced to improve separation performance and enhance mechanical strength. However, the composite structure might be disintegrated if the phases in the composite do not swell or expand in a coordinated manner (Shao and Huang, 2007). The asymmetric membrane and the mixed matrix membranes (MMMs) are the examples of composite membrane.

A typical asymmetric membrane consists of a thin layer homogenous membrane supported on a porous substrate. This type of membrane offers higher permeation flux than the conventional homogenous membrane due to the negligible resistance to mass transport within the porous layer (Shao and Huang, 2007, Koops et al., 1993).

On the other hand, mixed matrix membranes (MMMs) composed of a polymer and inorganic fillers is introduced. It is claimed that the pervaporation performance can

be enhanced by incorporation of appropriate fillers (Jia and Wu, 2016). Typical example of inorganic filler is aluminosilicates or zeolite particles which give rise to high separation factor due to the combined effects of molecular sieve, selective adsorption and difference in diffusion rates (Kittur et al., 2003). To overcome the drop of selectivity due to grain boundary defect arise from the weak interfacial bonding, incompatibility and mismatching of the thermal expansion coefficient between the inorganic filler and polymeric phases, metal-organic frameworks (MOFs) is introduced as new species filler. MOFs are crystalline nanoporous materials made up of a metal centers and organic linkers (Jia and Wu, 2016).

Idealised MMM structure

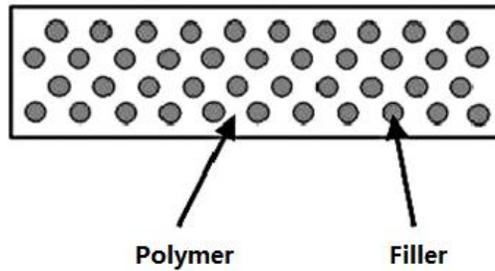


Figure 2.3: Schematic diagram of mixed matrix membranes (MMMs)

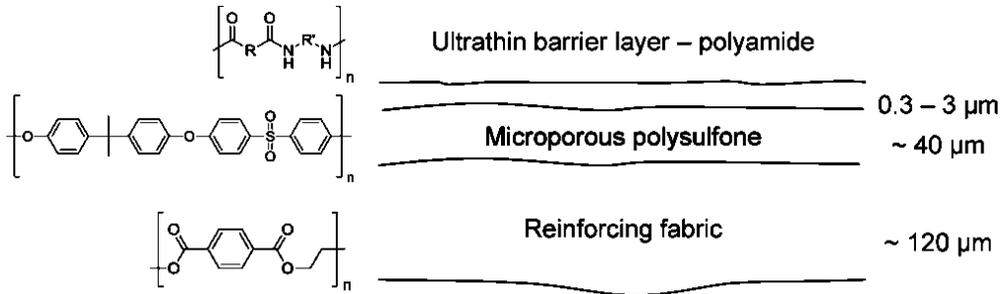


Figure 2.4: Schematic diagram of asymmetric membrane

2.3. Material of pervaporation membrane

As discussed in previous section, more components make up of pervaporation membrane are introduced as innovative modification approaches to enhance the properties of pervaporation membrane. These components are polymeric membrane layer, porous support layer and filler. Suitable material for these components will be discussed in this section.

2.3.1. Polymeric membrane: Poly (vinyl alcohol) (PVA)

Poly (vinyl alcohol) (PVA) based pervaporation membrane focusing dehydration of organic solvent had drawn a lot of research attention. Also, it has been applied in a number of commercial membranes due to the favorable properties. It is a hydrophilic polymer with excellent water perm-selective properties, high-abrasion resistance, elongation, tensile strength and flexibility (Chapman et al., 2008).

2.3.2. Asymmetric composite membrane: PVDF porous supports

The porous supports are commonly prepared from a polymeric substance including polypropylene, polyvinylidene fluoride and polysulfone via a phase inversion process (Jian et al., 1996, Ong and Tan, 2015).

The polyvinylidene fluoride (PVDF) has been used as porous support consisting an active alinate layer or chitosan layer as selective layer. Pervaporation to dehydrate water from ethanol and isopropanol mixtures shows promising permselectivity. This is due to the suitable ratio between hydrophobic PVDF and the hydrophilic alinae and chitosan layer. Also, the hydrophobicity of PVDF is improved by blending 1 wt. % of relatively hydrophilic polymethyl methacrylate (PMMA). On top of that, the chemically inert fluoropolymer present in PVDF able to tolerate high temperature feed solution (Huang et al., 2000).

2.3.3. Filler: Nanoparticles

Moreover, the encouraging preliminary results from the implementation of nanoparticles as filler promises a trend that focus on the nanocomposite pervaporation membrane in the near future (Shao and Huang, 2007). A novel chitosan/titanium dioxide nanocomposite membranes is synthesized using tetrabutyl titanate (TBT) as precursor and acetyl acetone as chelating agent by in situ sol-gel process to dehydrate 90 wt. % aqueous ethanol solution at 80 °C via pervaporation. Characterization and analysis show the presence of titania nanoparticle contributes to the best pervaporation performance with permeation flux and separation factor recorded at 0.340 kg m⁻² h⁻¹ and 196 respectively (Yang et al., 2009). Also, PVA-silica nanocomposite pervaporation membrane fabricated by in situ sol-gel technique for dehydration of 80 wt. % aqueous ethylene glycol solution at 70 °C showed desirable separation factor of 311 and a permeation flux of 67 g m⁻² h⁻² due to the formation of more compact crosslinked structure (Guo et al., 2007). Moreover, the carbon derivatives, graphene oxide (GO) and carbon nanotubes (CNTs) are another emerging nanomaterial for pervaporation membrane due to its good mechanical and thermal properties (Liu et al., 2015, Yeang et al., 2013). It is reported that the addition of CNTs are helpful in breaking the trade-off curve between total permeate flux and separation factor which usually limit the pervaporation operation (Sae-Khow and Mitra, 2010).

2.3.4. Filler: Carbon nanotube (CNT)

The extraordinary mechanical, electrical and thermal properties of CNTs drawn interest among researchers to utilize it as nanofillers in MMMs (Delozier et al., 2006). CNTs are rolled-up cylinders or tubes of graphite sheet with a nanometer diameter which tend to aggregate due to strong van der waals attraction among the tubes (Georgakilas et al., 2008). The dispersion efficiency of CNTs into polymer matrix becomes a crucial factor that affects the effectiveness of pervaporation membrane. Various modification techniques like surface oxidation, attaching functional groups onto the surface of the CNTs, functionalisation by chemical agents, non-covalent surface coating with surfactants and long polymer chains and non-covalent adsorption of hydrophilic non-charged polymer chains have been introduced to promote the homogeneousness of CNTs in MMMs and its structural integrity (Yeang et al., 2013). A review on various research articles regarding pervaporation dehydration of aqueous ethanol solution shows an increase in both total permeate flux and separation factor when mutli-walled carbon nanotubes (MWCNT) is immobilized in PVA polymeric membrane. It is believed that the inherent CNT walls contributes to the high mass transport rate (Kim et al., 2007) .Also, the presence of CNTs in the nanocomposite membrane modified its bulk properties, thus enhancing the solubility and diffusivity of a permeant in the membrane (Hu et al., 2012). In 2005, a research is conducted by Panahian et al. (2005) to study the effects of implementing different types MWCNT filler in PVA bases MMMs in the pervaporation dehydration of 90 wt. % aqueous ethanol solution. The MWCNT introduced in this studied are CNTs functionalized with carboxyl functional groups and TiO₂-CNT. The results showed that the present on functionalized MWCNT in MMMs gives rise to

lower swelling degree, improved hydrophilicity and higher crosslinking density resulting to higher separation factor and lower permeate flux (Panahian et al., 2015).

2.4. Membrane fabrication method

Suitable fabrication method need be employed in order to produce the desired membrane. For example, the solution casting method is suitable to produce polymeric membrane while the wet phase inversion method can produce porous membrane. A vacuum filtration process can be used to fill up the porous sites of porous support layer with the polymeric material.

2.4.1. Solution casting

This method is suitable for small scale production of membrane. A polymer solution can be prepared by dissolving the polymer pallet in a solvent. The polymer solution is then spread on a flat glass plate with a casting knife consist of a steel blade placed on two runners. The spread thin film is left for solvent evaporation to produce membrane. This method is simple, low cost and the produced membrane is crystalline and isotropic (Baker, 2004)

2.4.2. Phase inversion

The porous layer (PVDF in this study) is synthesis via wet phase inversion process which is usually governed by two mechanisms namely liquid-liquid de-mixing and solid-liquid de-mixing (Sardarabadi et al., 2016). Usually, liquid-liquid de-mixing is preferred as it able to produce a membrane with a relatively dense skin layer and a cellular network structure with macrovoids or fingered-like pores (Ong et al., 2011). As discussed above, these porous structure account for the smaller mass transfer resistance. Among the phase inversion methods, the procedure of non-solvent induced phase inversion involves casting a wet film of polymer solution onto a porous non-woven polymeric support, immersion of the casted film in a non-solvent bath and drying. The non-solvent, which is a poor polymer solvent that miscible with the solvent of polymer, promotes the mass transfer of solvent from polymer, resulting the finger-like porous structure (Guillen et al., 2011).

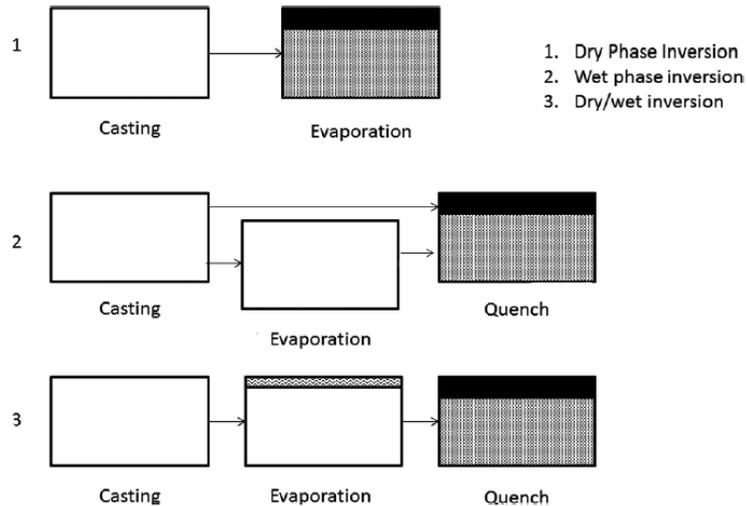


Figure 2.5: Schematic diagram phase inversion processes (Pinnau and Freeman, 2000)

2.4.3. Vacuum filtration process

A vacuum filtration process is proposed to immobilize liquid membrane or polymeric material into the porous site of the support layer. By using the simple filtration set, the porous support layer is fixed on the membrane support. The liquid membrane or polymer solution to be immobilized is being fed to the porous support layer. A vacuum pump connected to the permeate side is switched on to provide driving force. Allow the filtration process to take place until a thin visible layer of liquid membrane or polymeric membrane is observed on the top of the porous support layer (Ong and Tan, 2015).

CHAPTER 3: MATERIALS AND METHODS

3. Materials and methods

3.1. Material

Table 3.1: List of the materials and its specification

Material	Specifications	Supplier
PVDF Pellets	Average Mw ~ 180,000 by GPC Average Mn ~ 71,000, Beads or pellets	Aldrich Chemistry
DMF Solvent	Anhydrous, 99.8 %	Signal - Aldrich
PVA Powder	Fully hydrolized	Merck
MWCNT	Carboxyl MWCNT OD ~ 5 – 15 nm -COOH Content ~ 2.56 wt. % Length ~50 μ m Purity >95 % Ash <1.5 wt.% SSA >233 m ² /g EC 10 ² s/m MFG Code: MC2/21224	Timesnano.Com
Non-Woven Cloth	N/A	-
Distilled Water	N/A	Produced in lab
Deionized Water	N/A	Produced in lab
Ethanol	96 % purity	Signal Aldrich

3.2. Preparation of PVDF Solution

PVDF solution is prepared by dissolving 15 wt. % of PVDF pellets in DMF solvent. The solution is stirred overnight using magnetic stirrer at 85 °C. While for PVDF-MWCNT solution, the oxidized MWCNT are added to the prepared 15 wt. % PVDF solution. The solution is sonicated for 15 min and stirred overnight to ensure the MWCNT are homogeneously dispersed in PVDF solution.

3.3. Fabrication of porous PVDF layer

Porous PVDF layer is prepared according to phase inversion procedure suggested by Jian et al. ,(1996). The casting solution prepared in section 3.2 above is casted on non-woven cloth fixed on a glass plate. The resulting film on the glass plate is immersed in the precipitation bath consist of deionized water for 15 min. Afterward, the porous PVDF layer is allowed to dry in room temperature.

3.4. Preparation of PVA Solution

5wt. % PVA powder is dissolved in distilled water vigorous stirring at 80 °C for 6 h. The stirring process is continued overnight at room temperature once the PVA powder is dissolved totally in the water in order to form a homogenous PVA solution. To prepare PVA-MWCNT solution, 0.5wt.% of MWCNT is added to the 5wt.% PVA solution. The solution is sonicated for 15 minutes and stirred overnight to ensure even distribution of MWCNT.

3.5. Fabrication of asymmetric PVDF-PVA membrane

5wt. % PVA solution is immobilized in the pores of PVDF layer by vacuum filtration process using a procedure suggested by Ong, (2015). The PVDF layer is sliced into circle with a diameter of 4.7 cm and fixed on the membrane filter. With the vacuum pump switched on, the PVA solution is allowed to pass through the PVDF layer slowly until a thin visible layer of excess PVA solution is observed on the surface of PVDF layer. The excess PVA solution is removed using a transfer pipette. Afterward the asymmetric PVDF-PVA membrane is allowed to dry in the membrane filter set at room temperature.

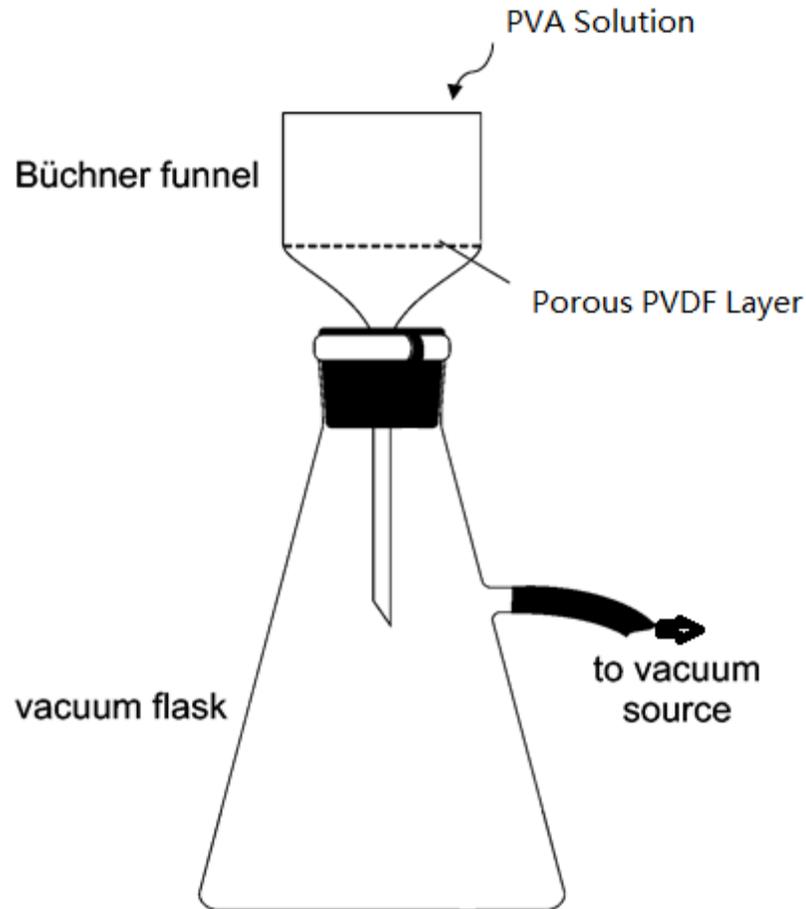


Figure 3.1: Schematic diagram of vacuum filtration process

3.6. Liquid sorption test

The casted membranes are cut using scissors into 1 cm x 2 cm dimensions. The dry weight of membrane was weighed using a digital balance. After that, the membrane is then immersed into sealed glass bottle composed of 95.0 wt. % ethanol and 5.0 wt. % water. The membranes were allowed to stand immersed at room temperature for 72 h to enable the membrane sorption to attain equilibrium. The swollen membranes were then removed from the vessel and weighed immediately after blotting the excess adhered liquid. The total amount of liquid sorbed was determined using the following equation:

$$\text{Degree of swelling} = \frac{M_s - M_d}{M_d} \times 100 \% \quad (3.1)$$

Where M_s = Swollen weight of the membrane in mg

M_d = Dry weight of the membrane in mg

3.7. Scanning Electron Microscopy

The surface morphology and cross section of the casted membranes and the elemental compositions of the samples were visualised using a SEM, Zeiss Supra 35 VP scanning electron microscope (SEM).

3.8. Determination of the mechanical properties

The mechanical properties of the membrane were examined using an Instron table-mounted universal testing machine. Each of the specimens was cut into a dumbbell shape with a gauge length of 22 mm. The load cell was set to maximum with a constant crosshead speed of 1 mm/min. The tensile strength and elongation at break were determined.

3.9. Pervaporation test

The pervaporation experiments were conducted using a laboratory-scale pervaporation test rig. The membrane is mounted on the permeation cell supported with a porous stainless-steel plate. The feed solutions containing 95.0 wt.% ethanol and 5.0 wt.% water is circulated between the feed tank and the permeation cell at a constant flow rate using peristaltic pumps. The temperature of the feed solution is maintained at 30 °C using a hot plate magnetic stirrer.

After circulation of the feed solution for 20 minutes, the permeate outlet is connected to a vacuum pump. The vacuum pump is switched on to maintain the permeate side pressure at 0.667 kPa. After steady state is achieved, the pervaporation process is operated for 4 h.

The permeate vapor was condensed and collected in a cold trap with liquid nitrogen. The total weight of collected permeate is weighed using electronic balance. The water percentage in permeate is analyzed using Karl Fischer Moisture Titrator (MKS-500). During the analysis, approximately 3 µl of permeate sample was measured using a micro syringe. The weight of the permeate sample is obtained by weighing the weight of micro syringe before and after sample collection. The sample is then injected quickly into