PERVAPORATION OF AQUEOUS ETHANOL SOLUTION BY CARBON NANOTUBE-INFUSED POLYVINYL ALCOHOL MEMBRANE SUPPORTED BY POLYVINYLIDENE FLUORIDE

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by

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LIST OF SYMBOLS

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

LIST OF ABBREVIATIONS

μm	Micrometre (Unit for length)
ºC	Degree Celsius (unit for temperature)
CNT	Carbon Nanotube
cm	Centimetre (Unit for length)
DMF	Dimethylformamide
g	Gram (Unit for mass)
hr	Hour (Unit for time)
MPa	Mega Pascal (Unit for pressure)
NMP	N-Methylpyrrolidone
min	Minute (Unit for time)
mg	Milligram (Unit for mass)
ml	Millilitre (Unit for volume)
N/A	Not available
OA	Oleyl alcohol
PVA	Poly(vinyl alcohol)
PVDF	Polyvinylidene fluoride

PSI	Pervaporation separation index
PDMS	Polydimethylsiloxane
PVA-It	Polyvinyl alcohol-co-itaconic acid
PVA-N	Polyvinyl alcohol co- N-3-trimethyl-ammonio-propyl-acrylamide-chloride
RH	Relative humidity
SEM	Scanning electron microscope
VPFESEM	Variable Pressure Field Emission Scanning Electron Microscope
VOCs	Volatile Organic compound

PENYEJATTELAPAN LARUTAN AKUEUS ETANOL OLEH NANOTIUB KARBON DISEMAI DI DALAM ALKOHOL POLIVINIL MEMBRAN DISOKONGAN OLEH POLIVINILIDENA FLUORIDA

ABSTRAK

Dalam projek ini, membran komposit yang mengandungi kain fabric tanpa tenun dan polivinilidena fluorida (PVDF) sebagai lapisan sokongan, dan poli(vinil alkohol) (PVA) yang digabungkan dengan nanotiub karbon (CNT) sebagai lapisan pemilih telah dihasilkan untuk dehidrasi campuran etanol dan air melalui proses penyejattelapan. Lapisan PVA-CNT telah dihasilkan melalui teknik penuangan larutan acuan dan lapisan sokongan PVDF telah dihasilkan menggunakan kaedah fasa penyongsangan. Keputusan pengimbasan elektron mikroskopi (SEM) menunjukkan bahawa isian CNT telah tersebar dalam polimer PVA matriks. Keputusan darjah pengampulan menunjukkan bahawa CNT dengan kumpulan fungsi hidroksil (-OH) dan karboksil (-COOH) dalam lapisan PVA membantu untuk meningkatkan tahap pengembangan membran. Kajian mekanikal untuk PVA yang digabung dengan CNT mempamerkan kekuatan terikan tertinggi sebanyak 11.6 MPa dan kekuatan tegangan sebanyak 220 %. Keputusan penyejattelapan menunjukkan bahawa membran dengan CNT mempunyai lebih tinggi jumlah fluks, faktor pemisahan dan indeks pengasingan penyejattelapan (PSI) iaitu masing-masing 8, 7 dan 54 kali ganda.

PERVAPORATION OF AQUEOUS ETHANOL SOLUTION BY CARBON NANOTUBE-INFUSED POLYVINYL ALCOHOL MEMBRANE SUPPORTED BY POLYVINYLIDENE FLUORIDE

ABSTRACT

In this project, composite membranes containing non-woven cloth and polyvinylidene fluoride (PVDF) as support layer, and poly(vinyl alcohol) (PVA) incorporated with carbon nanotubes (CNT) as a selective layer were prepared for dehydration of ethanol/water mixtures by the pervaporation process. The PVA-CNT layer was fabricated via solution casting technique and the PVDF support layer was fabricated through phase inversion method. The scanning electron microscopy (SEM) results showed that the CNT fillers were dispersed in the PVA polymer matrix. The degree of swelling results showed that the CNT with the hydroxyl (–OH) and carboxyl (–COOH) functional groups in the PVA layer help to increase the degree of swelling of the membranes. The mechanical test results showed that the membrane with the PVA incorporated with CNT exhibited the highest tensile strength of11.6 MPa and strain 25.9 %. The pervaporation results showed that membranes incorporated with CNT have higher total flux, separation factor and pervaporation separation index (PSI) which were 8, 7 and 54 times, respectively.

CHAPTER ONE

INTRODUCTION

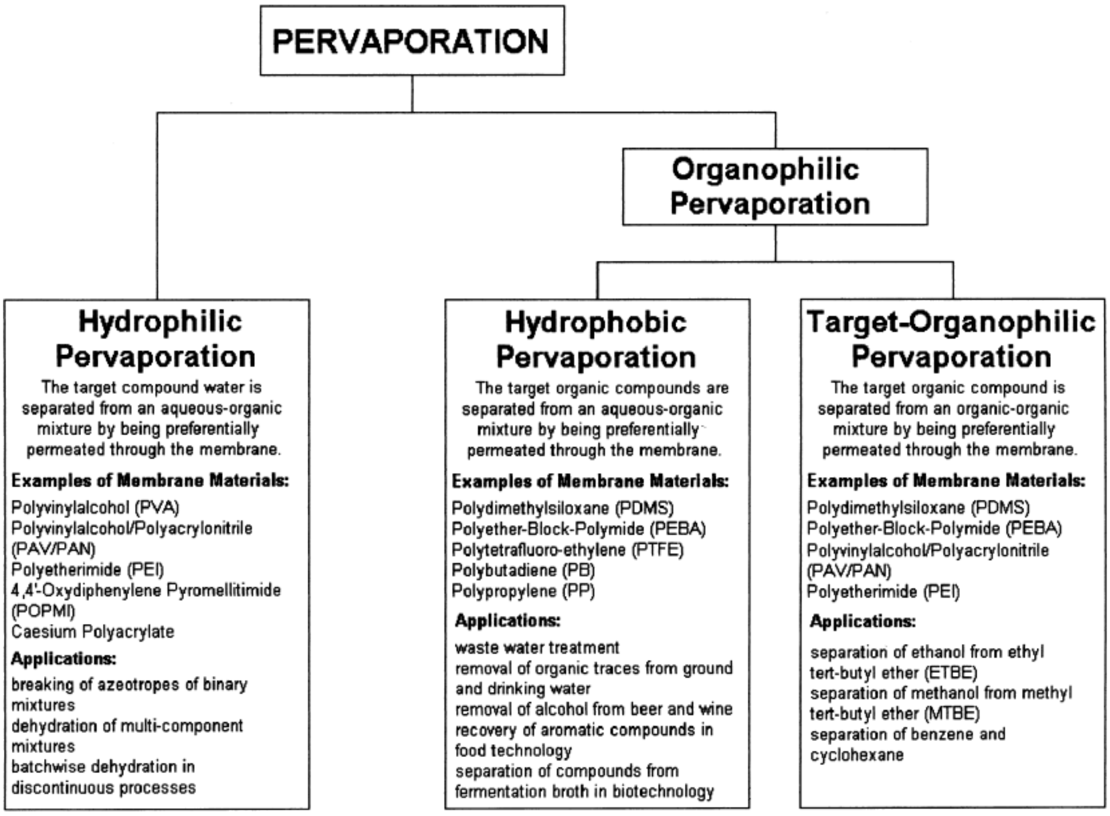
1.1 Research background

1.1.1 Pervaporation process.

Separation processes are very important in industries for the contaminants removal, recovery and purification. Distillation and liquid-liquid extraction are two of the most common and traditional technologies used for separation, however these two methods have major drawback. Thus, researcher started to find another alternative like membrane separation.

Membrane separation process possesses numerous industrial applications with many advantages. Pervaporation is one of the membrane separation processes in which a binary or multicomponent liquid is passed across a membrane that preferentially permeates one or more of the components. The term of ‘pervaporation’ from the abbreviation of ‘permeation’ and ‘evaporation’ defined by Kober after observing the selective permeation of water through the collodion and parchment membrane (Philip, 1917).

Generally, pervaporation can be labelled as a new technology. Depending on the permeating component two main areas of pervaporation can be determined: (1) hydrophillic pervaporation, and (2) organophilic pervaporation. The overview of the pervaporation areas, membranes applied and applications are shown in Figure 1.1.



Hydrophilic Pervaporation

The target compound water is separated from an aqueous-organic mixture by being preferentially permeated through the membrane.

Examples of Membrane Materials:

Polyvinylalcohol (PVA)
Polyvinylalcohol/Polyacrylonitrile (PAV/PAN)
Polyetherimide (PEI)
4,4'-Oxydiphenylene Pyromellitimide (POPMI)
Caesium Polyacrylate

Applications:

breaking of azeotropes of binary mixtures
dehydration of multi-component mixtures
batchwise dehydration in discontinuous processes

Hydrophobic Pervaporation

The target organic compounds are separated from an aqueous-organic mixture by being preferentially permeated through the membrane.

Examples of Membrane Materials:

Polydimethylsiloxane (PDMS)
Polyether-Block-Polymide (PEBA)
Polytetrafluoro-ethylene (PTFE)
Polybutadiene (PB)
Polypropylene (PP)

Applications:

waste water treatment
removal of organic traces from ground and drinking water
removal of alcohol from beer and wine
recovery of aromatic compounds in food technology
separation of compounds from fermentation broth in biotechnology

Target-Organophilic Pervaporation

The target organic compound is separated from an organic-organic mixture by being preferentially permeated through the membrane.

Examples of Membrane Materials:

Polydimethylsiloxane (PDMS)
Polyether-Block-Polymide (PEBA)
Polyvinylalcohol/Polyacrylonitrile (PAV/PAN)
Polyetherimide (PEI)

Applications:

separation of ethanol from ethyl tert-butyl ether (ETBE)
separation of methanol from methyl tert-butyl ether (MTBE)
separation of benzene and cyclohexane

Figure 1.1: Areas of pervaporation: membranes and applications (Lipnizki et al., 1999).

The most widely accepted transport mechanism for pervaporation is solution diffusion model as well as for reverse osmosis and gas separation processes (Baker, 2012). These transport mechanism consists of three steps which are sorption of the permeating component from the feed liquid into the membrane, diffusion of the permeating component through the membrane and desorption of the permeating component to the vapour phase on the downstream of the membrane.

Figure 1.2 shows the overview of the pervaporation process. The desired component in the feed which is in the liquid form permeates through the membrane and evaporates while passing through the membrane because the partial pressure of the permeating component is kept lower than the equilibrium vapour pressure. The separation performance of pervaporation membranes can be increased by enhancing the solubility selectivity and/or diffusivity selectivity of the penetrants across the membranes (Ong et al., 2016). Pervaporation performance can be evaluated according to its productivity and capability to separate the components from the feed mixture which can be expressed by two type of parameters which are process performance specify by flux and separation factor or driving force normalized performance specify by permeability or permeance and selectivity.

The main advantage of pervaporation is that it uses much less energy than other phase-change separations such as distillation (Shao and Huang, 2007). Pervaporation is an economical separation method as compared to conventional processes especially for separating azeotropic and close boiling mixtures due to its high separation factor and flux rates

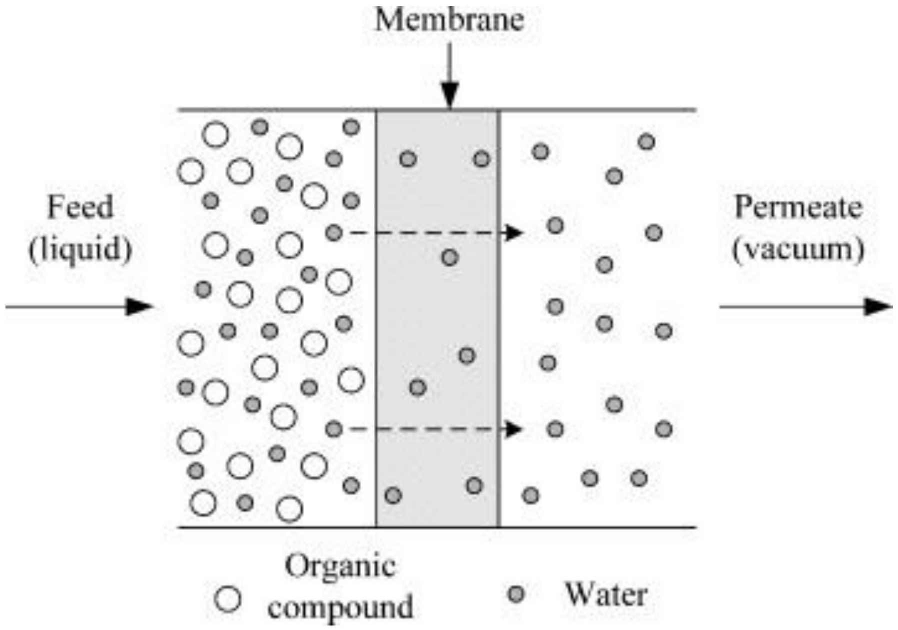


Figure 1.2 : Overview of the pervaporation process for aqueous organic mixtures (Wee et al., 2008).

1.1.2 Type of Membrane used.

There are different types of membranes used for the pervaporation of organic compounds from aqueous solution which are (a) organic membrane, broadly covers polymeric membranes, (b) inorganic membrane, covers ceramic membranes and (c) composite membrane, also called hybrid membrane and covers polymeric as well as inorganic membrane. Figure 1.3 shows the schematic representation of a supported membrane morphology used in the pervaporation process. The membrane which acts as the separating layer is coated on top of a porous support and allows only certain species to permeate through it selectively.

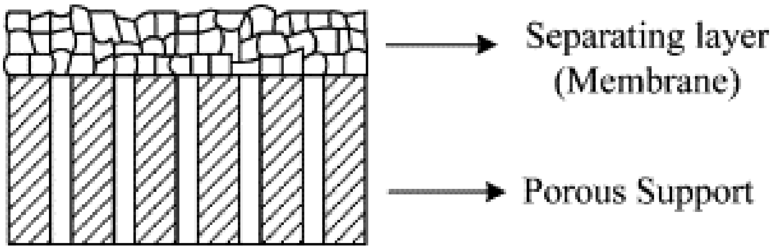


Figure 1.3 : Schematic representation of supported membrane morphology (Wee et al., 2008).

Most pervaporation membranes used in industrial applications are polymeric type. Polymers are important and common base materials, they are preferable alternatives to fabricate separation membranes for their multifunctional groups and excellent performances in structural strength and manufacturability (Yuan et al., 2014). For porous membrane, the most well-known preparation method is phase inversion. Inorganic membranes or known as ceramic membranes made from zeolite, silica or alumina, they are high solvent-resistant, high temperature stability and free of swelling (Wee et al., 2008). Therefore, these membranes can be used for broad range of applications and at the same time have both high selectivity and permeability. On the other hand, composite membranes are prepared by casting hydrophilic polymers on porous substrates which provides mechanical strength and the casting layer provides separation efficiency to the membrane. The formation of organic–inorganic hybrid shows certain achievement on membrane stabilization in terms of thermal, chemical and mechanical properties (Wee et al., 2008).

Recent membrane development is to use polymer-inorganic nanocomposite, where nanofillers are dispersed in a polymer matrix, and such membranes are sometimes referred to as mixed matrix membranes (MMMs). Zeolites, silica, carbon molecular sieves and activated carbons have been studied intensively as fillers for fabrication of MMMs. In addition, carbon nanotubes (CNTs) have also attracted significant attention as nanofillers due to their unique structures and properties (Ismail et al., 2009). CNTs are rolled-up cylinders of graphite sheets with a nanometer diameter and a tubular structure. The as-produced CNTs tend to assemble into bundles due to strong van der Waals attraction among the tubes. Therefore, the effectiveness of using CNTs in MMMs to improve the separation performance depends on a large extent on ability to disperse the CNTs uniformly in the polymer matrix. Attaching functional groups to the CNTs is considered to be an effective way to prevent nanotube aggregation, which helps better dispersion of the CNTs in a polymer matrix (Sahoo et al., 2010), and surface treatments of CNTs with strong acids (e.g., sulfuric acid, nitric acid) are commonly used for this purpose.

1.2 Problem Statement

The dehydration of organic solvent generally used hydrophilic membranes because of the favourable solubility and diffusivity for selective permeation of water. Particularly poly(vinyl alcohol) (PVA), it has been widely used as a membrane material for solvent dehydration due to its strong affinity to water molecules, good mechanical strength and membrane forming properties . However, the pure PVA has a very poor stability in the aqueous solutions, which makes it impossible to use it directly for the separation of the aqueous and organic solutions. Therefore, there are numerous studies being done in order to understand how to increase the stability of this material. One of the methods is to crosslinking PVA polymer. This method is usually achieved by reacting the polymer with a chemical solution. Several crosslinking methods have been studied for PVA membranes, for instance, by crosslinking PVA with CNTs. The effectiveness of using CNTs in MMMs to improve the separation performance depends on a large extent on the ability to disperse the CNTs uniformly in the polymer matrix. To support the composite membrane, a semi-crystalline polymer, poly (vinylidene fluoride) (PVDF) is chosen because of its excellent chemical resistance, physical and thermal stability, high strength and flexibility. However, the hydrophobicity of PVDF remains a problem and limits its application. It is well known that poly(vinyl alcohol) (PVA) is one of the polymeric materials for fabricating membranes which possesses good hydrophilicity and other advantages. Some reserachers have indicated that PVA is a polymer miscible with PVDF and a high degree of intermolecular interaction presents between PVDF and PVA chains (Paul and Barlow, 1980, Mijovic et al., 1997, Linares et al., 1997). Thus in this project, CNTs were used as the filler in PVA to reduce its degree of swelling and PVDF as the support layer since it is compatible with the PVA. The resultant membrane will use for dehydration of ethanol-water mixture.

1.3 Research Objectives

- To synthesis composite membrane of PVA incorporated with and without CNT supported by PVDF.
- To characterize composite membrane of PVA incorporated with and without CNT supported by PVDF via scanning electron microscope, swelling test and mechanical test.
- To study the performance of the synthesis membrane via pervaporation.

CHAPTER TWO

LITERATURE REVIEW

2.1 Carbon Nanotube

The carbon nanotubes (CNTs) were discovered in 1999 by lijima (Iijima, 1991), they possess unique atomic structure, very high aspect ratio, remarkable electronic structure and extraordinary high mechanical strength. Since then many researches have been conducted on CNTs because of its unique properties and various applications in nanotechnology related fields (Ebbesen, 1994). They have size in the order of nanometer and large surface area which offers excellent gas absorption properties.

The absorption of gas on the CNT surface at room temperature differ its electrical properties with fast response, which allows them to be a possible candidate for gas sensing applications (Modi et al., 2003). Gas sensors made from individual nanotubes have good sensitivity at room temperature, can be compared with the commercially available semiconductor sensors that operate at a temperature above 200 ºC (Kong et al., 2000). The absorbing of analyte on the surface of the nanotubes is due to a partial transfer of charges occurred, resulting in the charge carrier concentration variation. The adsorbed analyte differ the potential barriers present at the tube-electrode contacts, causing in the changes of electrical resistance and produce a sensor signal. Gas sensors made up of multiwalled carbon nanotubes (MWCNTs) functionalized with oxygen display high responsiveness to low gas level.

Carbon nanotube based materials have inspired scientists for a range of potential applications such as catalyst support (Planeix et al., 1994), electronic device (Saito, 1997), Li-ion batteries (Che et al., 1996), nanoelectronic devices (Collins et al., 1997), and chemical sensor (Ong et al., 2000). Detecting polluting gases using CNT arises due to its high surface area which provided by central hollow cores and outside side-walls that leading to the change in the electrical conductivity at room temperature on exposure to gas analyte. The electrical resistance in MWCNTs is mainly determined by the atom at the surface which means that no diffusion is required thus causing impact on the response time of the gas sensor. Vital role in the process of gas-sensing can be achieved by modifying the surface of the CNT thus altering the electronic properties of CNT effectively.

CNTs are very difficult to break down physically because of its agglomerate structures. This cause the fabrication of homogeneous nanocomposites with carbon tubes remains a challenge. The fabrication of nanotubes-polymer composites were generally by direct mixing or in situ polymerization. From through study we can say that in situ polymerization is a better way for homogenous dispersions because nanotubes are more likely to disperse in a precursor monomer than in the polymer.

Ajayan et al. (1994) initially reported about carbon nanotubes-polymer composites which what they did just mechanically mixed the purified MWNTs with epoxy resin, resulting high attention to composite materials with uniform and high nanotubes loading. It is known that, epoxy composites are most widely studied as nonconjugated polymer-based composites. Untreated CNTs dispersed in an epoxy matrix were reported by Sandler et al. (1999), it reduces the percolation threshold to below 0.04 wt%, and increases the overall conductivity. Even though the extreme stirring and ultrasound in ethanol process enhance the dispersion of the nanotubes, there is still possibility for it to break up all the entanglements of the CNTs (Sandler et al., 1999). To enhance dispersion and thermomechanical properties of

CNTs/polymer(epoxy) composites Gong st al. (2000) has reported that to use surfactants as wetting agents, however even with the addition of the surfactant, complete homogeneous dispersion of the nanotubes cannot be obtained (Gong et al., 2000).

2.2 Polymeric membrane preparation

2.2.1 Phase Inversion

The most versatile technique to prepare polymeric membranes is phase inversion. Many of morphologies can be obtained that are suitable for different applications, from microfiltration membranes with very porous structures, to more dense reverse osmosis membranes, to gas separation and pervaporation membranes, with a complete defect-free structure. The overviews of the techniques that are commonly implied for the preparation of synthetic polymeric membranes are shown in Table 1. It is well known that, phase inversion is the most commercially available membranes preparation by which the process transformed a liquid or soluble state to a solid state polymer. The first paper on the preparation of porous nitrocellulose membranes by phase inversion appeared in 1907, from that we can see the phase inversion technique has been available since decades ago (Bigelow and Gemberling, 1907).

Table 2.1**:** Frequently used techniques for the preparation of synthetic polymeric membranes

Process	Techniques
Microfiltration	Phase inversion, stretching, track-etching
Ultrafiltration	Phase inversion
Nanofiltration	Phase inversion, interfacial polymerization[a]
Reverse osmosis	Phase inversion, interfacial polymerization[a]
Pervaporation	Dipcoating[a], plasma polymerization[a]
Gas separation	Phase inversion, dipcoating[a], plasma polymerization[a]
Vapour permeation	Dipcoating[a]

[a] Support layer prepared by phase inversion.

Any polymer-solvent mixture that forms a homogeneous solution under specific conditions of temperature and composition, but separates into two phases when these conditions are changed can be used to synthesize membrane for phase inversion. As an example, volatile solvent from a homogeneous polymer solution or by cooling a casting solution which is homogeneous only at elevated temperatures can induce phase inversion (Durra, 1993). The available processes for the fabrication of integrally skinned asymmetric membranes from a homogeneous dope are abundant. There are three main processes in phase inversion which shown in Figure 2.1: (i) dry process, (ii) wet process, (iii) dry/wet process. Mainly the difference between the dry and wet process is whether the outlet of the spinneret or casting knife is submerged directly in a nonsolvent coagulant (Pinnau and Freeman, 2000).

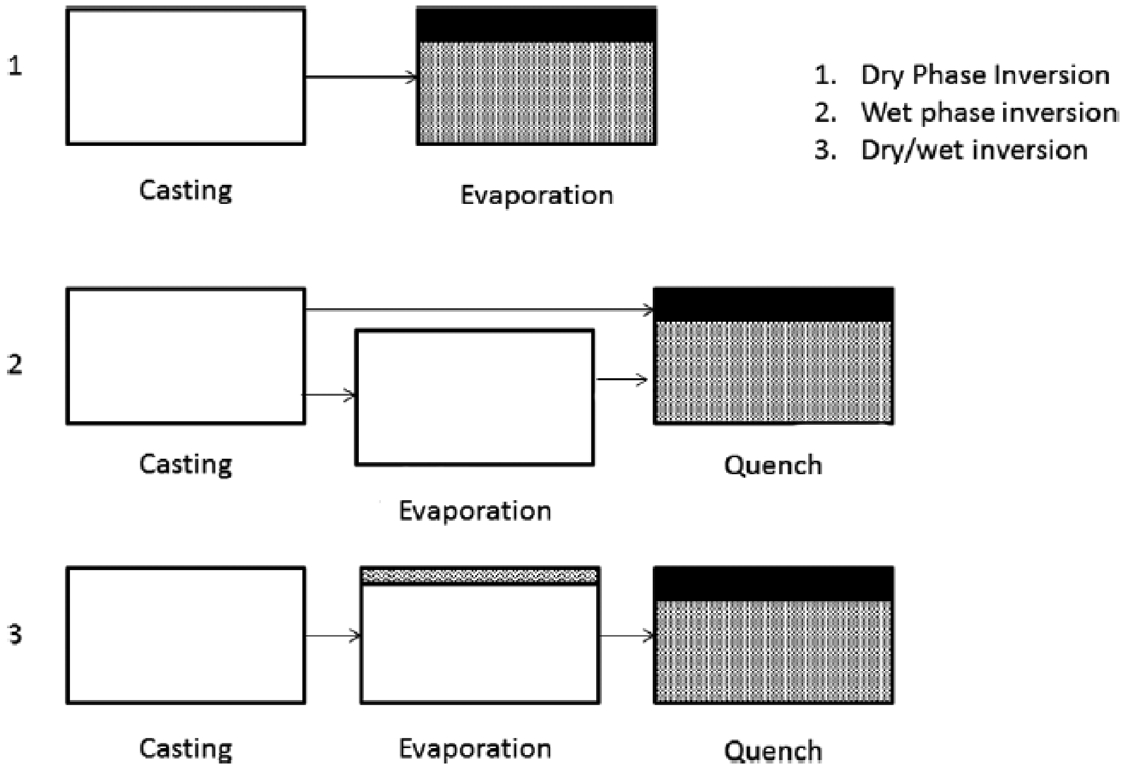


Figure 2.1: Phase-inversion processes (Pinnau and Freeman, 2000).

By combining two methods of immersion precipitation (wet phase inversion) and the dry-casting process (dry phase inversion), a new process called dry–wet phase inversion is created in which the dope solution is exposed to a nonsolvent vapour (usually water) for a while before immerse into a coagulation bath. The properties of the membrane can be altered by varying the casting solution and the formation conditions by changing the main factors, such as the composition of the polymer solution like additives, the temperature of solvent evaporation, also the coagulation media nature and temperature (Mosqueda-Jimenez et al., 2004). Furthermore, evaporation time and the relative humidity also have a great effect on the morphology and property of the membranes. For instance, researched on the duration of the evaporation step on the occurrence and prominence of macrovoid pores in cellulose acetate membranes via the dry–wet phase inversion process had been conducted by (Paulsen et al., 1994).

Moreover, a ternary diffusion model to analyse the mass transfer dynamics of the evaporation step the development have been developed by Tsay and McHugh (1991). Apart from that, in the recent papers there had been several morphological studies relating the relative humidity of the humid surroundings. Researched by Sun et al. (2007) had emphasized that the pore size was strongly affected by the relative humidity (RH) in the environment. The similar influence of the RH and a symmetric morphology were also reported by Park et al. (1999) for the polysulfone/NMP(N-Methylpyrrolidone) system and Caquineau et al. (2003) for polyetherimde/NMP system. The above systems shows the relation of the relative humidity were about the vapour-induced phase inversion. This shows that the relative humidity is also important to membrane performances and morphologies during dry–wet phase inversion, particularly for a hydrophilic casting system. Nevertheless, there are rarely reports on the relative humidity influence and evaporation time under a certain RH on membrane performance and morphologies for a charged casting system.

2.2.2 Solution-Casting Method

One of the oldest film productions is solution casting method. Later this method has been replaced with extrusion, pressing and polymer blowing from the melt. Nonetheless, it is still being used for fabrication of high quality thin films, particularly the combination of spin coating technique for substrates application. In this method there are various condition must be met which are the polymer must be soluble in a liquid solvent or in water, a solution with the appropriate viscosity should be formed, a homogenous film and easily extractable from the mould should be formed (Siemann, 2005).

Solution-Casting method is suitable for small-scale membrane samples preparation. With the use of casting knife the polymer solution is spread on a flat glass plate. The knife composed of a steel blade placed on two runners. After being left for solvent evaporation the thin film of the membrane were formed (Richard, 2004). Membrane fabricate using this method is crystalline and isotropic and the cost is cheap due to it simple operation (Zheng, 2009). There is a problem in the solution-casting method of formation of MMMs which is void creation between polymer and molecular sieve phase. Mahajan et. al. (2002) tried to solve and developed the membrane in two steps under high temperature. Various studies were performed for making casting solutions for MMM fabrication (Mahajan et al., 2002, Vu et al., 2003). These solutions were prepared by adding a molecular sieve to the solvent, and then a polymer powder was mixed into this slurry.

2.3 Mixed matrix membrane

Currently, numbers of different inorganic membrane materials are available commercially or have been investigated within the literature. Even though they pose good selectivities for a number of significant fermentative separations, there are still drawbacks to utilizing the inorganic membranes. Generally, the productions of membrane are brittle and difficult, and excess thicknesses of 10 µm usually are produced, causing in low permeances (Baker, 2004). Therefore, although there are a many of novel fabrication techniques being developed to reduce the cost of highly permeable inorganic membranes, inorganic membranes are still very expensive to produce (Buekenhoudt et al., 2010). Thus, mixed-matrix membranes (MMMs) have been developed to overcome the disadvantages of inorganic membranes.

In MMMs, inorganic materials were dispersed within a polymer matrix as shown in Figure 2.2 mainly to combine high separation performance of inorganic membranes with the processability and low cost of polymer membranes. Even though it has been enhance in permeabilities and separation aspects, most of polymer membranes also still suffer from various ageing processes over time and can be sensitive to the cleaning agents used in the removal of fouling from the membrane surface (Madaeni et al., 2015).

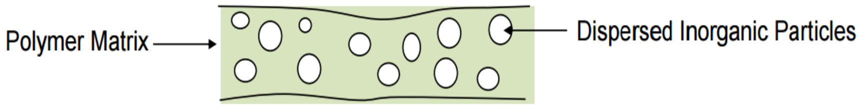


Figure 2.2: Schematic of a Mixed-Matrix Membrane (Christopher John Davey et al., 2016).

Nowadays, polymeric membranes are widely used in solvent dehydration. The performance of the membrane is depended on the material and structure of the membrane and its support. They assimilate high-selective diffusion and high-selective sorption that are dependent on the inter- and intra-molecular structure. They are made of rigid chain polymers that capable of interactions with ion–dipole or hydrogen bonding with water. Polymeric membranes with hydrophilic trait act as molecular sieves that are durable to water and prefer water molecules over other molecules in the process stream. (Semenova et al., 1997) mention that to have high sorption centres needs a good polymer for the selective permeation of water. It must interact with water by the action of dipole-dipole, ion-dipole action (In the case of a polyelectrolyte) and/or hydrogen bonds. Therefore selecting a membrane which has one of the features that are incorporated in the polymer chains or modify present membrane to include those features is frequently justified.

2.3.1 Poly (vinyl alcohol)

Poly (vinyl alcohol) (PVA) films show high wear resistance, elongation, tensile strength, and flexibility. PVA is a hydrophilic polymer used in a number of commercial membranes having excellent water perm-selective properties. The effect of the degree of crosslinking on the performance of PVA membranes was studied by Huang (1991) and he was one of the first to study PVA membranes for pervaporation. PVA membrane cross-linked with amic acid was studied at the operating temperature of 45 ◦C using a 50% ethanol feed mixture achieving a separation factor of around 100 with a flux of 0.25 kgm^{-2} h^{-1}. This show that PVA a successful membrane for alcohol dehydration and thus lead other researchers to investigate PVA-based membranes for pervaporation.

There are studies in the surface modification of PVA by reacting it with monochloroacetic acid (Kang et al., 1990). This modification introduces carboxylic acid groups on to the surface of the membrane resulting in increasing the membrane hydrophilicity. Apart from that this surface modification also causing perm-selectivity almost doubled compared to the cross-linked PVA and a slight increase in flux. The research on the membrane surface and support was conducted to determine it effect on separation performance and conclude that both played a major role in overall separation

PVA also have been studied by Praptowidodo (2005) on how the degree of cross-linking in the PVA membrane affected performance. He utilization Glutaraldehyde as the cross-linking agent and copolymer membranes of polyvinyl alcohol-co-itaconic acid (PVA-It) and fabricate polyvinyl alcohol co- *N*-3-trimethyl-ammonio-propyl-acrylamide-chloride. The result of the membranes swelling was studied and it is found that membranes that were more highly cross-linked and with co-polymer membranes with a charged species present have lower swelling compared to PVA alone. In pure PVA membrane the increase of cross-linking and reduced swelling resulting to a reduction in flux and an increase in separation factor follow the theory by which reducing the free volume available for transport. Both PVA-It and PVA-N have lower fluxes than PVA but increased separation factors. The reason behind the improvement in water selectivity is due to the charged nature of the groups present in both these membranes.

From the researched by Lee et al. (1997) it showed that the degree of PVA hydrolysis was important to determined properties such as the polymer crystallinity and polarity. The result depicted the flux through the membrane was inversely proportional to the degree of hydrolysis and the separation factor was directly proportional and how crystallinity reduced flux by hindering solvent transport through the membrane. Nevertheless with the uses of PVA as the increased in hydrolysis the number of hydroxyl groups also increase and thus favours the transport of water resulting in increasing the separation factor.

2.4 Pervaporation Membrane

The main industrial applications in pervaporation from the beginning of research until today are the dehydration of organic solvents. However these membranes are susceptible to swell, so there is a need to modify the active layer of these membranes with different chemical compositions and structures which enabled the membrane to extract water with broad ranges of flux and selectivity (Zhang et al., 2010).

Many researchers have been investigating on hydrophilic membrane, which can be categorized into organic, inorganic, and organic-inorganic hybrid membranes (Wee et al., 2008). Generally, inorganic membranes such as zeolite and silica are used (Pereira et al., 2010). They are suitable for high temperature applications and harsh environments. These membranes are generally prepared by sol-gel method, which was appropriate to elaborate thin and porous layers with controllable porosity on a wide range of chemically resistant macroporous substrates (Agoudjil et al., 2008). Even though these inorganic membranes displayed high dehydration efficiency, due to its complicated large-scale preparation and high manufacturing cost, it may slow down the industrialization process. Additionally, several kinds of commercial organic membranes including PERVAP 2201 (Delgado et al., 2010), PERVAP 1005 (GFT)(Krupiczka and Koszorz, 1991), and GFT-1005 (Benedict et al., 2006) have been introduced to the pervaporation-esterification hybrid process. Nevertheless, the applications of these organic membranes are limited due to their permanent instabilities.

It has been proposed that organic-inorganic hybrid materials are the best choice because of the stability of inorganic moiety and the functionality of the organic moiety. Budd et al. (2004) have utilized zeolite/polyelectrolyte (chitosan/poly(4- styrene sulfonate)) multilayer pervaporation membranes to improve the yield of ethyl lactate

Budd et al. (2004) and Adoor et al. (2008) prepared aluminum-rich zeolite beta incorporated with sodium alginate pervaporation membranes (Adoor et al., 2008). These organic-inorganic hybrid membranes showed enhanced performance with better flux and for dehydration of solution.

The uses of hydrophobic membranes in pervaporation membrane are used to separate volatile organic compounds from water. The hydrophobic systems utilize molecules made from proprietary polymeric hollow fiber membranes where it only allow the volatile organic compound and prevent water molecule from entering due to its hydrophobic nature. Therefore, the integration of pervaporation with membrane separation technology displays a good prospect in the separation of organic compounds such as pollutants and high-value products like aromatic compounds. The uses of polymeric membranes are very common (Vane, 2005). However the uses of ceramic are rarely but they still can be used (Qureshi et al., 2001). Despite that, when recovering volatile polar organics from very dilute solutions in water, the selectivity displayed by polymeric membranes and ceramic membranes are not high (Chang and Chang, 2004).

In organic separation, one of the most used polymeric materials is polydimethylsiloxane (PDMS). PDMS or commonly known as silicon rubber is the most widely studied hydrophobic material and regarded as the benchmark material in this application (Ong et al., 2016). Due to its flexible structure, It displayed high selectivity and permeability towards organic substances thus it was preferred for the organic compounds removal from water (Djebbar et al., 1998). To recover species like n-butanol and acetone from simulated fermentation broths, organic liquid membranes of oleyl alcohol (OA) were found that demonstrate high selectivity (Thongsukmak and Sirkar, 2007).

In pervaporation, the transport of component across the membrane is described by solution desorption model that first proposed by Thomas Graham (Ong et al., 2016), which results these processes in series: (1) diffusion of the component through the liquid boundary layer to the membrane surface, (2) sorption/diffusion into the membrane, (3) transport through the membrane, and (4) diffusion through the vapor phase boundary layer into the bulk of the permeance as shown in Figure 6. When modelling the transport model for pervaporation, we need to assume that the boundary layer resistance at the vapor phase is negligible and due the permeant side is maintained at a low vacuum the concentration assumed is zero. However, when the increasing permeant pressure, the resistance to transport on the vapor side will increase and become significant.

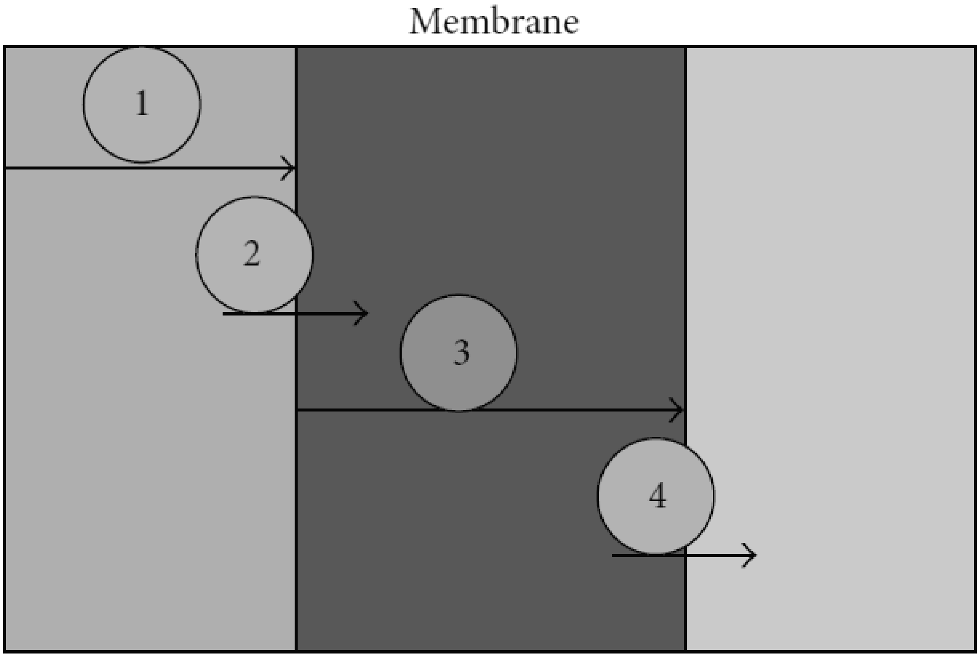


Figure 2.3: Steps involved in transport of component through a pervaporation membrane (Ghoshna et al., 2015).

2.5 Pervaporation

Membrane is an interphase between two adjacent phases that act as a selective barrier which regulate the transport of substances between the two compartments and prevents unwanted solutes from permeating through causing the impurity to be separated from the target (Ulbricht, 2006). The selective barrier can be classified according to their porous characters which are named as microfiltration, ultrafiltration, and nanofiltration membranes as shown in Figure 7. Membranes are either porous or nonporous and the separations are based on sizes, commonly porous membranes are used. The separation specifications for pervaporation are different since it is the distinction class among above membranes. The membranes for pervaporation are nonporous and have been widely utilized for liquid mixtures separation. The separation is based on affinity of the feed with membrane materials, when the feed molecules have higher affinity it will be adsorbed and diffuses through the membrane while feed molecules having low affinity are retained.

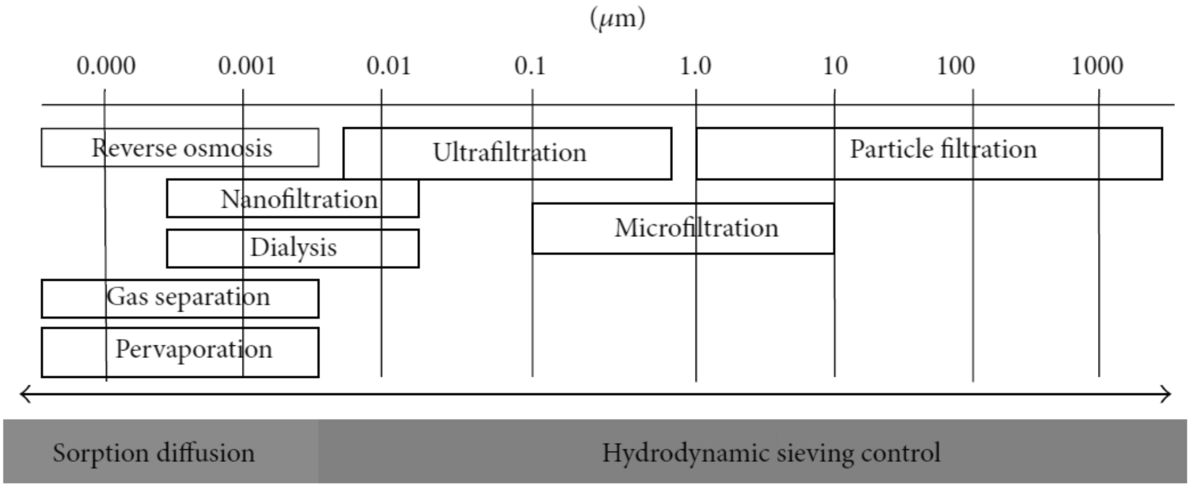


Figure 2.4: The choice of membrane with respect to the size of particles encountered (Ghoshna et al., 2015).

Pervaporation is a type of membrane-based separation technology. It have advantages over conventional separation techniques such as distillation and absorption processes in separating azeotropic mixtures, organic–organic mixtures and thermally sensitive compounds, in addition in removing dilute organic compounds from wastewater (Smitha et al., 2004). The separation principle in pervaporation is by separation of liquid mixtures by partial vaporization through a membrane (nonporous or porous), resulting in accumulation of permeating component in vapor form that can be removed by flowing an inert medium or applying low pressure on the permeant side. The pervaporation process driving force is the difference in chemical potential, correlate with the concentration gradient between phases on the opposite sides of the interfacial barrier. Sorption diffusion model is used to describe the transport mechanism of pervaporation based on the basis of difference in the molecular size instead of volatility as in the case of distillation (Ong et al., 2016) and could effectively acts as substitute for azeotropic separation. In addition, pervaporation does not use additional third component as in azetropic distillation and it is low energy consumption (Crespo and Brazinha, 2015).

Over the last decades, researcher have found a wide range of areas for it pervaporation application such as liquid hydrocarbons separations for petrochemical application, alcohol/ether separations (Aouinti et al., 2012), volatile organic compounds (VOCs) removal from water (Kujawa et al., 2015), water removal from glycerin (Mah et al., 2009), and dehydration to intensify esterification reaction (Delgado et al., 2009). Based on these applications, pervaporation are a single process that often need to compete with conventional processes like distillation, liquid–liquid extraction, adsorption, and stripping, which are much reliable and have thoroughly imply in industries.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Table 3.1: List of the purchased material with it specification and supplier.

Materials	Specification	Supplier
PVDF Pallets	Average M.W~180,000 by GPC	Sigma Aldrich
Dimethylformamide (DMF)	99.8%	Sigma Aldrich
PVA	96% hydrolysed	Acros Organics
CNT	> 95 wt% with -COOH 2.56 wt%	Timesnano
Ethyl Alcohol	96%	Acros Organics
De-Ionized Water	N/A	Produce in Lab
Dacron fabric	Style 0715	Texlon/USA

3.2 Membrane preparation

3.2.1 Preparation of PVDF/non-woven cloth membranes

PVDF/non-woven cloth membranes were prepared by phase inversion method. 15 gram of PVDF was dissolved in 47.8 ml of DMF at 80°C under a constant stirring rate for overnight to form a homogenous PVDF casting solution. The obtained casting solution was uniformly spread on non-woven cloth which was prior wrapped onto a glass plate. After the nascent membrane was evaporated in the air for 10 s, it was transferred into the coagulation bath composed of de-ionized water at room temperature for 15 minutes. Subsequently, the membranes were dried at room temperature overnight. The obtained membranes were cut with diameter 47mm and stored for further uses.

3.2.2 Preparation of PVA/ PVDF/non-woven cloth membranes with and without CNT filler.

PVA-CNT/PVDF/non-woven cloth homogeneous nanocomposite membranes were prepared by casting a blend of PVA solution containing 0.01 wt % amount of MWCNTs. First of all, an aqueous solution of PVA was obtained by dissolving 5 g of PVA powder into 95 ml of de-ionized water at 90ºC with constant stirring for overnight. Subsequently, a PVA-CNT solution was prepared by dispersing 5 mg of MWCNTs into 50 g of PVA aqueous solution and the resultant solution was sonicated for 20 min using an ultrasonic water bath to facilitate the dispersion. The PVA-CNT solution then was stirred overnight to form a uniform suspension, and then used for membrane fabrication. Dense films of PVA-CNT/PVDF/non-woven cloth were formed by casting the PVA-CNT solution on a petri dish with diameter 50 mm, followed by covering the top of solution with 47 mm diameter PVDF/non-woven cloth membrane and let it evaporate for 3-4 days. The PVA/PVDF/non-woven cloth membrane also formed with same technique but without CNT filler.