

POLY (VINYLIDENE FLUORIDE) (PVDF) MEMBRANES FOR PERVAPORATION OF BUTANOL/WATER MIXTURE: FABRICATION, CHARACTERIZATION AND APPLICATION

by

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LIST OF ABBREVIATIONS

ABE	Acetone-butanol-ethanol
BET	Brunauer, Emmet, Teller gas adsorption
DMAc	N,N-dimethyl acetamide
FTIR	Fourier transform infrared spectroscopy
IL	Ionic liquid
NaCl	Sodium chloride
N_2	Nitrogen gas
NMP	Nitrogen gas N-methyl-2-pyrrolidinone
FTIR	Fourier Transform Infrared Spectroscopy
EDS	Energy Dispersive X-ray Spectroscopy
PDMS	Polydimethylsiloxane
PES	Polyethersulfone
PI	Polyimide
РР	Polypropylene
PS	Polysulfone
PTFE	Polytetrafluoroethylene
PVDF	Poly(vinylidene fluoride)
RTIL	Room temperature ionic liquids
SEM	Scanning Electron Microscope
SILM	Supported Ionic Liquid Membrane
SLMs	Supported liquid membranes
TEP	Triethylphosphate
TIPS	Thermally induced phase separation
IP	Immersion precipitation

LIST OF SYMBOLS

V _{total}	- Total pore volume
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D_v	-	Volume pore size distribution
J	-	Liquid Flux across membrane
μ	-	Viscosity of water
3	-	Porosity
δ_{tP}	-	Total solubility parameter
Wa	-	Adsorbed mass at standard temperature and pressure
Wm	-	Maximum adsorbed mass at standard temperature and pressure.
P/Po	-	gas pressure relative to its saturation pressure
S	-	Specific surface area (m^2/g)
Ν	-	Avogadro number (6.022 x 10^{23}) atoms or molecules/mole
А	-	Cross sectional area of the absorbed gas molecule (cm ²)
М	-	Mass of the material tested (g)
Q	-	Weight of the collected butanol permeate (grams) passing through the
		membrane
A _m	-	Membrane surface area (cm ²)
t	-	Elapsed time (hour)
X_B	-	Butanol weight fractions in the feed

$\mathbf{Y}_{\mathbf{B}}$	-	Butanol weight fractions in the permeate
X _{H2O}	-	Water weight fractions in the feed
Y _{H2O}	-	Water weight fractions in the permeate
rpm	-	Revolutions per minute
m _p	-	Mass of the dry membrane
m _n	-	Mass of the absorbed octanol
$ ho_p$	-	Density of the PVDF membrane
ρ _n	-	Density of octanol.
	O T	Mass of the absorbed octanol Density of the PVDF membrane Density of octanol. Density of octanol.

POLY (VINYLIDENE FLUORIDE) (PVDF) MEMBRAN UNTUK PENYEJATTELAPAN CAMPURAN BUTANOL/AIR: PENGHASILAN, PENGHASILAN, PERINCIAN DAN APPLIKASI

ABSTRAK

Polemerik poly(vinylidene fluorida) (PVDF) membrane telah digunakan dalam pelbagai proses di mana satu daripada kegunaan ini adalah penyejattelapan. Dalam kajian ini, PVDF membran dengan mikrostruktur yang tak simetri telah difungsikan dengan cecair ionik untuk pemisahan butanol terpilih dalam campuran air melalui proses membran penyejattelapan. Penghasilan PVDF membran berprestasi tinggi masih lagi memberi cabaran dan sukar untuk dilaksanakan. Kajian ini menekankan penghasilan pelimerik membran dari polimer jenis poly(vinylidene fluorida) (PVDF) dengan penambahan N-Metil-2-Pyrrolidinone sebagai satu pelarut disediakan dengan memanipulasikan beberapa parameter yang optimum. Untuk menghasilkan polimerik menghasilkan keadaan membran bagi membran yang optimum, pembentukan struktur "finger-like" perlu ditingkatkan dengan memanipulasi dua parameter utama iaitu, kepekatan etanol didalam larutan pembekuan (0 w/w % sehingga 75 w/w % kepekatan etanol) dan masa penyejatan (0 minit sehingga 3 minit) semasa "phase inversion". Teknik-teknik perincian bahan komprehensif melalui mikroskop elektron pengimbasan (SEM), Spektroskopi infra-merah jelmaan Fourier (FTIR) Spectroscopy, analisis luas permukaan BET, analisis keliangan bahan dan spektroskopi x-ray (EDS) telah diikuti tenaga sebaran untuk menentukan sifat rekaan membran dan ciri bahan sedia yang ada. Dalam ujian prestasi membrane menggunakan eksperimen penyejattelapan, suhu dan kadar kesan aliran suapan dikaji untuk mendapatkan hasil produk yang tinggi. Suhu 50°C dengan kadar aliran 20L/j merupakan keadaan optimum untuk proses ini. Menggunakan membran PVDF jenis 15 w/w % kepekatan etanol dan masa penyejatan 2 minit menghasilkan factor pemisah yang tinggi iaitu 32 dan fluk yang rendah iaitu 4.9 kg.m⁻²j⁻¹ berbandingan jenis membrane yang lain. Dengan menambah cecair ionic pada membrane jenis tersebut mengakibatkan peningkatan faktor pemisah dari 32 hingga 78. Sementara itu fluks juga bertambah dari 4.9 kg.m⁻²j⁻¹ kepada 7.9 kg.m⁻²j⁻¹.

POLY (VINYLIDENE FLUORIDE) (PVDF) MEMBRANES FOR PERVAPORATION OF BUTANOL/WATER MIXTURE: FABRICATION, CHARACTERIZATION AND APPLICATION

ABSTRACT

The polymeric poly (vinylidene fluoride) (PVDF) membranes are in current used for a number of process applications in which one of these applications are pervaporation. In this work, PVDF membrane with controlled asymmetric microstructure has been functionalised with ionic liquid for selective separation of butanol in water mixture via membrane pervporation process. The fabrication of polymeric membrane from poly (vinylidene fluoride) (PVDF) polymer with N-methyl-2-pyrrolidinone (NMP) serves as a solvent is prepared using phase inversion method with several parameters to produce the optimum membrane condition. To produce the optimum polymeric membrane, the formation of finger-like structure needs to be increased by manipulating two major parameters, the coagulation bath medium (0 until 75 w/w% ethanol concentration) and evaporation time (0 minutes to 3 minutes) during phase inversion. Comprehensive material characterization techniques via scanning electron microscopy (SEM), fourier transform infrared (FTIR) spectroscopy, surface area analysis, porosity analysis and energy dispersive x-ray spectroscopy (EDS) were followed to ascertain the nature of the membrane fabrication and their inherent material properties. In membrane performance test using pervaporation experiment, the effect of feed temperature and feed flow rate was investigated in order to get the optimum membrane separation. Temperature 50°c with the flow rate 20 L/hr had become optimum condition for this process. Using PVDF membrane with 15 w/w% ethanol concentrations at 2 minutes evaporation time gives better selectivity with higher separation factor (32) and low permeation flux (4.9 kg m⁻² hr⁻¹) compared to other type of membrane. This type of membrane was improved by adding the ionic liquid and results in increasing the separation factor from 32 to 78. Meanwhile the permeation flux also increases from 4.9 kg m⁻² hr⁻¹ to 7.9 kg m⁻²hr⁻¹.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The increasing price of petroleum due to its high demand and shortage contributes to the utilization of biofuels produced from renewable biomass. Currently, butanol has been widely used as a biofuel. Butanol as a new liquid fuel has superior properties such as having higher energy content, low evaporative losses, being easier to transport, and it can be directly used without modification to the car engine (Liu et al., 2011). One of the largest biotechnological processes that produce butanol are from acetone-butanol-ethanol (ABE) fermentation. Butanol is conventionally produced by ABE fermentation through the anaerobic conversion of carbohydrates by strains of *Clostridium* into acetone, butanol and ethanol. Biobutanol can be found from sugar cane, sugar beet and sugar cereal crops, and can also be produced from *cellulosic* raw materials (Meagher and Huang, 2001). However, due to price issues, relatively low yield and sluggish fermentations, as well as problems caused by end product inhibition and phage infections (Meagher and Huang 2001).

In the recovery of butanol, several methods can be applied such as adsorption, distillation, gas stripping, membrane reactor and pervaporation. Traditionally, distillation process is the method to remove butanol from fermentation broth using boiling point difference to purify the mixture. However, this technique requires much energy and increases the cost due to butanol has a higher boiling point compare to water (Kaminski et. al., 2011). Adsorption is another method to remove butanol from fermentation broth using silicalite as a common absorbent in this process. Nevertheless, this separation

cannot be used on industrial or semi-industrial plant due to small-capacity of adsorbent for butanol (Kaminski et. al., 2011). Another option of butanol to remove is by immobilization of microorganisms in membrane or the use of membrane reactors. In industrial scale, this method gives plenty of disadvantages like low mechanical strength, increase mass transfer resistance and leakage of cells from the matrices (Kaminski et. al., 2011). Among these techniques, pervaporation is the most promising option due to its general advantages in environmental issues which no harmful effects on microorganisms. Besides that recovery of butanol using pervaporation technique can be done in a single step without alcohol recovery from extractants with low energy requirement (Liu et al. 2011)

Polyvinylidene fluoride (PVDF) received great attention as a membrane material due to its outstanding properties such as thermally stable, possessing high mechanical strength and having excellent resistance to the most corrosive chemical and organic compounds. PVDF, a semi-crystalline polymer is a popular membrane material which is relatively more hydrophobic compared to other materials such as polysulfone (PS), polyethersulfone (PES) and polyimide (PI) (Ooi et. al., 2012). Although polypropylene (PP) and polytetrafluoroethylene (PTFE) are more hydrophobic than PVDF, these materials are limited by the complexity in solvent selection during the phase inversion process.

In preparing the PVDF, there are several different methods that can be used to produce specific membrane morphologies and properties to suit application requirement (Liu et al., 2010). One of the methods is a phase inversion, also known as a de-mixing process where a polymer solution transforms from a liquid to a solid phase. The homogeneous casting solution is cast into thin film membrane and then submerged in a non-solvent coagulation medium. The membrane is formed by demixing of the solvent solution and the precipitation of the polymer. This process is also known as solution precipitation or polymer based on the phenomenon of liquid-liquid phase separation, and it is commonly used in preparing a variety of polymeric membranes. In polymeric membrane formation, the immersion precipitation technique is commonly used which the polymer solution casts on a support and immersed into a coagulation bath containing a non-solvent. At this point, the skin or out layer is formed by gelation, and the porous sublayer is the result of liquid-liquid phase separation by nucleation and growth (Ahmad et. al., 2012).

The physio-chemical properties which is viscosity of the polymer casting solution effect the microstructure of membrane. The two main asymmetric membrane microstructure included sponge-like structure and finger-like structure. The membrane performance and morphologies depend on experimental parameters such as composition of casting solution (polymer concentration, type of solvent and non-solvent), the thickness and temperature of casting polymer film, the time and temperature of evaporation prior to immersion, relative humidity, the composition and temperature as the coagulation bath (Ahmad, 2012).

1.2 Problem Statement

The Prepavoration technique has been proven to be a suitable extraction method to separate organic solvent, including butanol from ABE fermentation broth. This method involves the selective transport by diffusion of some components through a membrane. Supported liquid membranes (SLMs) have become a tremendous potential in different application. However, this SLMs have poor stability due to loss of the organic phase. Recently, researchers have reported that SLMs impregnated with Ionic Liquids(IL) achieved selective transport of organic compound such as amines, alcohols, organic acids, ketones, ethers, aromatic hydrocarbons, mixed gases and metal ions. In separation of hydrophobic n-butanol from ABE fermentation broth, hydrophobic membranes such as polysiloxane, polyether block amide and poly(vinylidene fluoride) (PVDF) (Lozano et. al., 2011) By mixing the PVDF solution with an ionic liquid for separation of acetone and 1-butanol, the permeability and separation factor are enhanced. However, the liquid supported membranes have mechanical issues which; lacking long-term stability, caused by the leaking of the ionic liquid from the membrane due to the large pressure differences during the pervaporation process. In this study, the mixture of butanol-water solution has been used and attempts are being made to improve membrane stability, flux and permeation through the addition of ionic liquid.

1.3 **Research Objectives**

The objectives of the project are:

- 1. To study the parameters to achieve optimum membrane structure and control the morphology with respect to the formation of finger-like structure and sponge-like structures.
- To prepare the ILs incorporate with PVDF support membrane using the phase 2. inversion technique.
- To characterize the polymeric membrane by evaluate the physio-chemical 3. properties.
- To evaluate the performance of ILs incorporates with PVDF support 4. inalcop membrane in pervaporation experiment.

1.4 Scope and Significance of Research

This research is focus on the preparation of polymeric membrane and functionalized this membrane using ionic liquid by studying the effects of certain parameters. To produce the optimum polymeric membrane, the formation of finger-like structure needs to be increased by manipulating two major parameters, the coagulation bath medium and evaporation time during phase inversion. These techniques will influence the membrane structure formation allowing higher ionic liquid uptake during the impregnation process. In this research, the performance of the membrane is investigated using the pervaporation technique by separating the mixture of butanol/water.

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Polymeric Membrane

In general, a membrane can be defined as a barrier which not necessarily solid that separates two phases as a selective wall to the mass transfer, making the separation of the components in a mixture possible (Mulder, 2000). In order to produce the excellent membrane, the membrane should be designed to have a high and stable filtration flux, low filtration pressure, and a simple and highly reliable process based on the use of membrane (Ng et. al., 2013).

A polymeric membrane is a microporous film which acts as a semi-permeable barrier to separate two different medium phase (Mathias, 2006). The major benefits of polymeric membranes have overconventional counterpart technologies are low operation cost and complicity with environmental regulator (Ng et. al., 2013). There are several methods to prepare the polymeric membrane such as preparation by evaporation, vapour phase, control evaporation thermal precipitation and immersion percipitation. Among of the techniques, evaporation is simplest way of polymeric membrane and this method gives a relatively thick membrane (Mulder, 2000). However, to prepare integrally skinned dense membranes with a thin selective layer, the phase inversion technique can be applied. In this method, a polymer solution is brought into contact with an appropriate non-solvent, leading to the precipitation of the polymer. The membrane formed will have a top layer with carefully controlled pore structure and a porous support layer which provides its mechanical resistance (Johannes, 2013). The use of polymeric membranes has increased in popularity recently in a wide range of applications due to its various advantages such as easy-forming properties, selective transfer of chemical species, and inexpensive (Ng, 2013).

In commercial use, inorganic membranes commonly composed of metal oxides are currently in competition with polymeric membrane. Inorganic membranes are more resistant to chemical attack, have good mechanical strength, and high tolerance to pH extremes and oxidation. However, inorganic membranes are not used extensively because of its high costs, harsh operational environments and relatively poor control in pore size distribution. Thus, the use of organic-inorganic polymer hybrids has been considered as an approach to make polymeric membranes more attractive for Classification of Membrane Polymer commercialization (Ng, 2013).

2.2

Membrane can be classified according to structure, morphology and application. Symmetric membrane and asymmetric membrane are the two types of membrane. The thickness of symmetric membranes (porous and nonporous) ranges roughly from 10 to 200 µm. A decrease in membrane thickness result in an increased permeation rate. Most commercially available membrane is in asymmetric structure. An asymmetric membrane has either a thin microporous or dense permselective layer supported by a more-open porous substrate (Mulder, 2000).

Porous Membrane 2.2.1

Porous membranes with fixed pores in the range $0.1 - 10 \ \mu m$ are called microporous, and 2 - 100 nm is used in ultrafiltration (Mulder, 2000). The selectivity and transport rate are mainly influenced by viscous flow, and sieving or size exclusion (Ulbricht, 2006). Hydrophobic membranes such as polytetrafluoroethylene (PTFE), poly (vinylidene fluoride) (PVDF) and isotactic polypropylene (PP) are often used as microfiltration membranes. PVDF has good thermal and chemical resistance and high solubility in aprotic solvents such as dimethylformamide (DMF) and triethylphosphate (TEP). These qualities make PVDF suitable for preparation by phase inversion technique. PVDF also exhibits hydrophobic behaviour, which means water cannot wet these membrane spontaneously. The membrane can be used in membrane distillation, simply because they are not wetted by water or other liquids with high surface tension (Mulder, 1 copyright 2000).

2.2.2 **Nonporous Membrane**

Nonporous membrane is regularly used in gas and vapour separation particularly in membrane pervaporation process. A composite and asymmetric type membrane is commonly used in these processes. Figure 2.1 shows a typical cross-sectional view of an asymmetric membrane which consists of two layers. The upper layer is a very thin dense layer (also called the top skin layer), and the bottom is a porous sub-layer. The top dense layer governs the permeation properties, while the porous sub-layer provides the mechanical strength (Khulbe, 2008). The permeability and selectivity of the membrane are determined by the material's intrinsic properties and its transport mechanism can be described by the solution/diffusion model (Ulbricht, 2006). In the asymmetric membrane, if the top layer and bottom porous sub-layer are made of the same polymer, the membrane is called an integrally skinned asymmetric membrane (Khulbe, 2008). If the top layer polymer type is different from the one that is the bottom porous sub-layer, the membrane is called a composite membrane (Mulder, 2000). One of the advantage of composite membranes have over the integrally skinned asymmetric membranes is that the material