BLENDED CHITOSAN AND POLY(VINYL ALCOHOL) MEMBRANES FOR THE PERVAPORATION OF METHANOL AND METHYL TERT-BUTYL ETHER

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To my beloved family

abah, umi, ekin, enun, ela, epa, apis, chik & adik

and my lovely husband, anas

Thanks for everything

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ABSTRACT

In this research project, blended chitosan/poly(vinyl alcohol) (PVA) membranes were produced by mixing PVA and chitosan solutions. Chitosan (CS) was first dissolved in acetic acid aqueous solution before PVA solution was added. The mixture was then cured at room temperature. The modified composite membrane was prepared by coating the mixture of chitosan and PVA solution onto the porous polysulfone membrane by the solution casting technique. The porous polysulfone substrate was prepared via phase inversion process from a casting solution containing 12 wt% polysulfone, 11 wt% polyethylene glycol and 77 wt% N,N- dimethylacetamide. The weight percent of chitosan in the membrane was varied from 20 wt. % to 100 wt. % while the membrane thickness was in the range of 15-30 µm. The unmodified and modified composite membranes with PVA were used in pervaporation separation of methanol/methyl-tert-butyl ether (MTBE) mixture. The swelling degree and the total flux increased with increasing chitosan content in the membranes. 30 wt. % of methanol (MeOH) in feed was chose since it gave the optimal overall pervaporation characteristics in terms of flux and separation factor. The membrane containing chitosan 20 wt. % to 40 wt. % performed the best. At operating temperature of 50 ^{o}C for 20 wt % to 40 wt % of chitosan, the fluxes obtained are at 52.28 g/m^2.hr and 66.92 g/m^2.hr with the separation factors of 81.00 and 53.22 respectively. The effect of temperature on flux followed the Arrhenius relationship. The membrane showed excellent performance for separation of MeOH/MTBE mixture when the quantity of MeOH in feed is small. It is a very suitable process for the recovery purpose in order to remove excess MeOH in the MTBE system.

ABSTRAK

Dalam kajian ini, membran campuran kitosan/poli(vinil alkohol) (PVA) telah dihasilkan dengan mencampurkan larutan PVA dan larutan kitosan. Kitosan (CS) telah dilarutkan terlebih dahulu dengan asid asetik sebelum larutan PVA dicampurkan. Campuran tadi kemudiannya dikeringkan pada suhu bilik. Membran komposit diubahsuai dengan menyelaput campuran larutan kitosan dan PVA ke atas membran poros polisulfona dengan menggunakan kaedah penebaran larutan. Membran poros polisulfona disediakan melalui proses pembalikan fasa daripada larutan penebaran yang mengandungi 12 % berat polisulfona, 11 % berat polietilen glaikol dan 77 % berat N,N-dimetilasetamida. Peratusan berat kitosan dalam membran adalah antara 20 % hingga 100 % manakala ketebalan membran adalah dalam lingkungan 15-30 µm. Membran komposit yang tidak diubahsuai dan yang diubahsuai dengan PVA ini digunakan dalam proses penelapsejatan untuk pemisahan campuran azeotropik metanol (MeOH) dan metil tert-butil eter (MTBE). Darjah pembengkakan dan jumlah penyerapan fluks meningkat dengan peningkatan kandungan kitosan di dalam membran. 30 % berat metanol di dalam suapan dipilih kerana sifat penelapsejatan yang optima secara keseluruhannya dari segi fluks dan faktor pemisahan. Membran yang mengandungi 20 % berat hingga 40 % berat kitosan menunjukkan prestasi terbaik. Pada suhu operasi 50 ^{o}C bagi 20 % berat hingga 40 % berat kitosan, fluks yang diperolehi masing-masing ialah 52.28 g/m^2.j dan 66.92 g/m^2.j dengan faktor pemisahan sebanyak 81.00 dan 53.22. Kesan suhu terhadap penyerapan fluks adalah mengikut hubungan Arrhenius. Membran telah menunjukkan prestasi yang baik untuk pemisahan campuran MeOH/MTBE apabila kandungan MeOH dalam suapan sedikit. Ini adalah sesuai untuk proses perolehan semula untuk menyingkirkan lebihan MeOH dalam sistem MTBE.

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PV	pervaporation
MTBE	methyl-*tert*-butyl ether
PVA	poly (vinyl alcohol)
CS	chitosan
MeOH	methanol
PS	polysulfone
DMAc	N,N-dimetilacetamide
PDMS	polydimethyl siloxane
J	permeation rate, $g/m^2.hr$
α	pervaporation separation factor
x	weight fractions in the feed
y	weight fractions in the permeate
A_p	Arrhenius
A	area, m^2
t	time, hr
Q	weight of permeate, g

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CHAPTER 1

INTRODUCTION

1.1 Background

A membrane has been defined by the European Society of Membrane Science and Technology as "an intervening phase separating two phases and/or acting as an active or passive barrier to the transport of matter between phases. Membrane also can be simply defined as a barrier. This barrier separates two phases and restricts the transportation of various chemicals in selective manner. Geankoplis (2003) defines; membrane can act as a semi-permeable barrier where the separation occurs by the membrane controlling the movement of various molecules between two liquid phases, two gas phases, or a liquid and a gas phase.

Membranes can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid can carry a positive or negative charge or be neutral or bipolar. Transportation through a membrane can be affected by convection or by diffusion of individual molecules. Other factors are induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as

100 micron to several mms. A summary of technically relevant membranes, their structure and area of application is tabulated in Table 1.1.

Table 1.1: Properties and applications of technically relevant synthetic membranes (Strathmann, 1986)

Membranes	**Basic Materials**	**Manufacturing Procedures**	**Structures**	**Applications**
Ceramic membranes	Clay, silicate, aluminium oxide, graphite, metal powder	Pressing and sintering of fine powders	Pores from 0.1 to 10 micron diameter	Filtering of suspensions, gas separations, separation of isotopes
Stretched membranes	Polytetrafluoro-ethylene, polyethylene, polypropylene	Stretching of partially crystalline foil perpendicular to the orientation of crystallyst	Pores of 0.1 to 1 micron diameter	Filtration of aggressive media, cleaning of air, sterile filtration, medical technology
Etched polymer films	Polycarbonate	Radiation of a foil and subsequent acid etching	Pores of 0.5 to 10 micron diameter	Analytical and medical chemistry, sterile filtration
Homogeneous membranes	Silicone rubber, hydrophobic liquids	Extruding homogeneous foils, formation of liquid films	Homogeneous phase, support possible	Gas separations, carrier-mediated transport
Symmetrical microporous membranes	Cellulose derivatives, polyamide, polypropylene	Phase inversion reaction	Pores of 50 to 5000 nanometres diameter	Sterile filtration, dialysis, membrane distillation

Table 1.1: Properties and applications of technically relevant synthetic membranes (Strathmann, 1986) (*continued)*

Integral asymmetric membranes	Cellulose derivatives, polyamide, polysulfone	Phase inversion reaction	Homogeneous polymer or pores of 1 to 10 nanometres diameter	Ultrafiltration, hyperfiltration, gas separations, pervaporation
Composite asymmetric membranes	Cellulose derivatives, polyamide, polysulfone, polydimethylsiloxane	Application of a film to a microporous membrane	Homogeneous polymer or pores from 1 to 5 nanometres diameter	Ultrafiltration, hyperfiltration, gas separations, pervaporation
Ion exchange membranes	Polyethylene, polysulfone, polyvinylchloride	Foils from ion exchange resins or sulfonation of homogeneous polymers	Matrix with positive or negative charges	Electrodialysis, electrolysis

There are many reasons why the membrane separation process is commercially being practiced in industrial applications such as to recover hydrogen from off-gases, or to fractionate, concentrate and purify molecular solutions in chemical and pharmaceutical industry (Strathmann, 1986). The main reason is due to the fact that the membrane process replaces the conventional processes such as filtration, distillation, ion-exchange and chemical treatment systems which is more energy savings and environmental benign. On top of that, this ease of operational process is able to produce high and better quality products.

Nowadays, membranes are significantly being preferred in chemical technology and being used in variety of applications in our daily life routines. Various types of membrane separation have been developed for specific industrial applications such as reverse osmosis, ultrafiltration, microfiltration, electrodialysis, gas separation and pervaporation. Yamada and Nakagawa (1980) reported that membrane separation techniques have a great importance in chemical and petrochemical because it is believed to be much less energy consuming process than conventional separation techniques.

According to Bruschke and Tusel (1986), separation of liquid mixtures by means of membrane, whereby a vaporous product is obtained on the permeate side of the membrane, has been known for about 80 years. Separation of liquid mixtures using pervaporation process is considered as a basic unit operation with significant potential for the solution of environmental problem and energy cost compared to the distillation process (Kim *et al*., 2000). The separation mechanism in pervaporation is not based on the relative volatility of components like distillation process. It is based on the difference in sorption and diffusion properties of the feed components as well as permselectivity of the membrane (Dubey *et al*., 2005).

Pervaporation, which name originates from a combination of the terms permeation and vaporization, is a hybrid between a liquid and a gas separation process (Nawawi, 1997). There are three applications of pervaporation; dehydration of organic solvents (water removal from organics), removal of organic compounds from aqueous solution (organic removal from water) and the separation of organic mixtures like methanol and MTBE. Among the membrane processes, pervaporation technique is considered to be the best process in separating the organic mixtures especially for the close boiling point and azeotropic mixtures due to its high separation efficiencies coupled with energy saving (Durmaz-Hilmioglu and Tulbentci, 2004). Pervaporation is also being recognized as an effective process for separating mixtures consisting of heat-sensitive compounds and isomers (Kim *et al*., 2000).

The separation of methanol from methyl tert-butyl ether (MTBE) is an organic-organic separation whose economic importance has increased with the industrial production of octane enhancers (Gozzelino and Malucelli, 2004). MTBE is produced by reacting isobutene with excess methanol, and the reacted methanol is subsequently distilled off and recovered. However, the distillation of methanol (bp 64.7^{0}C) and MTBE (bp 55.3^{0}C) mixtures involves the formation of minimum-boiling azeotrope (bp 51.6^{0}C) (Ray *et al*., 1999) with a composition of 14.3 wt. % methanol at 760 mmHg (Yang *et al*., 1998) and it is very difficult to be separated (Kim *et al*., 2000). In the conventional process, the operation requires high capital cost and is not energy efficient. Therefore, pervaporation process has been considered as a favourable alternative separation technique for the separation of methanol and MTBE mixture.

The selection of the right polymer is a key in the development of pervaporation membranes. Membranes used for pervaporation separation process are generally dense (non-porous), homogeneous thin polymer films, or membranes that have a dense polymer top-layer (skinned of composite). In fact, the characteristics of pervaporation processes are a rate-controlled process. Thus asymmetric and composite membrane structures have been introduced into the membrane. The basic idea is to reduce the flow resistance by depositing thin and dense active layers on the supporting membrane (Huang *et al*., 1999).

Blending a hydrophilic polymer with a hydrophobic polymer can control the hydrophilic-hydrophobic balance properties of a membrane (Nawawi, 1997). Thus, an optimal combination of flux and separation factor can be achieved. A membrane with high flux gives a low separation factor and *vice versa*. Besides, the hydrophilic group swells the membranes significantly under aqueous mixture due to its plasticization action which results in poor separation factor (Huang and Xu, 1989; Uragami and Takigawa, 1990).

1.2 Problem Statement

Many studies have been done for chitosan as membranes (Nawawi, 1997; Hamdan, 1999; Yaakub, 1999; Yunus 1999; Muda, 2000; Nawawi and Pamin, 2000; Tan, 2000; Zakaria, 2000; Tan *et al*., 2002; Ahmad *et al*., 2005 and Taib, 2006) because of its good film forming properties, highly hydrophilic and good chemical resistant properties. However, Nawawi, (1997) found that chitosan has a reasonably poor stability in water and in aqueous mixtures because of the existing of amino group in its chain. The stability has to be improved to fully utilize its potential as a membrane especially in aqueous solution.

On the other hand, the separation factor or flux also needs to be improved in order to achieve a better result of separation. These problems may be solved by implementing some modifications. Many attempts have been made using various techniques to improve the separation factor of chitosan membrane and also to control degree of swelling by crosslinking, grafting, zeolite filled and blending. Researchers have reported modified chitosan membranes by blending it with other polymers such as PVA (Muthukamaru, 1999; Wei, 1999; Tan *et al*., 2001; Wong, 2002; Jalil, 2005 and Svang-Ariyaskul *et al*., 2006). As it is well known, PVA exhibit enhanced mechanical properties such as tensile strength, modulus elasticity and elongation (Mohd, 1999). Besides, its many hydroxyl groups cause it to have high affinity to water, with strong hydrogen bonding between the intra- and intermolecular hydroxyl groups, greatly impeding its solubility in water (Nawawi, 1997).

Tan *et al*. (2001) studied the separation of aqueous isopropanol through chitosan/PVA blended membranes by pervaporation. Yusof (2005) and Magedonna (2006) studied the pervaporation separation of ternary DMC/methanol/water mixtures and DMC/water respectively. Svang-Ariyaskul *et al*. (2006) studied the pervaporation dehydration of isopropanol using blended chitosan and PVA membranes. Through this research, blended chitosan/PVA membranes were used for the pervaporation separation of organic-organic solvent mixture which is methanol/methyl tert-butyl ether. Thus, it is best hope that the separation of methanol/MTBE will be improved after combination chitosan with PVA using pervaporation process.

1.3 Objective

Based on the background of this study, objectives of this study are categorized as following:

i. To determine an optimum preparation condition of chitosan composite based membranes for membrane pervaporation separation process.

ii. To analyze the performance of membrane in pervaporation separation of methanol/MTBE in terms of separation factor and flux using the membrane that has been developed.

1.4 Scopes of Work

In order to achieve the objectives mentioned in 1.3, below are the steps in order to accomplish this experiment. The scopes of work will be carried out:

i. Preparing unmodified chitosan/polysulfone composite based membrane where their characteristics will be studied.
ii. Preparing chitosan blended with PVA and polysulfone composite based membrane where their characteristics will be studied.
iii. Determining an optimum preparation condition chitosan composite based membrane for membrane pervaporation separation process. The composition chitosan and polyvinyl alcohol of modified composite membrane will be studied to reach the effective wt. % of chitosan-PVA membrane.
iv. Pervaporation separation of methanol/MTBE mixtures, the membranes will be used for separation of methanol/MTBE. This experiment will use several different feed compositions of methanol/MTBE mixture. This is to compare and investigate the effective composition of mixture for pervaporation. The membranes performance will be studied based on the flux and separation factor.
v. Determining the separation condition for the membranes been developed in the range of separation temperature at 27 ^oC, 35 ^oC, 40 ^oC, 45 ^oC and 50 ^oC while permeate pressure is maintained at 0.07 bar.
vi. Characterizing and determine the structure and morphology of modified and unmodified membranes using Nikon Microscopes and PHILIPS XL-40 Scanning Electron Microscopy (SEM).

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