

CHAPTER I

INTRODUCTION

Pervaporation, a type of membrane separation techniques, is well-known for separating azeotropic and close-boiling point mixtures. It plays an important role in production of ethanol fuel from ethanol-water mixture due to its advantages over the other separation processes in many aspects, including; less intensive energy, no azeotrope, no need for harsh chemicals, less space requirement for installation, etc. (O'Brien *et al.*, 2000). However, because the economic feasibility of the pervaporation is significantly dependent of the production cost and the membrane performance, thus, the deployment of a high performance membrane must be a major focus for developing a cost-effective ethanol manufacturing process (Di Luccio *et al.*, 2002).

A polymeric membrane is commonly selected due to its high processability and low production cost. One of the most interesting polymer for preparing a polymeric membrane is polybenzoxazine (PBZ), a novel class of high performance phenolic resin, due to its many interesting aspects, such as high thermal, chemical, and mechanical stability (Takeichi *et al.*, 2005). However, similar to most of the pervaporation membranes, partially crosslinked PBZ membrane still faced a problem of swelling, drastically reducing the membrane stability and separation performance (Pakkethati *et al.*, 2011; Qiao and Chung, 2005; Zhang *et al.*, 2006). To overcome this issue, use of the fully crosslinked polymeric membrane is one way for reducing the swelling and improving the membrane durability. Although an increase in the degree of the polymer crosslinking causes a reduction of the swelling behavior, the resulting lower permeation flux and flexibility become major drawbacks (Hilmioglu and Tulbentci, 2004; Praptowidodo, 2005).

The ceramic-supported, crosslinked polymeric membrane should be a promising solution for producing higher stability and separation performance of the membrane while

the permeation flux is still maintained if the thickness of the polymer membrane is thin enough (Huang *et al.*, 1999). Many researchers found that using a ceramic support could improve not only the membrane stability, but also its separation performance (Liu *et al.*, 2012; Zhu *et al.*, 2010).

Objectives

The purpose of this research is to determine the optimum conditions for preparing ceramic-supported PBZ-based membranes, which are; α -Al₂O₃ supported PBZ membranes, α -Al₂O₃ supported NaA-PBZ double layered membranes, and α -Al₂O₃ supported NaA-PBZ mixed matrix membranes (NaA-PBZ MMM), by investigating the effect of preparation parameters, such as; PBZ precursor concentration, dipping time, NaA zeolite coating time, and amount of NaA zeolite loading, on the membrane formation and performance of ethanol/water separation via pervaporation. The operation parameters, such as; feed ethanol concentration and operating temperature, were also studied and discussed, as well.

CHAPTER II

LITERATURE REVIEW

2.1 Bioethanol

Bioethanol is a natural alcohol obtained via fermentation, mostly from starches, sugars, and cellulosic materials, by microorganisms (Mamma *et al.*, 1996; Sheikh *et al.*, 2013). It was considered as a renewable energy source and has received more attentions as an alternative energy for replacing fossil fuel usage due to the increasing of global concerns about the depletion of fossil fuel in over the last decade (Tao *et al.*, 2005). However, due to the limitations of fermentation process, the produced ethanol has a very low concentration, approximately 10-12 wt%. To overcome the problem, a purification process is necessary (Chen *et al.*, 2014).

2.2 Pervaporation

2.2.1 Introduction to pervaporation technology

Pervaporation is a separation of liquid-liquid mixture using a selective membrane. It is a well-known technique that used to break the azeotropic mixture and separate close-boiling point mixture that cannot be accomplished by using normal distillation (Chapman *et al.*, 2008). Pervaporation is also known as a less energy-intensive technique for separating ethanol-water mixture when comparing to distillation and other conventional separating techniques (Kunnakorn *et al.*, 2013).

The liquid mixture is fed at upstream side (ambient pressure) to contact with the selective membrane that allows the desired component to transport through (which is called “permeate”) and prevents the other components from passing through (which is called “retentate”). Meanwhile, the downstream side is being held under

vacuum that causes permeate to be evaporated. The retentate is concentrated by recycling back to the feed reservoir, as shown in Fig. 2.1.

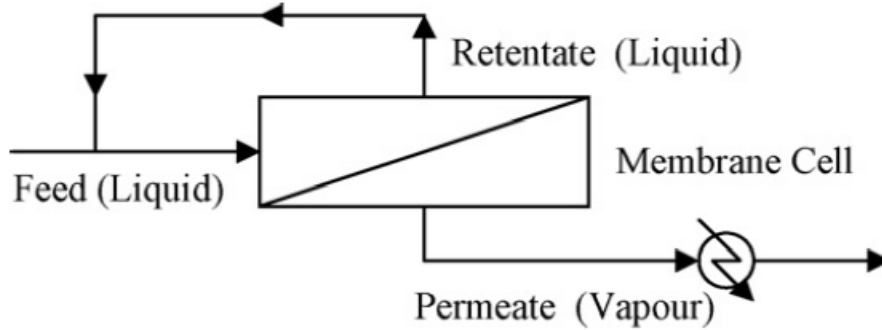


Figure 2.1 Schematic diagram of pervaporation process (Chapman *et al.*, 2008)

The pervaporation performance can be determined by two parameters, permeation flux and separation factor, that imply to productivity and quality of the separation, as given in eq. 2.1 and 2.2, respectively.

The permeation flux (J , $\text{g m}^{-2} \text{h}^{-1}$) is expressed as:

$$J = \frac{W}{A \cdot t} \quad (2.1)$$

where W is the weight of permeate (g), A is the effective membrane area (m^2), and t is the pervaporation time (h).

The separation factor (α , dimensionless) is expressed as:

$$\alpha = \frac{\left(\frac{w_{H_2O}}{w_{EtOH}} \right)_{Per}}{\left(\frac{w_{H_2O}}{w_{EtOH}} \right)_{Ret}} \quad (2.2)$$

where w_{H_2O} and w_{EtOH} are the weight fractions of water and ethanol from the permeate side (denoted as Per) and the retentate side (denoted as Ret), respectively.

2.2.2 Membranes for pervaporation dehydration of ethanol

To maximize the pervaporation performance, a development of membrane that has high separation performance, high chemical stability, and high mechanical strength must be a major focus (Sun *et al.*, 2013).

2.2.2.1 Polybenzoxazine membrane

Polybenzoxazine (PBZ) is a class of high performance thermosetting phenolic resin, obtaining from the polymerization of benzoxazine resin via thermally activated ring-opening reaction (Fig. 2.2). A primary amine, phenol, and phenolic compound are used as a starting materials for synthesize benzoxazine resin (Burke and Stephens, 1952; Ghosh *et al.*, 2007).

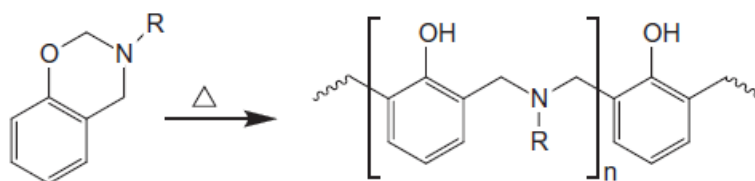


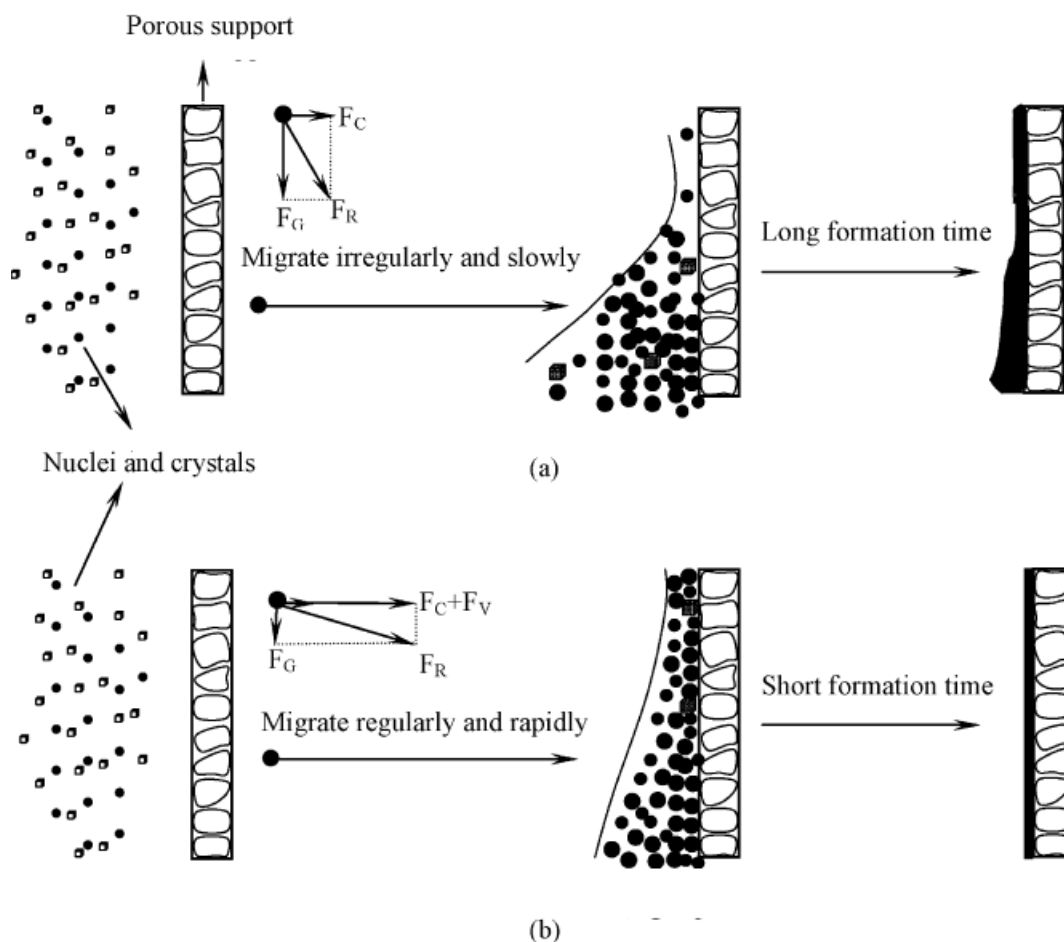
Figure 2.2 Benzoxazine polymerization (Hacaloğlu *et al.*, 2011)

PBZ has been attracted great attention for serving as separating membrane in pervaporation applications due to its high thermal, mechanical, and chemical stability (Takeichi *et al.*, 2005). The potential of using PBZ as the pervaporation membrane for separating ethanol/water mixture was studied by Pakkethati *et al.* (2011). They synthesized three different PBZs from bisphenol-A (BPA), formaldehyde, and three different primary diamines; hexamethylenediamine (HDA), tetraethylenepentamine (TEPA), and tetraethylenetriamine (TETA) to prepare poly(BA-hda), poly(BA-tepa), and poly(BA-teta) membrane, respectively. It was found that all PBZ membranes exhibited an excellent thermal stability up to 240 °C. The pervaporation of 10 wt% feed ethanol

mixture at 70 °C showed that the poly(BA-hda) membrane provided the highest durability with a service time longer than 120 h, a maximum permeation flux of $1.52 \text{ kg m}^{-2} \text{ h}^{-1}$, and separation factor of more than 10,000, indicating outstanding separation performance for the ethanol/water separation, leading to a great potential of using PBZ membrane in water/ethanol separation applications.

2.2.2.2 Sodium A (NaA) zeolite membrane

NaA zeolite (also referred as zeolite A or 4A zeolite) is sodium aluminosilicate with Linde Type A (LTA) framework. Because NaA zeolite has a well-defined pore opening of about 4 Å, it provides molecular-sieving effect for separating water (kinetic diameter of 2.6 Å) and ethanol molecules (kinetic diameter of 5.2 Å) (Shah *et al.*, 2000). In 2006, Kuanchertchoo *et al.* proposed an effective method for synthesizing uniform nano-sized NaA zeolite particles by using silatrane and alumatrane as a precursor. They also found that the optimum conditions for synthesizing the most uniform and smallest size of NaA zeolite particles was to use $\text{SiO}_2:\text{Al}_2\text{O}_3:3\text{Na}_2\text{O}:410\text{H}_2\text{O}$ synthesis formula with addition of 3 wt% NaA zeolite seed and using microwave heating at 80 °C for 6 h (Kuanchertchoo *et al.*, 2006). However, in order to prepare a NaA zeolite membrane, the continuous layer of NaA zeolite must be formed. One of the most effective technique to prepare a continuous NaA zeolite layer was proposed by Huang *et al.* (2004), see Fig. 2.3. They successfully synthesized NaA zeolite membrane on a tubular alumina support by using a technique called secondary growth with vacuum seeding method. The result showed that vacuum could help in reducing the influence of gravitational force on the NaA zeolite particles, allowing them to be attached on the support surface more homogeneously, resulting in the NaA zeolite membrane formed on the support more uniformly (Huang *et al.*, 2004).



F_C : capillary force, F_V : vacuum force, F_G : gravitation force, F_R : resultant force

Figure 2.3 Mechanisms of zeolite membrane formation by hydrothermal synthesis. (a) Without vacuum assistance, (b) with vacuum assistance. F_C : capillary force, F_V : vacuum force, F_G : gravitation force, and F_R : resultant force (Huang *et al.*, 2007).

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CHAPTER III

EXPERIMENTAL

3.1 Materials

Formaldehyde (CH_2O , 37 wt% in water; Merk), bisphenol-A (BPA, 97% purity; Aldrich), tetraethylenepentamine (TEPA, 85% purity, Aldrich) and diethylenetriamine (DETA, 99% purity; Aldrich), and hexamethylenediamine (HDA, 98% purity; Aldrich) were used for PBZ precursor synthesis in 1,4-dioxane (analytical grade; RCI Labscan) as a solvent. Ethanol (absolute; RCI Labscan) mixed with deionized water was used as pervaporation feed. Sodium hydroxide (NaOH , 99% purity; RCI Labscan), aluminum hydroxide hydrate ($\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$; Sigma), and fumed silica (SiO_2 , AEROSIL® 380; supported by Evonik) were used to synthesize NaA zeolite. Tubular α -alumina support with inner and outer diameters of 9 and 11 mm, respectively, was purchased from the National Metal and Materials Technology Center (MTEC). It was cut to 6 cm long, cleaned with deionized water using an ultra-sonic bath, dried in an oven, and calcined in a furnace at 400 °C for 3 h to remove any organic impurities before being used.

3.2 Synthesis of PBZ precursors

The PBZ precursor was synthesized using quasi-solventless method with 1:1:4 (phenolic compound : primary amine : formaldehyde) formula (Pakkethati *et al.*, 2011). Prior to the synthesis, phenolic compound (i.e. BPA) and primary amine (e.g. HDA, TEPA, and DETA) were prepared according to their state obtained from vendor, for example, BPA and HDA are solid at room temperature so they are required to dissolved into 1,4-dioxane to prepare BPA and HDA solution before being used for synthesis; on the other hand, TEPA and DETA are liquid thus they can be used directly from the bottle. To synthesize PBZ precursor, formaldehyde was added into BPA solution and stirred until a

homogeneous mixture was obtained. The amine was then added dropwise into the mixture and stirred until a yellow viscous solution of PBZ precursor was obtained. However, in case of using HDA, it is important to keep the BPA/CH₂O mixtures in an ice bath under 10 °C before adding HDA solution into it, to suppress the side reactions. After that, the pretreatment at 80 °C was also required for obtaining the yellow viscous solution. Finally, the obtained PBZ precursor was diluted with solvent to 5–25 wt% PBZ concentrations before being used in membrane preparation step.

3.3 Synthesis of NaA zeolite particles

The NaA zeolite particles was synthesized via oxide one-pot synthesis (OOPS) using Al₂O₃:SiO₂:3Na₂O:410H₂O formula as was described elsewhere (Kuanchertchoo *et al.*, 2006). Firstly, Sodium hydroxide was dissolved in deionized water, followed by adding aluminum hydroxide hydrate, and fumed silica, respectively. The mixture was stirred overnight before heating treatment in a microwave oven (Milestone - ETHOS SEL) set at 60 °C for 10 h. The obtained particle was washed with deionized water, dried, and calcined at 550 °C for 3 h.

3.4 Preparation of PBZ membrane

The PBZ was coated on the outer surface of the support using dip-coating technique. A PTFE cap was used to clog at both ends of the support to prevent coating at inside. The support was then dipped into the PBZ precursor solution and dried in oven at 100 °C for 30 min. The process between dipping and drying were continuously done in cycle which was counted as the number of dipping cycle. The final sample was heated in an oven to convert PBZ precursor to PBZ membrane.

3.5 Preparation of NaA-PBZ double layered membrane

A NaA zeolite particles was coated on the support using vacuum-assisted method according to seeding method proposed by Huang *et al.* (Huang *et al.*, 2004; Huang *et al.*, 2007). The support was closed at one side using a PTFE cap and connect with a vacuum pump the other side. The support was immersed in the NaA zeolite suspension and applied vacuum. After the coating, the support was dried in oven. Finally, the support was coated with PBZ precursor in a similar way as preparing PBZ membrane.

3.6 Preparation of NaA-PBZ mixed matrix membrane

The method for preparing the PBZ membrane as was described previously is also used in this case, except that NaA zeolite was first added to the PBZ precursor and dispersed by ultra-sonication before the dip-coating procedure.

3.7 Characterizations

1 Equipment

Differential scanning calorimeter (DSC; Mettler Toledo – DSC-822e) was used to determine the crosslinking temperature of the PBZ precursor using a heating rate of 10 °C min⁻¹ under N₂ flow. Thermogravimetric analyzer (TGA; PerkinElmer) was used to investigate thermal behavior of the PBZ using heating rate of 20 °C min⁻¹ under N₂ flow. X-ray diffractometer (XRD; Rigaku - Smartlab), using CuK α as the X-ray sources, was used to confirmed the structure of zeolite. Scanning electron microscope (SEM; Hitachi – TEM 3000) and field emission scanning electron microscope (FE-SEM; Hitachi – S-4800) were used to identify the morphology of the synthesized zeolite and to measure the thickness of the prepared membrane.

2 Pervaporation testing

The pervaporation system was carried out at 70 °C and the pressure of permeate side was maintained constantly at 10 mmHg using vacuum pump (Edwards). A peristaltic pump (Masterflex) was used to feed the mixture of ethanol and water. The effect of number of dipping cycle and PBZ concentration on separation performance were investigated using fixed 50:50 (ethanol:water, w/w) feed mixture. The effect of ethanol-water ratio in feed on optimized membrane was studied with feed ratios of 10:90, 30:70, 50:50, 70:30 and 90:10. The quantities of ethanol and water from both retentate and permeate sides were determined using Gas Chromatography (GC; Agilent – 3890N) equipped with TCD detector using He as a carrier gas.

3 Swelling behavior of membrane

The test on swelling was conducted to investigate the separation mechanism of the membrane. A piece of thin membrane film was submerged under various solvents ranging from pure water, ethanol/water mixture, to absolute ethanol in a closed container. The system was kept at 70 °C, similar to the actual pervaporation temperature, for 48 h. The degree of swelling (D_s) was calculated using Equation (3.1) (Pakkethati *et al.*, 2011):

$$D_s (\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (3.1)$$

where W_s is the weight of the swollen membrane and W_d is the weight of dry membrane.

CHAPTER IV

NOVEL POLYMERIC MEMBRANE MATERIALS FOR ETHANOL/WATER SEPARATION VIA PERVAPORATION

4.1 Abstract

In this research, novel polybenzoxazine (PBZ) membranes, synthesized from bisphenol-A, formaldehyde and diamines, were coated on a tubular alumina support by dip-coating technique for ethanol purification application via pervaporation. The effects of dipping time and precursor concentration on the membrane preparation and the separation performance showed that both PBZ membranes were remarkably stable, resistant to swelling, and provided an impressively high separation factor of higher than 10,000 for all ethanol concentration ranges, characteristics implying that they could be a good candidate for high purity ethanol production.

4.2 Introduction

An increase in energy use has spurred greater interest in producing ethanol fuel for vehicle use. The ethanol fuel, however, must be highly pure to prevent damage to vehicles. It is well known that in obtaining highly pure ethanol, membrane technology can be much more energy efficient than conventional technology. Thus, a membrane with high mechanical strength and chemical resistance is required [1,2]. Polybenzoxazine (PBZ), a thermosetting phenolic resin, is a good candidate for serving this purpose because it has a high performance in both mechanical and chemical properties due to its thermally activated structure, allowing the ring polymerization to occur and form strong network structures [3-5]. Pakkethathi et al. [6] studied three different partly crosslinked PBZ membranes for separating 10:90 ethanol:water mixture via pervaporation, and found that only one membrane revealed a good performance in both permeation flux and

selectivity. However, all membranes have low mechanical strength and chemical resistance since they cannot tolerate both vacuum force and higher ethanol concentration. In this research, fully crosslinked PBZ membranes were studied to overcome these problems. To prevent brittleness from fully crosslinking PBZ as well as to improve membrane strength, a tubular alumina support was employed [7]. The effect of PBZ type on swelling behavior and separation performance was also investigated.

4.3 Experimental

1 Tubular alumina supported membrane preparation

Two different partly crosslinked PBZ precursors were first synthesized using two different diamines, viz., tetraethylenepentamine (tepa, 85% purity, Aldrich) and diethylenetriamine (deta, 99% purity, Aldrich), as described elsewhere [4,6]. Meanwhile, the α -alumina tube (effective length = 43 mm, purchased from National Metal and Materials Technology Center (MTEC), Thailand) was cleaned with deionized water in an ultrasonicator bath before calcining at 400 °C for 3 h to remove organic dirt.

The PBZ precursors synthesized from tepa or deta were denoted as poly(BA-tepa) and poly(BA-deta), respectively. Using dip-coating technique, PBZ precursors were first diluted by 1,4-dioxane (analytical grade, Labscan) to prepare 10 to 30 wt% of poly(BA-tepa) and poly(BA-deta) solutions. The calcined alumina support (one end closed with Teflon cap) was dipped into the solution before drying at 100 °C in oven, followed by polymerization at 200 °C or 180 °C, for poly(BA-tepa) or poly(BA-deta), respectively. Both dipping and drying steps were carried out as a cycle, the so called dipping cycle, and were repeated until a functional membrane (or a membrane giving a good separation performance) was obtained.

2 Membrane characterization

Surface morphology and thickness of membranes were characterized by scanning electron microscope (SEM, JEOL JSM-540LV). Gas chromatography (GC, Agilent 6890N) equipped with TCD detector was used to determine the quality of ethanol in both permeate and retentate while testing performance.

To study the swelling behavior, three different solvents (pure ethanol (EtOH, absolute, Labscan), water, and 50:50 (w/w) (ethanol/water), were used. Into each solvent, 0.1 g PBZ thin film was immersed, and the system was maintained at 70 °C similar to the actual performance study. The degree of swelling (D_s) of the membrane sample was defined as [6]:

$$D_s = \frac{w_t - w_0}{w_0} \times 100 \quad (4.1)$$

where w_0 is the initial weight of the membrane sample and w_t is the weight of the membrane swollen.

3 Performance study

The performance of PBZ membranes was carried out in batch pervaporation with a feed flow rate of 900 ml min⁻¹ using a peristaltic pump (Masterflex). The interior pressure was maintained constantly at 10 mmHg using a vacuum pump (Edwards). The ethanol concentration and temperature in the feed were varied to study the pervaporation performance of each PBZ membrane. The amount of permeate was measured to determine the total permeation flux and the ethanol concentrations in both permeate and retentate were determined for the separation factor, as follows [7,8].

Total permeation flux (J) (g m⁻² h⁻¹) is defined as:

$$J = \frac{W}{A \cdot t} \quad (4.2)$$

where W is the weight of permeate, A is the membrane effective surface area, and t is the pervaporation time.

Separation factor (α) is defined as:

$$\alpha_{H_2O/EtOH} = \frac{\left[\frac{X_{H_2O}}{X_{EtOH}} \right]^{permeate}}{\left[\frac{X_{H_2O}}{X_{EtOH}} \right]^{retentate}} \quad (4.3)$$

where X_{H_2O} and X_{EtOH} are the weight fractions of water and ethanol in permeate and retentate, respectively.

4.4 Results and discussion

1 Membrane fabrication

The images of the prepared membranes are shown in Fig. 4.1. The surface image of α -alumina support shows that the particle size varied from 0.5 to 3 μm (Fig. 4.1a). After finishing the dipping process, the surface is completely covered with a smooth and dense polymer layer, as shown in Fig. 4.1b. Because the major separation mechanism occurs at this polymer layer [9], it is important to prepare the membrane with a minimum of defect. The cross-sectional images of poly(BA-tepa) and poly(BA-deta) are shown in Fig. 4.1c-4.1h. The thickness of the prepared polymer layer was analyzed and summarized in Table 4.1. As can be seen in Fig. 4.1c and 1f, no dense poly(BA-tepa) and poly(BA-deta) membrane layers prepared from 10 and 20 wt% precursors, respectively, were observed on the support surface even when they were continuously dipped up to 10 times (Table 4.1), indicating that those concentrations were too low for preparing the membranes. However, instead of coating on the surface, the polymers penetrated into the support, probably due to a very low solution viscosity. The dense polymer layer was observed when the precursor concentration was up to 20 and 30 wt% for poly(BA-tepa) and poly(BA-deta), respectively. It is worth noting that only 20 wt% poly(BA-tepa) was needed

to obtain a dense layer while poly(BA-deta) needed 30wt% concentration. Tepas contains more amine groups, resulting in more intermolecular H-bonding and making poly(BA-tepa) membrane fabrication easier to achieve [10]. This result can be confirmed by the thicker poly(BA-tepa) membrane layer. In addition, when comparing membranes produced at the same precursor concentration (i.e. 30 wt%, see Fig. 4.1e and 4.1g), poly(BA-tepa) also requires fewer dipping cycles to obtain a dense membrane. Not only were fewer dipping cycles needed to produce a membrane, but the resultant thinner membrane layer improved the membrane performance, resulting in a thinner polymer layer and consequently providing a higher permeation flux [6,9]. Conclusively, a defect-free polymer layer cannot be obtained if the precursor concentration is too high or too low. The optimal precursor concentrations for preparing poly(BA-deta) and poly(BA-tepa) membranes were at 30–40 and 20–30 wt%, respectively.

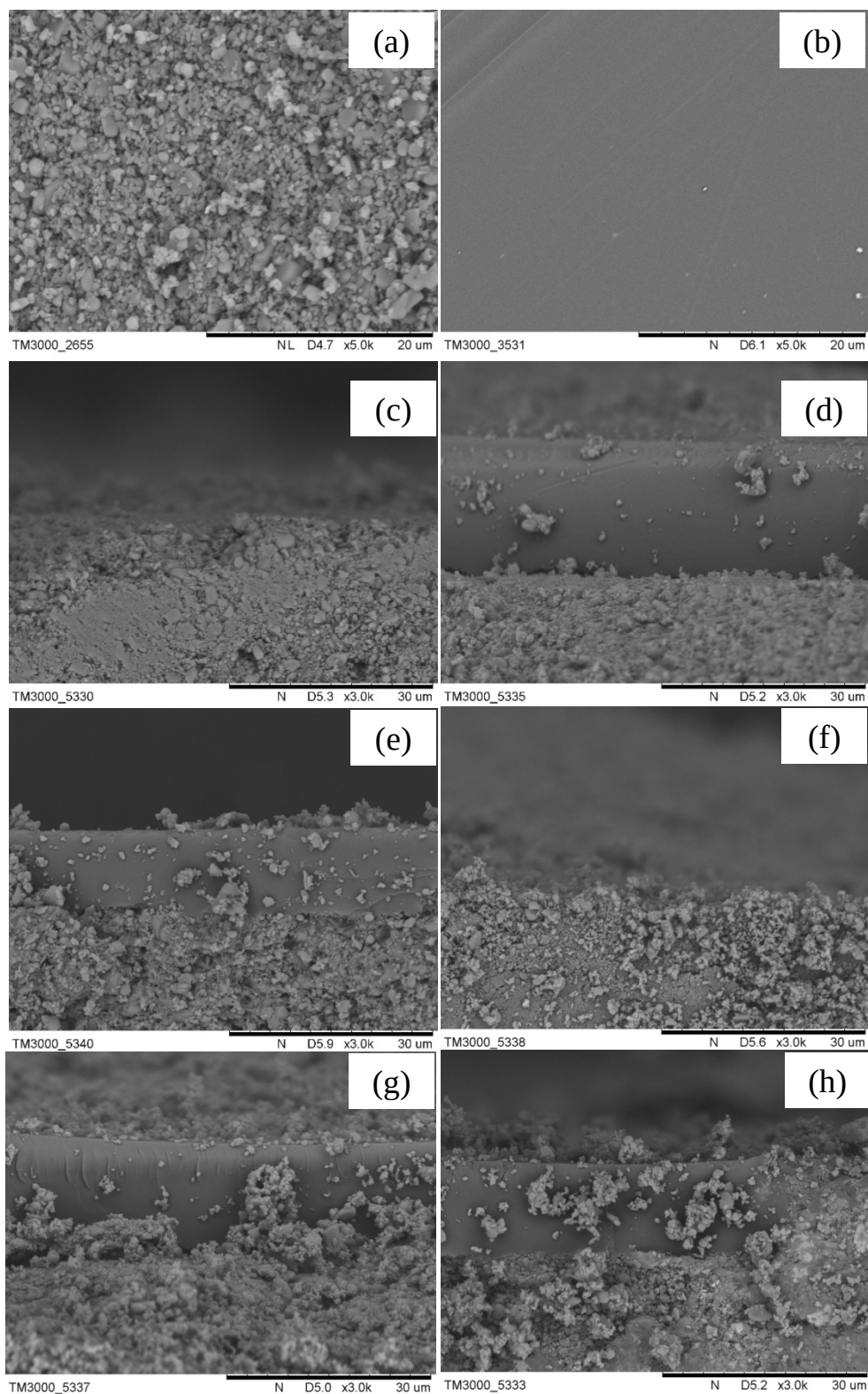


Figure 4.1 SEM surface images of (a) uncoated α -alumina support; (b) α -alumina supported PBZ membrane; cross-sectional images of poly(BA-tepa) at (c) 10 wt%; (d) 20 wt%; (e) 30 wt% and poly(BA-deta) at (f) 20 wt%; (g) 30 wt %; (h) 40 wt%, respectively

Table 4.1 Effect of PBZ concentration on number of dipping cycle requirement and membrane separation performance

Polymer	Precursor concentration/wt%	Number of dipping cycle requirement	Averaged membrane layer thickness/ μm^*
Poly(BA-tepa)	10	10**	...
	20	5	19.8
	30	2	11.9
Poly(BA-deta)	10	10**	...
	20	10**	...
	30	4	15.4
	40	2	13.0

* – measured from SEM

** – all membranes prepared up to 10 times of dipping cycles are leaked and no separation performance was observed

2 Membrane performance

To study the membrane performance, pervaporation is generally utilized and in this study a batch system containing a mixture of water-ethanol was operated, thus, retentate was recycled back to feed while water was permeated through the membrane. As expected, the feed ethanol concentration increased with time. A pervaporation experiment using a feed ethanol concentration ranging from 10 to 90 wt%

EtOH was conducted to study the performance and stability of the membranes. Poly(BA-tepa) and poly(BA-deta) membranes prepared from 30 and 40 wt% precursor concentrations, respectively, were chosen since the lowest number of dipping cycles in preparation was needed, taking the shortest time in fabrication. Moreover, the thinnest membrane layer was obtained, maximizing the permeation flux. From Fig. 4.2, the highest total permeation flux of both poly(BA-tepa) and poly(BA-deta) are observed at 10 wt%EtOH feed with a value of $20.25 \text{ g m}^{-2} \text{ h}^{-1}$ (Fig. 4.2a) and $19.45 \text{ g m}^{-2} \text{ h}^{-1}$ (Fig. 4.2b), respectively, with a separation factor higher than 10,000, indicating that the permeate contained mostly water. As the ethanol concentration gets higher; the water partial pressure in the feed should be lower, causing a lower permeation flux [11]. Although the separation factor of the membranes are not different, the poly(BA-tepa) membrane shows a greater reduction in the total permeation flux than the poly(BA-deta) membrane at higher feed ethanol concentrations. To clarify this result, a swelling behavior test was conducted in pure water, pure ethanol, and 50:50 water/ethanol solvents, and the results are shown in Fig. 4.3a to 4.3c, respectively. Neither membrane was swollen by water molecules after more than 10 days, but both were swollen by ethanol molecules, with the maximum swelling degree of 3.1 and 2.1 for poly(BA-tepa) and poly(BA-deta), respectively (Fig. 4.3b). Although these swelling degree results are considerably small, they could indicate that the membranes are more hydrophobic. Fu et al. [12] suggested that the sorption of ethanol in hydrophobic membranes restricts the molecular transport in the polymer layer, which would be the major reason in decreasing of permeation flux besides the lowering of water partial pressure. Thus, the drastic decrease of the total permeation flux of poly(BA-tepa) at higher ethanol concentration (Fig. 4.2a) may result from the higher molecular restriction by ethanol molecules adsorbed in the membrane, as confirmed by the larger amount of the swollen membrane in ethanol (Fig. 4.3b). The swelling behavior testing also revealed the multiple sorption of water and ethanol

molecules in a mixture of ethanol and water (Fig. 4.3c). The water molecules could adsorb in the membrane via H-bonding with ethanol, resulting in a higher degree of swelling than in pure ethanol conditions [13]. However, those swelling results are again very small, thus still resulting in a separation factor higher than 10,000 with no sign of being damaged since no drastic drop in the separation factor was observed in all ethanol concentrations [14,15]. The results could suggest the excellent stability of PBZ membranes in any ethanol/water mixture, leading to a great potential for the use of these membranes in the ethanol purification process, especially in a highly pure ethanol concentration for renewable energy.

4.5 Conclusions

Poly(BA-deta) and poly(BA-tepa) membranes on tubular α -alumina support were successfully fabricated. The PBZ precursor concentration was a major factor in controlling the membrane performance. Poly(BA-tepa) required less precursor concentration to obtain a functional membrane than poly(BA-deta). However, both membranes provide good stability and separation performance at all ethanol concentrations, indicating a potential material for high purity ethanol production.

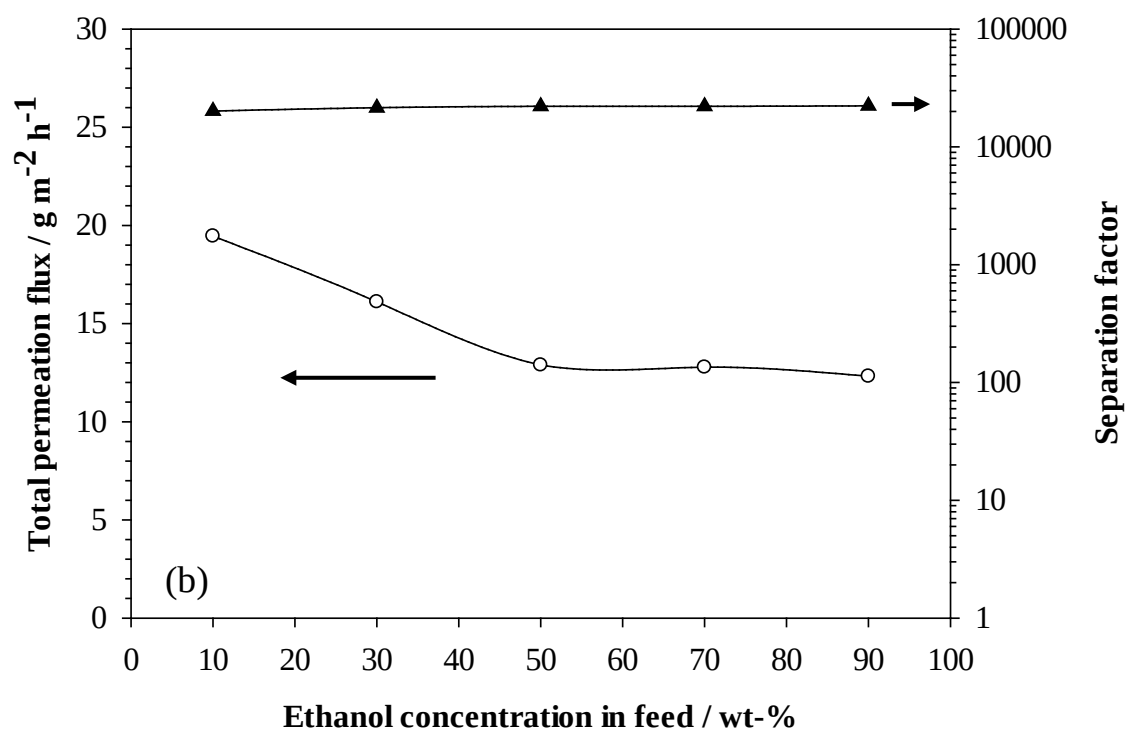
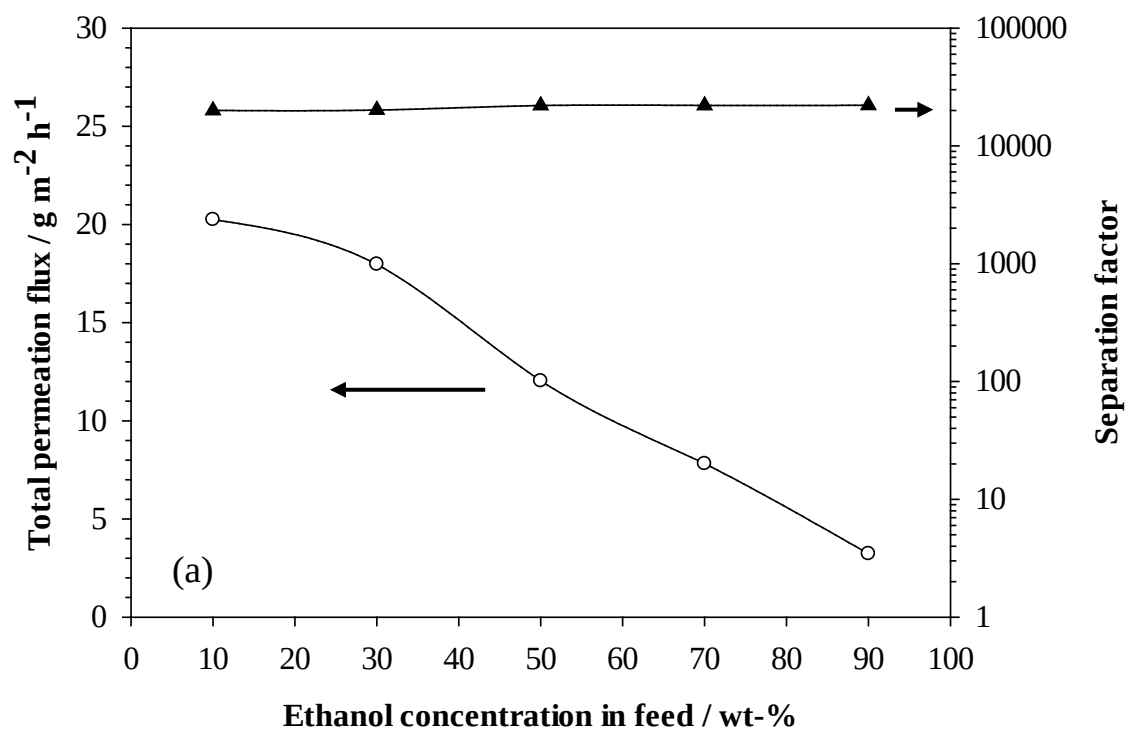


Figure 4.2 Effect of feed ethanol concentration on membrane separation performance of (a) poly(BA-tepa) and (b) poly(BA-deta)

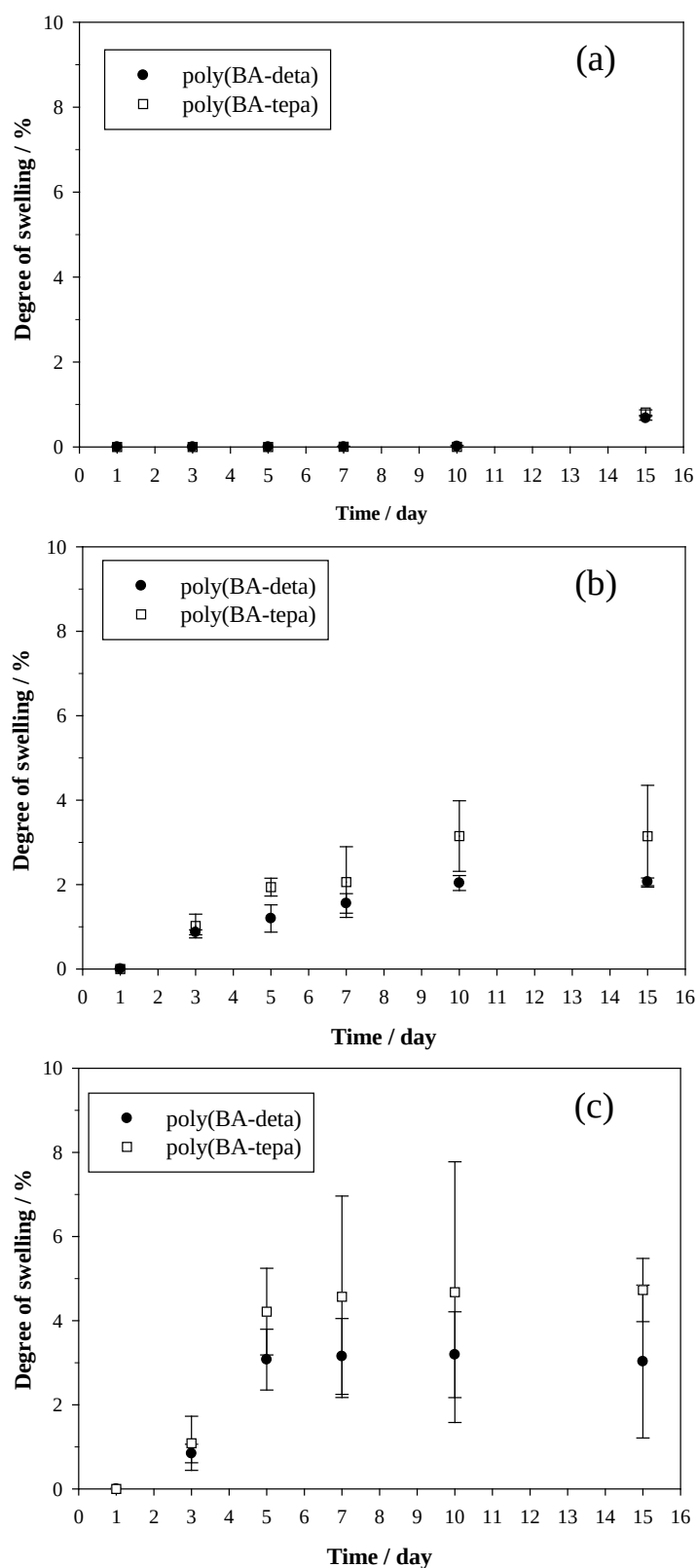


Figure 4.3 Swelling behavior of fully crosslinked PBZ thin film in (a) pure water; (b) absolute ethanol and (c) 50:50 water/ethanol mixture

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CHAPTER V

PREPARATION OF POLYBENZOXAZINE/NaA ZEOLITE DOUBLE LAYERED MEMBRANE FOR ETHANOL/WATER PERVAPORATION APPLICATIONS

5.1 Abstract

Polybenzoxazine (PBZ)/NaA zeolite double layered membrane was developed for ethanol/water separation purpose. The effects of membrane preparation parameters, including coating time and crosslinking temperature, on membrane separation performance were studied. It was found that the PBZ layer was well coated on the NaA zeolite layer regardless NaA zeolite coating conditions. The optimum crosslinking temperature to achieve the PBZ layer was found at 170 °C. The obtained membrane provided a high separation factor of more than 10,000 and was highly stable in the feed ethanol concentration of 35-90 wt% with multiple runs of pervaporation testing.

5.2 Introduction

Due to global concern on fossil fuel depletion over the last few years, the use of alternative renewable energy for the vehicle fuel substitution has received more attention. Bioethanol has a great potential for serving this purpose because it can be produced from abundantly natural resources, such as biomass. Moreover, it provides much less climate change due to much less carbon dioxide emission.[1] However, to produce ethanol fuel from bioethanol, an energy efficient separation process, such as pervaporation, is required. The pervaporation is a membrane separation process and well-known for purifying ethanol. Many researchers have focused on development of high performance membrane to improve the separation efficiency.[2-4]

Polybenzoxazine (PBZ) can be served as the pervaporation membrane due to its high thermal, chemical, and mechanical stability.[2,5,6] However, membrane stability is

another drawback to achieve a better separation performance. One strategy to overcome this drawback is to incorporate NaA zeolite into PBZ membrane to improve the ethanol/water separation performance into PBZ.[6,7]

In this work, a new preparation of the PBZ/NaA zeolite membrane for ethanol purification via pervaporation technique was developed by forming a double layered membrane. The effects of the membrane preparation parameters on pervaporation performance were studied and discussed. The membrane stability was also determined from multiple tests under the pervaporation condition.

5.3 Experimental

1. Chemicals

Fumed silicon dioxide (SiO_2 , AEROSIL® 380) was supported by Evonik. Aluminum hydroxide hydrate ($\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$), 1,6-hexamethylenediamine (HDA, 98 % purity), and Bisphenol-A (BPA, 97 % purity) were purchased from Aldrich. Sodium hydroxide (NaOH, AR grade), 1,4-dioxane, and ethanol (EtOH, absolute) were purchased from RCI Labscan limited. Formaldehyde (CH_3O , 37 wt% in water) was purchased from Merck. Tubular support with 11 mm O.D., 9 mm I.D., and 43 mm effective length was purchased from MTEC.

2. Equipment

A differential scanning calorimeter (DSC, Mettler DSC822) was used to study a polymerization process of PBZ precursor using a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under a N_2 flow. The morphologies of the support and the membrane were investigated using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800). A thermogravimetric analyzer (TGA, PerkinElmer) was used to investigate thermal behavior of the membrane using a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ under a N_2 flow. Gas chromatograph (GC, Agilent 6890N) equipped with TCD detector was used to determine chemical composition of

ethanol/water mixture. A microwave oven (Milestone ETHOS SEL) was used to synthesize NaA zeolite.

3. Synthesis of NaA zeolite particles

NaA zeolite particles were synthesized according to the procedure described by Kuanchertchoo et al.'s work.[8] Sodium hydroxide, aluminum hydroxide hydrate, and fumed silica were mixed together in water using $3\text{Na}_2\text{O}:\text{SiO}_2:\text{Al}_2\text{O}_3:410\text{H}_2\text{O}$ formula. The mixture was stirred overnight and microwave heated at 60 °C. The obtained NaA zeolite was washed repeatedly with deionized water and dried in an oven.

4. Synthesis of PBZ precursor

PBZ precursor preparation was followed the procedure described elsewhere using BPA:HDA:4CH₃O formula.[2] Two mixture solutions of BPA and HDA were separately prepared by dissolving 3.42 g of BPA and 1.74 g of HDA in 1,4-dioxane before mixing them together in an ice bath with addition of formaldehyde. The mixture was then stirred until homogenous, followed by pretreatment at 80 °C to obtain a transparent yellow liquid of PBZ.

5. Preparation of PBZ/NaA zeolite double layered membrane

Prior to the preparation, a tubular alumina support was cut, cleaned with deionized water, dried, and calcined at 400 °C for 3 h to remove any organic dirt. NaA zeolite particles were coated on the support using vacuum-assisted method according to seeding method proposed by Huang et al. [8] One side of the support was sealed with PTFE tape and the other side was connected with a vacuum pump. The support was immersed in the NaA zeolite suspension, which was prepared by dispersing 7 g of NaA particles in 1 liter of deionized water using an ultrasonic bath. Vacuum was then applied

for various times (2-6 min). After the coating, the support was dried in an oven before dip-coating with PBZ following the procedure described elsewhere. [6,9] The support was dipped into a PBZ precursor solution twice before crosslinking at a suitable temperature for 30 min. The final membrane was gently cooled to room temperature.

6. Pervaporation process

The process was set at 70 °C with the pressure of the permeate side was kept constant at 10 mmHg. A feed mixture was circulated between a feed tank and the retentate side using a feed pump with a flow rate of 900 ml min⁻¹. The permeate was condensed using a liquid nitrogen cold trap to determine the permeation flux. The quantities of ethanol and water from both permeate and retentate were used to calculate the separation factor. The permeation flux and the separation factor are calculated from the following equations:[10]:

Permeation flux (J , g m⁻² h⁻¹) is expressed by:

$$J = \frac{W}{A \cdot t} \quad (5.1)$$

where W is the permeate weight (g), A is the effective membrane surface area (m²), and t is the pervaporation time (h).

Separation factor (α) is expressed by:

$$\alpha = \frac{(X_{\text{water}} / X_{\text{ethanol}})_{\text{perm}}}{(X_{\text{water}} / X_{\text{ethanol}})_{\text{reten}}} \quad (5.2)$$

where $X_{\text{water}}/X_{\text{ethanol}}$ is the weight ratio of water to ethanol in permeate and retentate, denoted as perm and reten, respectively.

5.4 Results and discussion

1 Effect of NaA zeolite coating time

Vacuum coating time was varied to determine an optimal condition for preparing NaA zeolite layer. SEM images of α -Al₂O₃ support surface before and after the coating are shown in Fig. 5.1. The image of the plain support (Fig. 5.1a) revealed an irregular shape and non-uniform size of alumina particles varying from 0.5-5 μ m. After 2 min of the coating (Fig. 5.1b), the uniformly cubic shape of NaA zeolite particles with an average size of 0.5 μ m were found on the surface, but not fully covered. When increasing the coating time to 4 min (Fig. 5.1c), the α -Al₂O₃ support was fully covered by an orderly arranged NaA zeolite particles. However, if the coating time was extended to 6 min (Fig. 5.1d), the smoothness of NaA zeolite layer was reduced and the excessive particles were found on top since the excess NaA particles were unable to attach to the support. [8]

To determine the optimal coating time, the pervaporation of 50:50 (EtOH:H₂O) mixture was conducted to determine the membrane performance and the results are shown in Fig. 5.2. It was surprising that the surface roughness of 6 min of coating did not cause any negative effect to the membrane performance as both permeation flux and separation factor were still increasing with the coating time. This is implied that the PBZ outmost layer was well coated on the NaA zeolite layer and well protected the mixture from leaking, as confirmed by the almost identical values of the separation factor for all coating time. The presence of NaA zeolite facilitates the transportation of water, thus making the permeation rate of water be increased [7,11]. The maximum total permeation flux was found to be 106 g m⁻² h⁻¹ for the 6 min coating time with the separation factor of more than 10,000.

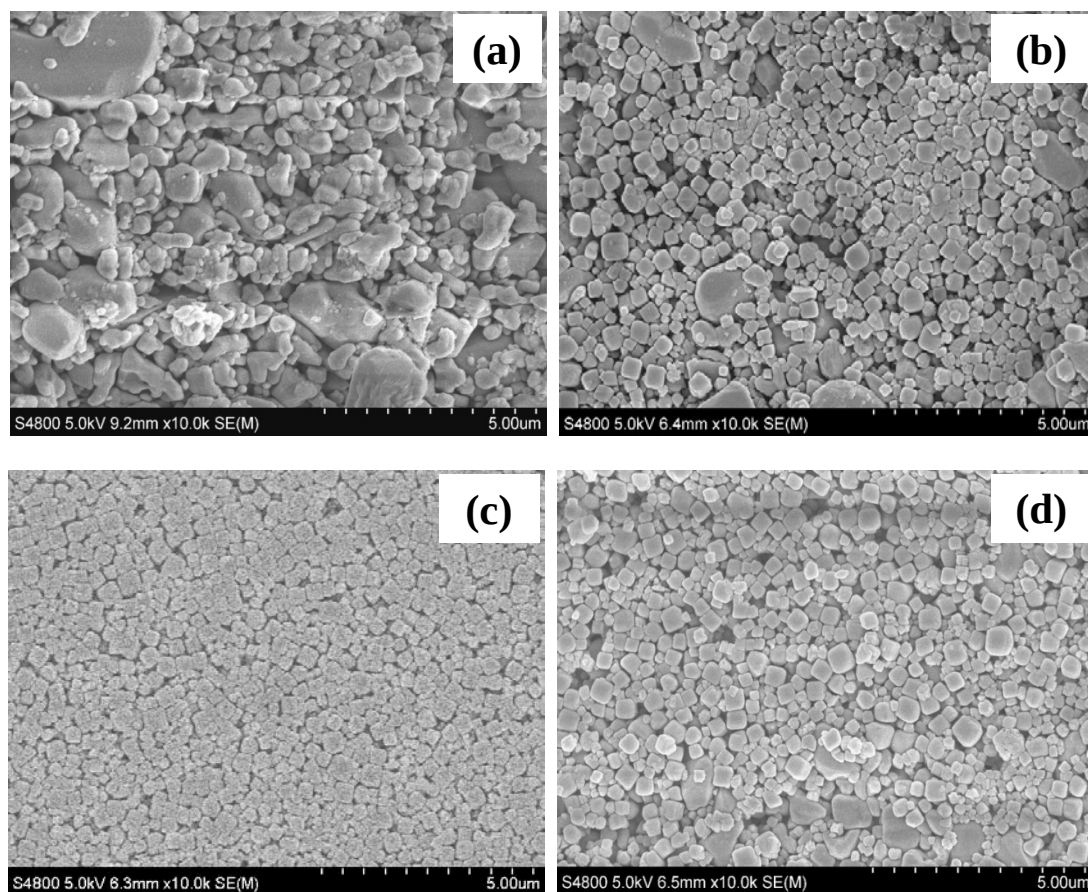


Figure 5.1 FE-SEM surface images of (a) plain α - Al_2O_3 support; NaA zeolite particles coated support with vacuum coating time of (b) 2 min; (c) 4 min; and (d) 6 min.

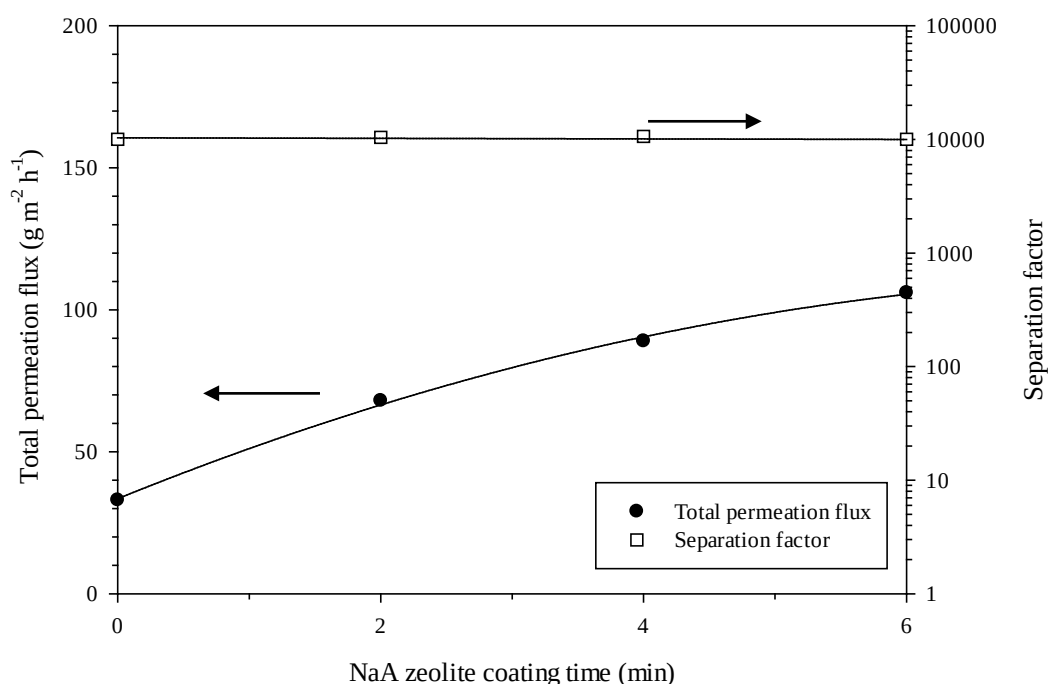


Figure 5.2 Pervaporation performance of 50:50 (w/w) ethanol/water mixture using PBZ/NaA zeolite double layered membrane

2 Effect of crosslinking temperature

DSC thermograms of PBZ after crosslinking at various temperatures are shown in Fig. 5.3. The exothermic peak was referred to crosslinking reaction of the PBZ precursor. At 100 °C crosslinking temperature, a large exothermic peak was observed, indicating the complete crosslinking of PBZ precursor [12]. The peak was reduced when increasing crosslinking temperature and also shifted its onset toward a higher temperature, meaning that higher crosslinking degree was obtained as more benzoxazine rings were opened and crosslinked. At the crosslinking temperature of 180 °C, no peak was observed, implying that the maximum crosslinking degree of PBZ precursor was reached as most of benzoxazine rings were opened and crosslinked [13].

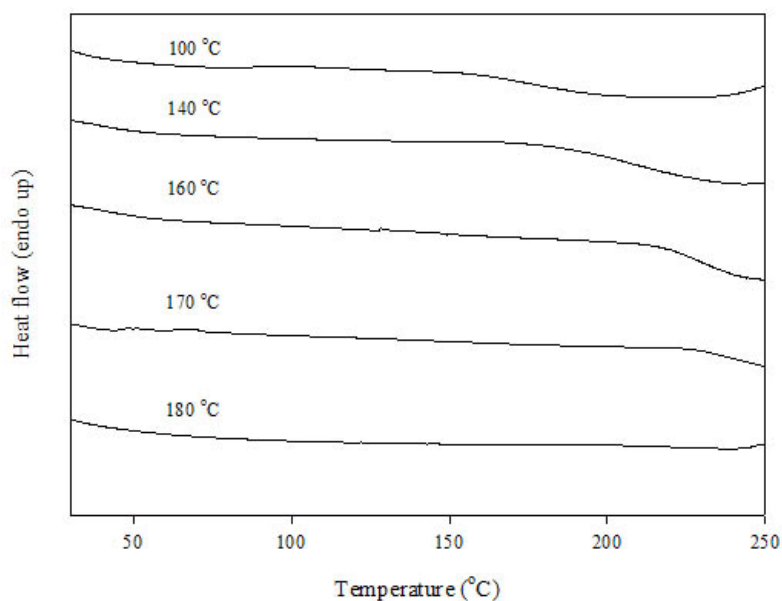


Figure 5.3 DSC thermograms of PBZ after crosslinked at various temperatures.

TGA thermogram shown in Fig. 5.4 revealed thermal behavior of PBZ. The thermogram showed two major weight loss at 150°-250 °C and 260°-470 °C, in agreement with the results observed by Takeichi and Agag. [14] The weight loss at 150°-250 °C can be visually observed from the changing of the membrane color as increasing the crosslinking temperature, see Fig. 5.5. The PBZ membrane was pearly yellow at the crosslinking temperature of 140 °C (Fig. 5.5a) and became orange at the crosslinking temperature of 160 °C (Fig. 5.5b), followed by brown at 170 °C (Fig. 5.5c). At 180 °C (Fig. 5.5d), the membrane became dark brown which reflected to a higher degree of degradation [2].

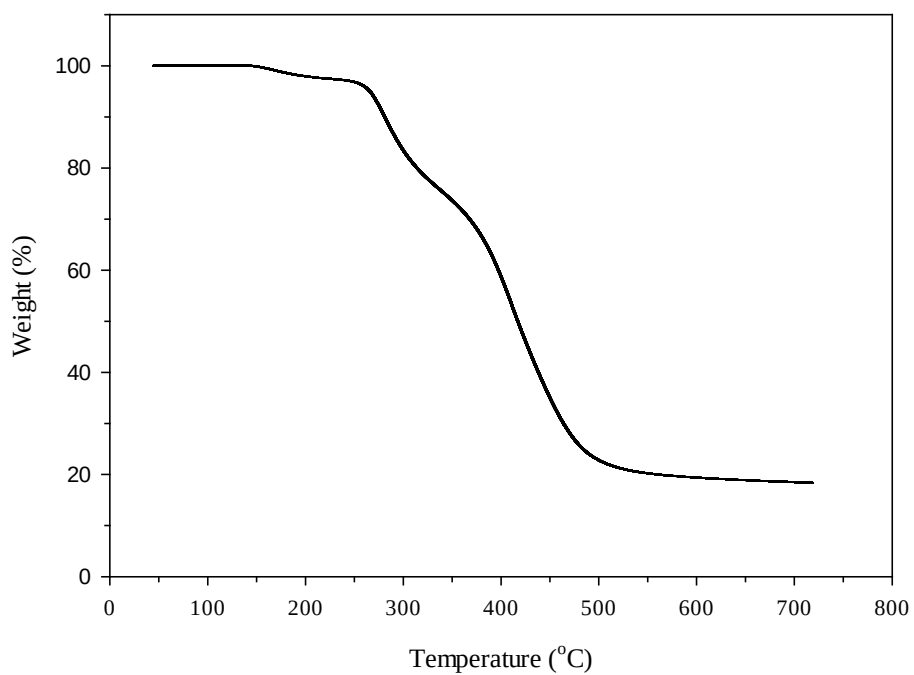


Figure 5.4 TGA thermogram of PBZ precursor

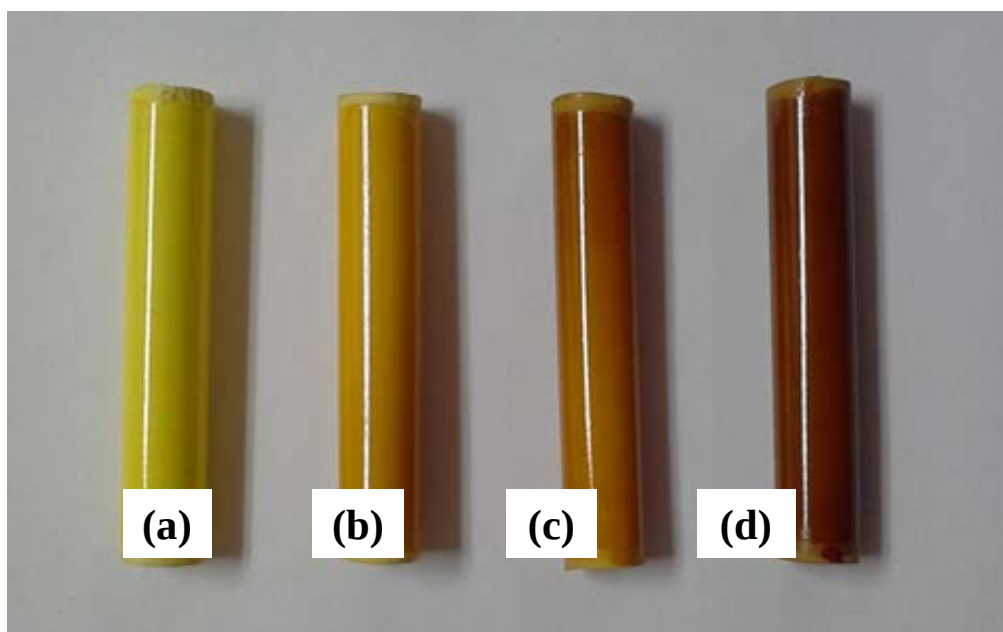


Figure 5 Physical appearance of the membranes crosslinked at (a) 140°; (b) 160°; (c) 170°; and (d) 180 °C

Figure 5.6 shows that the total permeation flux was increased with the crosslinking temperature up to 170 °C before decreasing. This result could be explained by the change of physical structure of polymer, as proposed a mechanism by Berean *et al.*'s [15]. They also found that the permeability of polydimethylsiloxane (PDMS) membrane was increased with crosslinking temperature, due to the increasing of intensity of bonds stretching at pendant groups, resulting in more polymer chain flexibility, and thus causing the decreasing of crosslink density. However, at the crosslinking temperature above 170 °C, the separation factor was found to decrease due to the degradation of PBZ layer, creating some defects on the membrane. Therefore, the optimum crosslinking temperature for preparing the membrane was 170 °C.

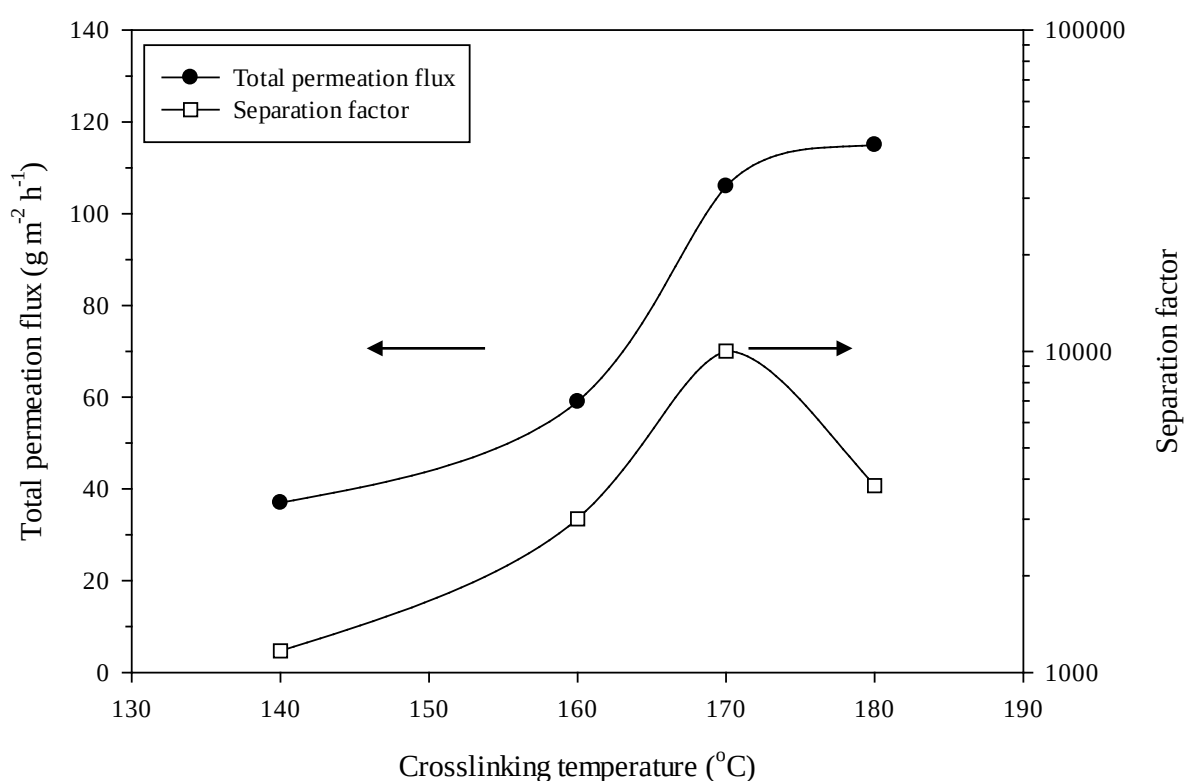


Figure 5.6 Total permeation flux and separation factor of PBZ/NaA double layered membrane as a function of crosslinking temperature

3 Membrane stability testing

The membrane was tested under various feed ethanol concentrations between 35-90 wt% and several cycles to check its performance and stability. After multiple runs (Fig. 5.7), the total permeation flux and the separation factor of the membrane exhibited the same trend, implying that this membrane has high stability and can tolerate a wide range of the feed ethanol concentrations, indicating a great potential for this material to serve as the pervaporation membrane.

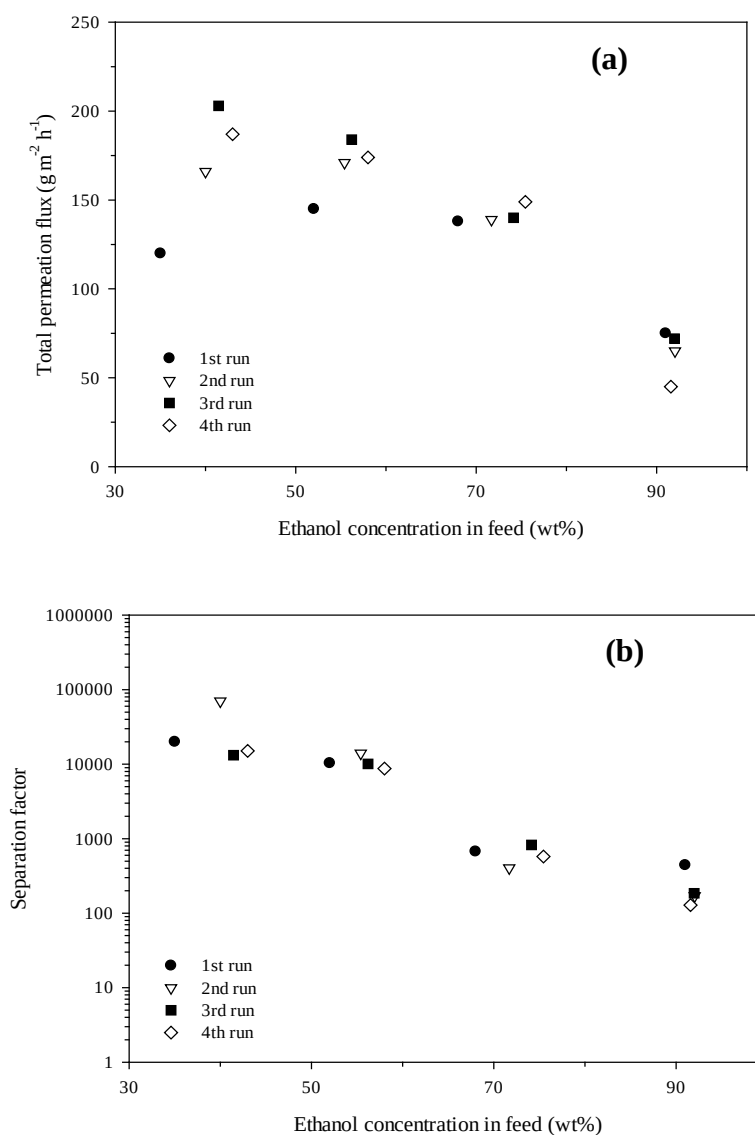


Figure 5.7 Pervaporation performance of PBZ/NaA double layered membrane at various feed ethanol concentrations.

5.5 Conclusions

The PBZ/NaA zeolite double layered membrane was prepared for separation of ethanol/water mixture via pervaporation. The presence of NaA zeolite layer was found to improve the total permeation flux to PBZ membrane. When increasing the amount of NaA zeolite particles, the performance was also increased. The several cycles of pervaporation testing confirmed that the membrane was highly stable in various feed ethanol concentrations, ranging from 35 to 90 wt%.

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CHAPTER VI

PERFORMANCE POLYBENZOXAZINE MEMBRANE AND MIXED MATRIX MEMBRANE FOR ETHANOL PURIFICATION VIA PERVAPORATION APPLICATIONS

6.1 Abstract

Polybenzoxazine (PBZ) membranes have caught great attention for serving as a high performance membrane for pervaporation process owing to their high mechanical properties, high chemical resistance, high thermal stability, and low synthesis cost. This study aims to develop PBZ membrane and NaA-PBZ mixed matrix membrane (MMM) for purification of ethanol/water mixture using pervaporation process and to investigate the effects of preparation parameters on the membrane performance, including precursor concentrations, number of dipping, amount of NaA zeolite loading, temperature, and ethanol concentration. It was found that PBZ membrane and NaA-PBZ MMM were found to exhibit an excellent stability in every feed ethanol concentrations with low degree of swelling. The highest separation factor of the pure PBZ membrane was more than 10,000 while the NaA-PBZ MMM was even higher, up to and in some cases even higher than 100,000 with the highest permeation flux of $1,071 \text{ g m}^{-2} \text{ h}^{-1}$ when using 25 wt% PBZ precursor with 15 wt% NaA zeolite loading. The permeation flux of MMM increased with an increase in the temperature or a decrease in the feed ethanol concentration. The swelling increased when the ethanol concentration increased, revealing a hydrophobic behavior of the NaA-PBZ MMM. The membranes are capable of purifying ethanol in any feed ethanol concentration ranges with an excellent performance and properties that would lead to a great potential for used in bioethanol purifying applications.

6.2 Introduction

Currently, ethanol fuel is one of the most attractive alternative fuels to gasoline due to its derivation from various biological renewable resources and its compatibility with internal combustion engines [1-3]. However, the ethanol produced from these resources contains only a 10–12 wt% concentration, and thus distillation, a conventional process for ethanol purification and considered an energy-intensive technique, is employed [4]. Moreover, the azeotrope of ethanol/water mixture at 95 wt% ethanol also restrains the maximum concentration of ethanol that can be achieved.

Pervaporation, a well-known technique for the separation of an azeotropic and close-boiling point mixture, not only has a great potential in producing ethanol fuel from fermented ethanol, but also is considerably more energy efficient than the distillation process [5]. Since the economic feasibility of the pervaporation process is significantly dependent on production cost and membrane performance, a membrane with a high separation factor, a better permeation flux, and good stability has been studied and developed [5,6]. A polymeric membrane is commonly selected due to its high processability and low production cost. However, most pervaporation polymeric membranes have a tendency to swell, drastically reducing the membrane stability and separation performance [7-9].

Polybenzoxazine (PBZ), a class of high-performance phenolic material, provides many interesting characteristics, including high mechanical properties, high thermal stability, tailorable chemical structure, and low synthesis cost. The potential of using PBZ as a separating membrane was studied by Pakkethathi et al. [10], who synthesized three different kinds of partially crosslinked PBZ membrane synthesized from bisphenol-A, formaldehyde, and three different types of multifunctional amines, viz., hexamethylenediamine (hda), tetraethylenepentamine (tepa), and tetraethylenetriamine (teta), and denoted as poly(BA-hda), poly(BA-tepa), and poly(BA-teta), respectively. They

studied the membrane performance on a 10:90 ethanol:water separation via pervaporation process and found that only poly(BA-hda) provided the best separation performance in both permeation flux and separation factor. However, poly(BA-hda) lost its performance after a few days due to its swelling. One way to overcome these drawbacks is to crosslink the polymeric membrane to suppress the swelling behavior and to improve its durability.

One promising method for increasing stability and separation performance is to crosslink the polymer on a ceramic support while the permeation flux is still maintained if the polymer membrane is sufficiently thin [11-14]. However, the diffusion of polymer into the support must be a primary concern in order to prepare a defect-free membrane. Many ceramic-supported polymeric membranes have been prepared using water to saturate the support and prevent polymer penetration into the support [15]; however, water caused pin holes and voids when making contact with polymer systems [12,16].

Our research thus aimed to develop a thin film PBZ membrane and a NaA-PBZ mixed matrix membrane (NaA-PBZ MMM) on a tubular α -alumina support for the ethanol purification process. The effects of membrane preparation parameters and operation parameters on pervaporation performance were systematically investigated. Swelling behavior of the membranes was also tested to study separation behavior of the membranes.

6.3 Experimental

1 Materials

Formaldehyde (CH_2O , 37 wt% in water; Merk), bisphenol-A (BPA, 97% purity; Aldrich), and, hexamethylenediamine (HDA, 98% purity; Sigma-Aldrich) were used for PBZ precursor synthesis in 1,4-dioxane (analytical grade; RCI Labscan) as a solvent. Ethanol (absolute; RCI Labscan) mixed with deionized water was used as pervaporation

feed. Sodium hydroxide (NaOH, 99% purity; RCI Labscan), aluminum hydroxide hydrate ($\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$; Sigma), and fumed silica (SiO_2 , AEROSIL® 380; supported by Evonik) were used for NaA zeolite synthesis. Tubular α -alumina support with inner and outer diameters of 9 and 11 mm, respectively, were purchased from MTEC.

2 Synthesis of PBZ precursor

The PBZ precursor was synthesized using the procedure described elsewhere [10]. BPA (5.13 g) and HDA (2.61 g) were separately dissolved into 15 ml of 1,4-dioxane. Formaldehyde was then added into the BPA solution and stirred until a homogeneous mixture was obtained. The mixture was kept under 10 °C before adding HDA solution and then pretreated at 80 °C until a yellow viscous solution was obtained. The final mixture was diluted to 5–25 wt% PBZ concentrations for membrane preparation.

3 Synthesis of NaA zeolite

NaA zeolite used as a dispersed phase in this study was synthesized using $\text{Al}_2\text{O}_3\text{:SiO}_2\text{:3Na}_2\text{O:410H}_2\text{O}$ formula [17,18]. NaOH was dissolved in deionized water, followed by adding aluminum hydroxide hydrate, and fumed silica, respectively. The mixture was stirred overnight before microwave heating treatment on a Milestone - ETHOS SEL microwave oven set at 60 °C for 10 h. The obtained product was washed with deionized water, dried, and calcined at 550 °C for 3 h.

4 Preparation of PBZ membrane

An alumina support tube was cleaned with deionized water using an ultrasonic bath to remove dirt and loose particles on its surface before drying in an oven and calcined in a furnace at 400 °C for 3 h to remove any organic impurities. The prepared PBZ solution was coated only on the outer surface of the tube, followed by drying in an

oven set at 100 °C for 30 min. The dipping procedure was carried out by repeatedly dipping and drying in a cycle, and the number of dipping cycles was counted. The final membrane was obtained by crosslinking the PBZ-coated alumina tube in an oven.

5 Preparation of NaA-PBZ MMM

The method for preparing the PBZ membrane is also used in this case, except that NaA zeolite was first added to the PBZ precursor and dispersed by ultrasonication before the dipping procedure. The optimum PBZ precursor concentration and the number of dipping cycles obtained from the PBZ membrane study were applied for preparing the NaA-PBZ MMM. In this part, various amounts of NaA zeolite were studied, thus *xNaA-PBZ membrane* refers to the NaA-PBZ MMM containing *x* amount (wt%) of NaA zeolite.

6 Characterization

A scanning electron microscope (SEM; Hitachi – TEM 3000) was used to identify the morphology of the prepared zeolite and the thickness of the prepared membranes. The structure of the prepared zeolite was determined by X-ray diffraction spectrometer (XRD; Rigaku - Smartlab) using $\text{CuK}\alpha$ as the X-ray source. Differential scanning calorimetry (DSC; Mettler Toledo – DSC-822e) was used to determine the crosslinking temperature of the PBZ membrane using a heating rate of 10 °C min⁻¹ under N₂ flow.

7 Pervaporation

A prepared membrane was installed in the module, as shown in Fig. 5.1. The pervaporation system was carried out at 30-70 °C with pressure of the permeate side maintained constantly at 10 mmHg using a vacuum pump (Edwards). A peristaltic pump

(Masterflex) was used to feed the mixture of ethanol and water at a feeding rate of 900 mL min⁻¹. The quantities of ethanol and water from both retentate and permeate sides were determined using Gas Chromatography (GC, Agilent 3890N) equipped with TCD detector using He as a carrier gas.

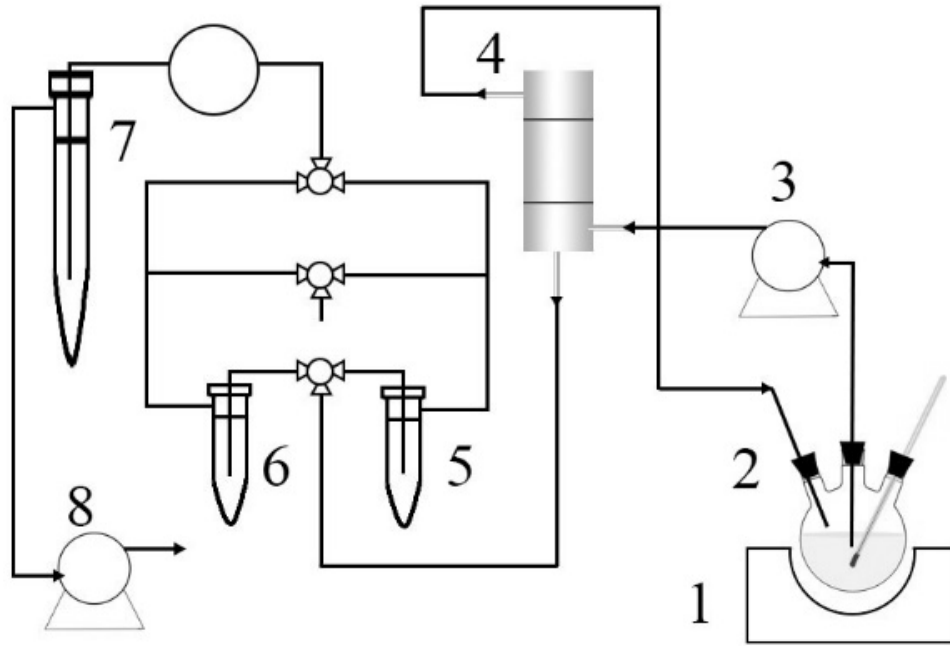


Figure 6.1 Schematic of pervaporation apparatus. (1) Heater; (2) Feed reservoir; (3) Peristaltic pump; (4) Membrane module; (5), (6) and (7) Condenser; and (8) Vacuum pump.

The separation performance of the membranes was determined by the total permeation flux and the separation factor from the following equations;

Total permeation flux (J , g m⁻² h⁻¹) is defined as:

$$J = \frac{P}{A \cdot t} \quad (6.1)$$

where P is the weight of permeate (g), A is the effective membrane area (0.00149 m²), and t is the pervaporation time (h).

Separation factor (α) is defined as:

$$\alpha = \frac{\left(\frac{w_{H_2O}^P}{w_{EtOH}^P}\right)}{\left(\frac{w_{H_2O}^R}{w_{EtOH}^R}\right)} \quad (6.2)$$

where W_{H_2O} and W_{EtOH} are the weight fractions of water and ethanol from permeate side (superscript of P) and retentate side (superscript of R), respectively.

8 Swelling behavior of membrane

The test on swelling was conducted to investigate the separation mechanism of the membrane. A piece of thin membrane film was submerged under various solvents ranging from pure water, ethanol/water mixture, to absolute ethanol in a closed container. The system was kept at 70 °C, similar to the actual pervaporation temperature, for 48 h. The degree of swelling (D_s) was calculated using Equation (3):

$$D_s (\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (6.3)$$

where W_d is the weight of dry membrane and W_s is the weight of the swollen membrane.

6.4 Results and discussion

1 Determination of membrane crosslinking condition

PBZ precursor was obtained after mixing BPA, HDA, and CH_3O together at low temperature. Heating the precursor causes ring-opening polymerization at the benzoxazine ring and creates a network structure of PBZ, so-called crosslinked PBZ, as shown in Fig. 6.2. The network structure provides better mechanical properties, chemical stability, and swelling resistance [19-21]. Therefore, the maximum degree of crosslinking must be focused to maximize the properties.

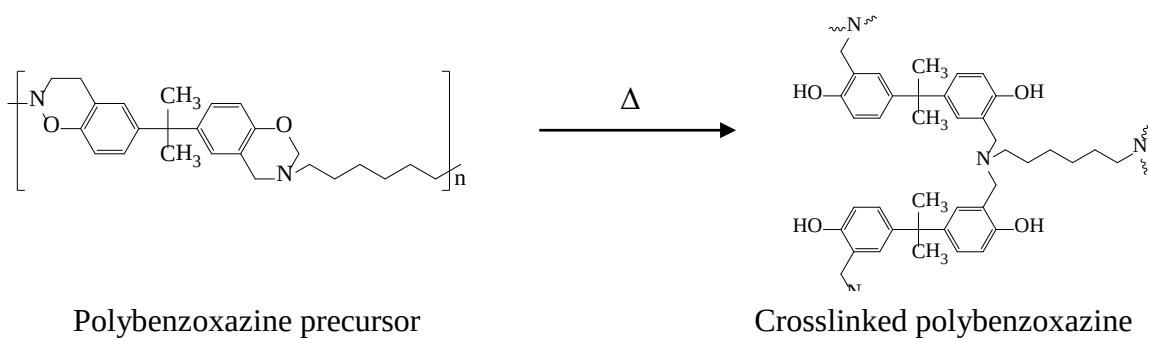


Figure 6.2 Thermal crosslinking of PBZ

DSC technique was used to track the ring-opening polymerization of the precursor, which is identified by an exothermic peak [10,22]. DSC thermograms of the PBZ precursor before and after heating are shown in Fig. 6.3. As can be seen from Fig. 6.3a, the highest crosslinking rate is indicated by the maximum exothermic peak of the PBZ precursor at 170 °C. This temperature was thus selected as the crosslinking temperature for all fabricated membranes in this experiment. The thermogram of the PBZ precursor after heat treatment at 170 °C for 30 min (Fig. 6.3b) shows no peak, indicating that 170 °C was the maximum temperature to fully crosslink the PBZ precursor.

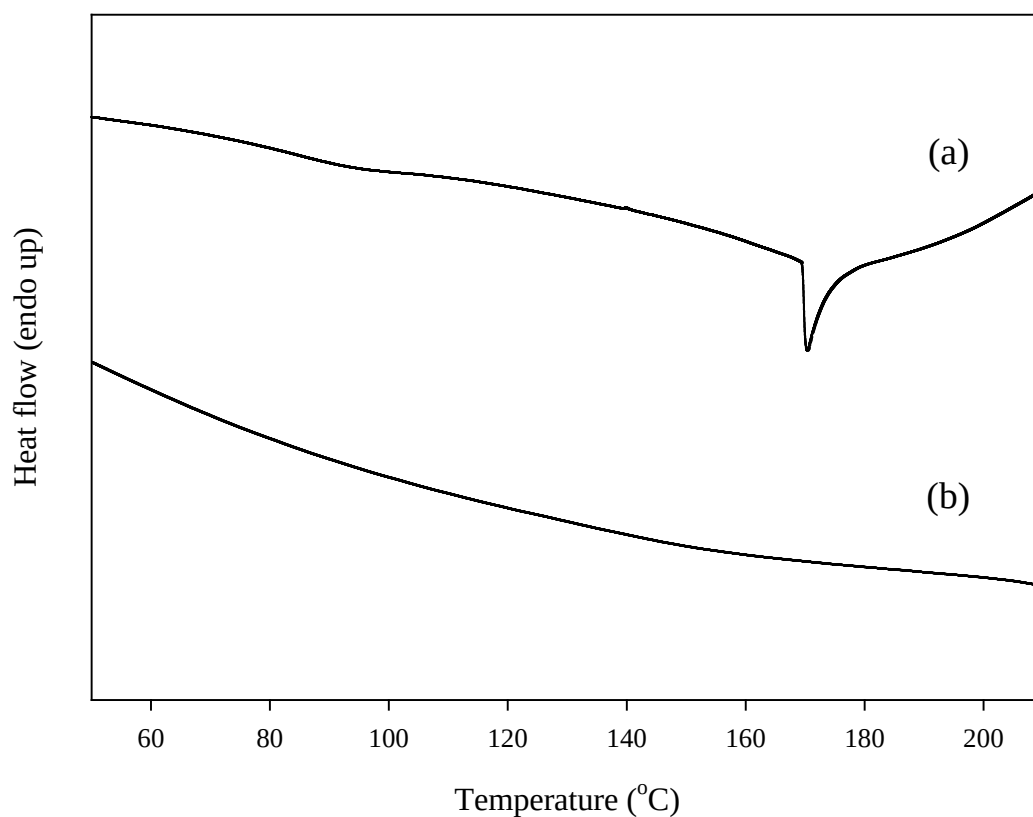


Figure 6.3 DSC thermograms of PBZ membrane. (a) Before and (b) After thermally crosslinked at 170 °C for 30 min.

2 Characterization of NaA zeolite

The crystal structure of synthesized NaA zeolite particles were characterized using XRD technique matching with the reference data from PDF card number: 00-038-0241, as shown in Fig. 6.4a. The obtained peaks were well-matched with the reference that indicated to cubic structure of NaA zeolite. To confirm the results, the SEM technique was used and the image was shown in Fig. 6.4b. It revealed the cubic shape of the synthesized NaA zeolite with the size was in a range of 0.24-0.74 μm .

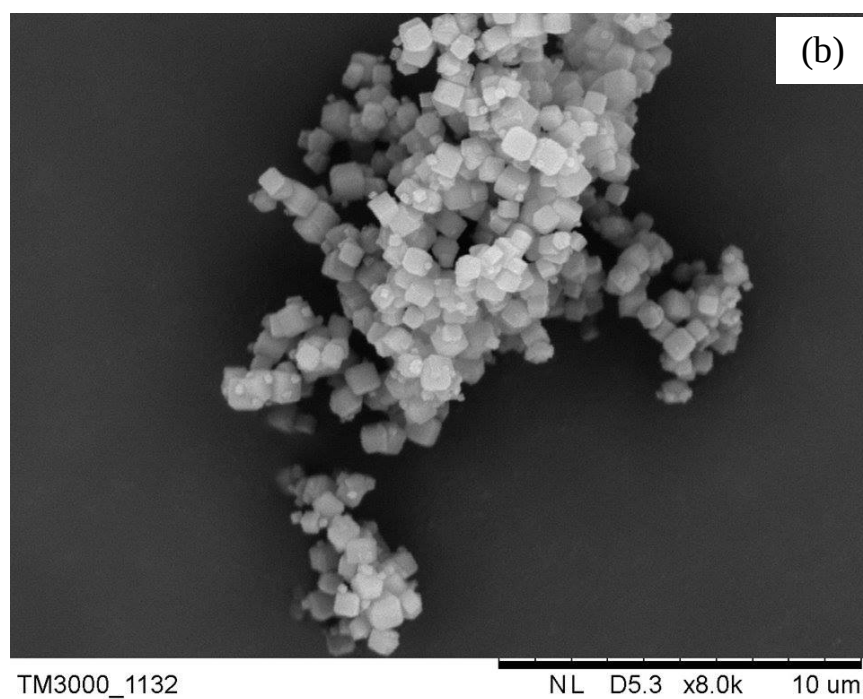
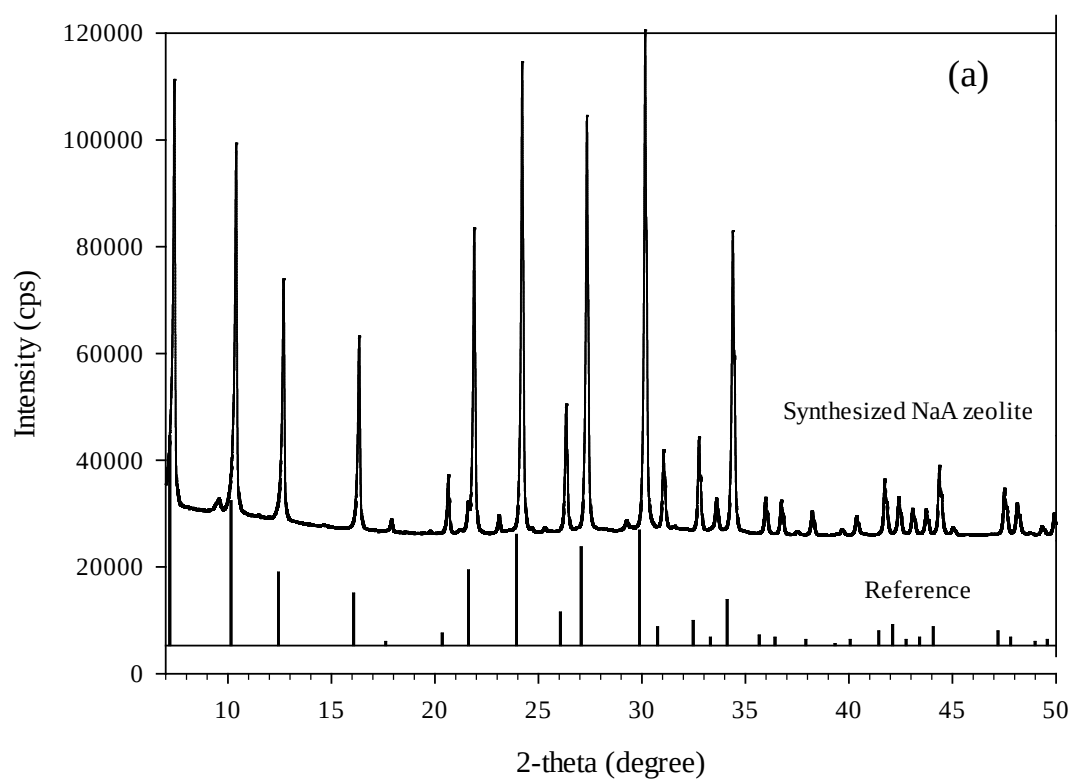


Figure 6.4 (a) XRD pattern and (b) SEM image of synthesized NaA zeolite particles

3 PBZ membrane

To obtain a good separation performance, the fabricated membrane must have no defects and be sufficiently thin. Study of the precursor concentration and the number of dipping cycles was thus conducted, and the results shown in Fig. 6.5. The pervaporation testing was carried out using 50:50 water:ethanol mixture at 70 °C. It was found that the number of dipping cycles required for preparing a good membrane significantly depends on the precursor concentration. None of the prepared membranes using 5 – 25 wt% precursors can be achieved from only one dipping cycle. The first dipping cycle might be a pretreatment for the ceramic support surface before the dense thin film layers, i.e., separation layers, started to form during the second dipping step. However, except for the 5 wt% precursor, the additional dipping did not affect the membrane performance since nearly constant values beyond 2 dipping cycles of each precursor concentration were obtained (Fig. 6.5). The relationship between the required number of dipping cycles, separation performance, and membrane thickness is summarized in Table 6.1. The minimum number of dipping cycles required was found to be 2 when using the precursor concentrations of 20 and 25 wt%. It was noticed that a precursor concentration higher than 25 wt%, e.g., 30 wt%, resulted in a very viscous polymer solution, which hindered the dipping step. The membrane prepared from 30 wt% precursor was either impermeable or highly defective. Therefore, the highest performance membrane with a separation factor >10,000 can only be obtained when using a precursor concentration of 25 wt%. Moreover, the membrane thickness undoubtedly increased with an increase in the PBZ precursor concentration. As described previously, the separation performance also depends on the membrane thickness. The thickness values obtained thus reflect the permeation flux and the separation factor of each membrane. The thicker membrane resulted in a lower permeation flux, but also a higher separation factor.

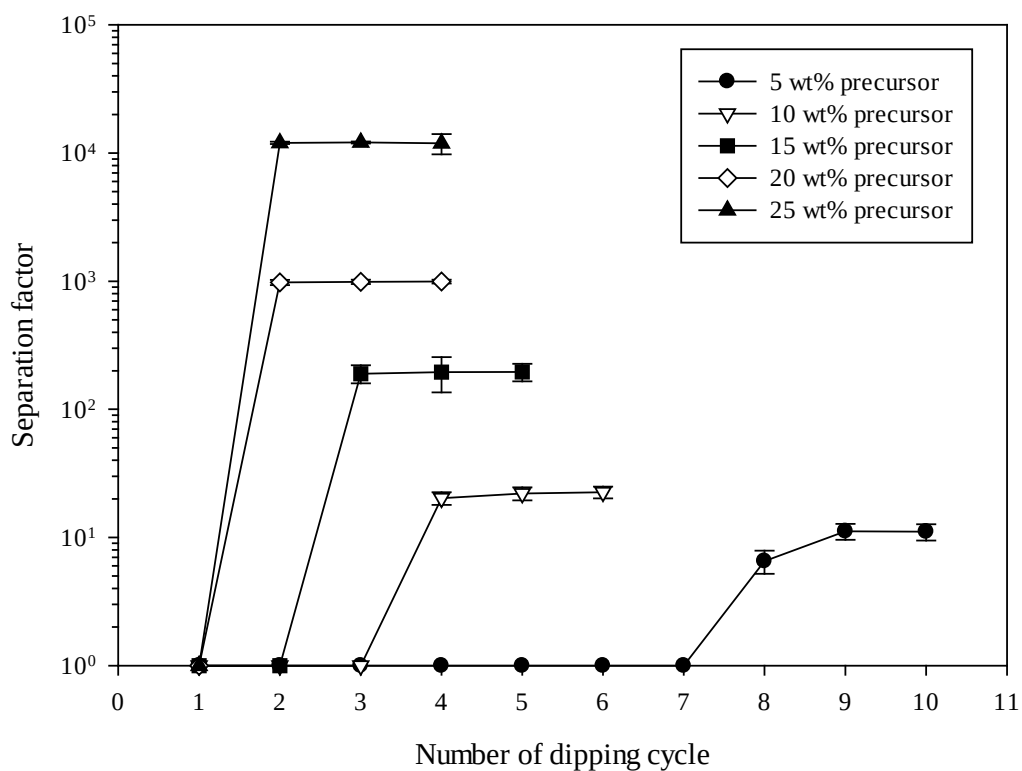


Figure 6.5 Effect of number of dipping cycle on membrane separation factor.

Table 6.1 Membrane pervaporation performance and thickness

PBZ precursor concentration (wt%)	Number of dipping cycle requirement	Separation factor (α)	Total permeation flux ($\text{g m}^{-2} \text{h}^{-1}$)	Separation layer thickness (μm)
5	8	6	67.16	1.8 ± 0.18
10	4	20	45.59	3.2 ± 0.15
15	3	190	37.09	4.3 ± 0.22
20	2	980	25.68	10.2 ± 0.99
25	2	12,012	21.84	15.1 ± 0.83

4 NaA-PBZ mixed matrix membrane (NaA-PBZ MMM)

The key component of a membrane process is the membrane itself. The two most basic requirements for selecting a membrane are selectivity or separation factor and permeation rate. Compared to polymeric membranes, a significant improvement in separation properties with trivial loss in membrane flexibility is expected for the resultant MMMs due to the presence of inorganic fillers. In this study, NaA zeolite is the filler used in the PBZ matrix which was prepared by using a precursor concentration of 25 wt%. The pervaporation performance results of the PBZ membrane containing no NaA zeolite and NaA-PBZ MMM, containing various amounts of NaA zeolite (5–25 wt%), and using 90 wt% ethanol feed concentration are shown in Fig. 6.6. Due to the fully crosslinked PBZ making the material become very dense, the permeation flux of the pure PBZ membrane was low ($22.9 \text{ g m}^{-2} \text{ h}^{-1}$). However, the separation factor was impressively high, above 10,000. This because, according to the mechanism proposed by Pakkethati et al. [10], the diffusion of ethanol molecule in the membrane was reduced by the attraction between ethanol and hydrophobic PBZ chain. Thus the only water molecules can permeate throughout the membrane which resulting in very high membrane separation factor.

The addition of 5 wt% zeolite not only increased flux, but also increased the separation factor. This reversal trade-off phenomenon occurred due to molecular sieving effect of the NaA zeolite. The pore opening of NaA zeolite is about $4 \text{ \AA}$ that permits water molecules (kinetic diameter of $2.65 \text{ \AA}$) to diffuse through but restricts the ethanol molecules (kinetic diameter of $4.46 \text{ \AA}$) [23]. Thus it enhances the membrane selectivity that increasing the separation factor. Moreover, the hydrophilicity of NaA zeolite also improves the water transportation in membrane, resulting in the increasing of total permeation flux as well [24]. As the zeolite increased up to 15 wt%, both the permeation flux and the separation factor remarkably increased to $1,071 \text{ g m}^{-2} \text{ h}^{-1}$ and over 100,000, respectively. However, at loading beyond 15 wt%NaA, the separation factor

dropped down from the maximum value of more than 100,000 to 943 and 6 at 20 and 25 wt%NaA, respectively. This is due to the agglomeration of zeolite causing a defective membrane and promoting ethanol leaking, resulting in a decrease in the membrane separation factor [24].

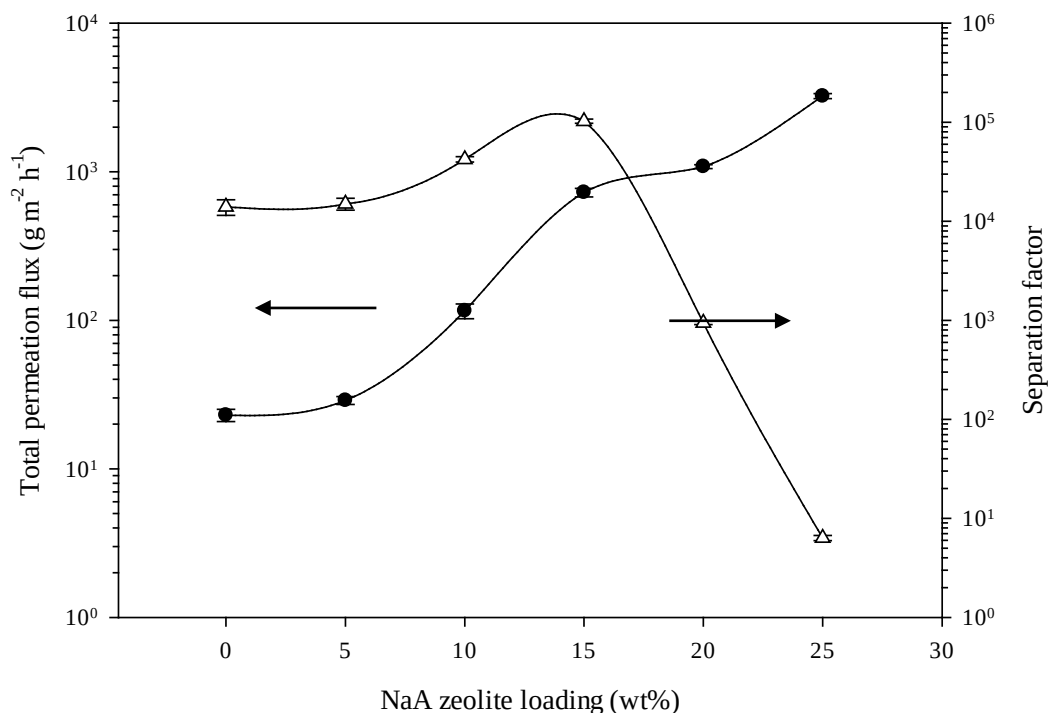
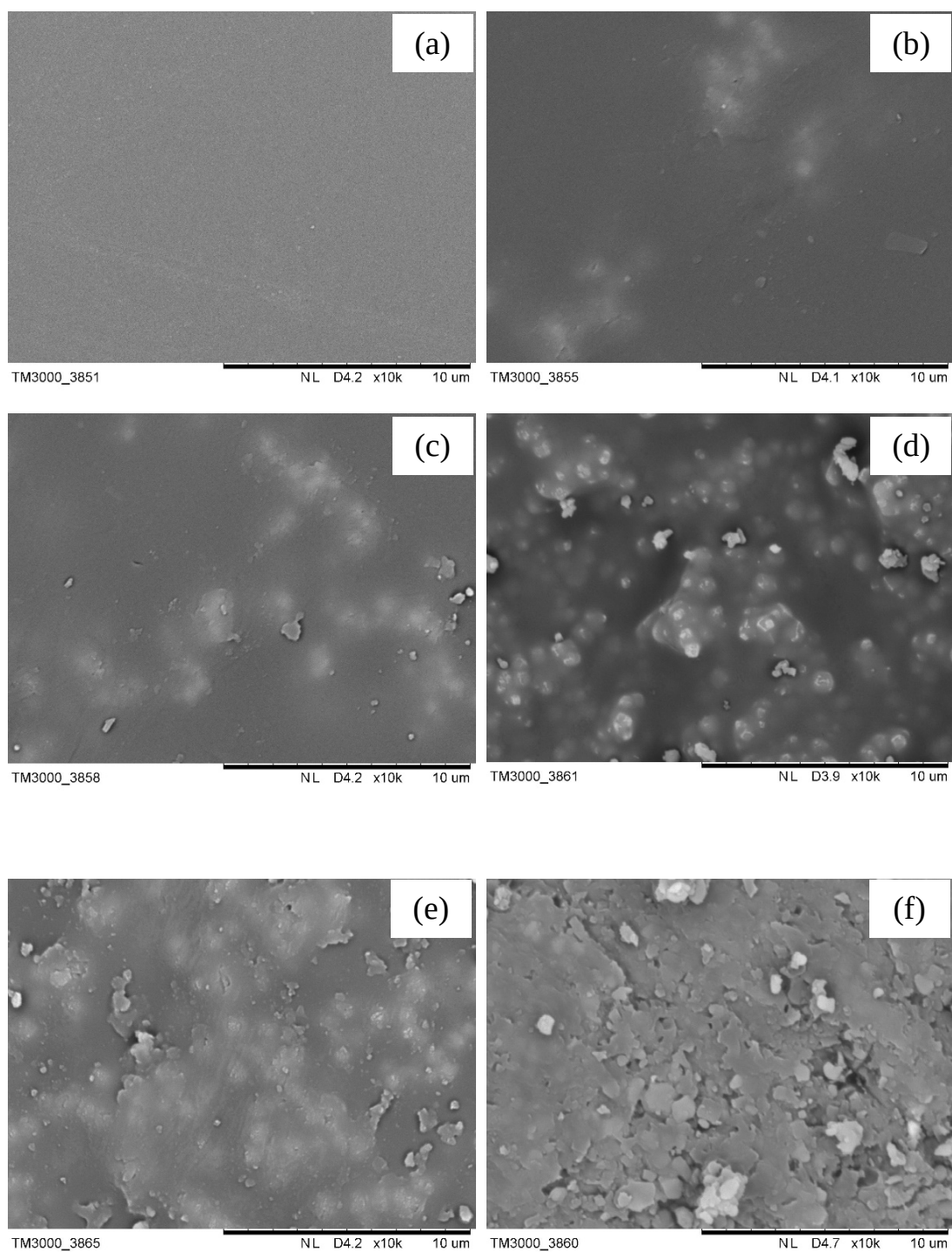


Figure 6.6 Membrane separation performance from various NaA zeolite loadings.

This incident can be clearly identified by SEM images shown in Fig. 6.7. The PBZ membrane surface is smooth and dense (Fig. 6.7a) while the PBZ membranes loaded with NaA zeolite show white particles dispersed underneath the PBZ smooth surface (Fig. 6.7b and 6.7c). The membrane surface started to become rough when loaded with 15 wt% of NaA zeolite (Fig. 6.7d). Voids and defects started to occur at 20 and 25 wt% NaA (Fig. 6.7e and 6.7f), leading to a greater chance for ethanol molecules to pass through the membrane, resulting in a drastic decrease of the separation factor, as shown in the results in Fig. 6.6. The 15 wt%NaA-PBZ MMM, exhibiting the highest separation factor of more

than 100,000, was thus selected as the optimum MMM used in further experiments. In addition, examples of the cross-sectional images of the PBZ membrane and the MMM (Fig. 6.7g and 6.7h), respectively) also revealed that the average membrane's thickness was in a range of 19 to 23 μm .



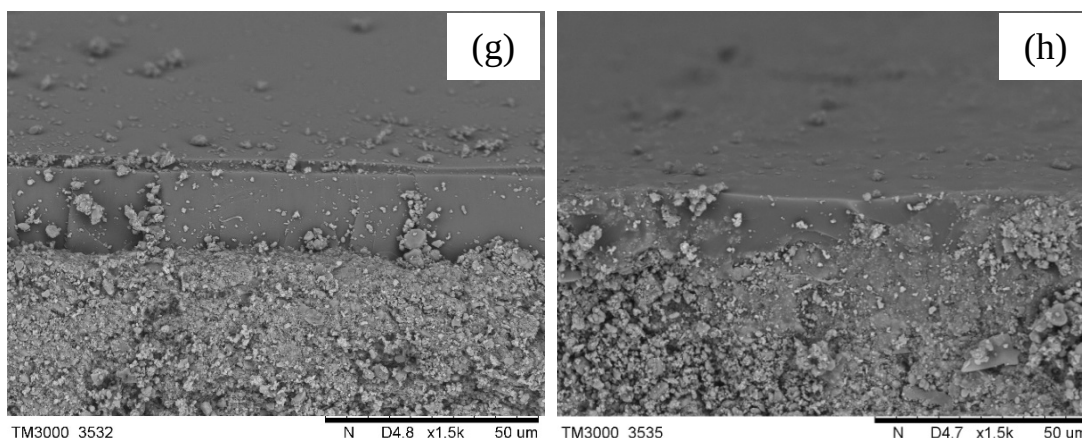


Figure 6.7 SEM surface images of (a) PBZ membrane; MMM with (b) 5; (c) 10; (d) 15; (e) 20; (f) 25 wt% NaA zeolite loadings; and cross-sectional images of (g) PBZ membrane and (h) 15 wt%NaA-PBZ MMM.

The effect of NaA zeolite on the reduction of surface smoothness can also be roughly determined through visual observation, as given in Fig. 6.8, showing the appearance of the support and the supported membranes. The α -alumina support exhibits a white, dull appearance (Fig. 6.8a) while a yellow, smooth glossy surface was achieved when coated with pure, fully crosslinked PBZ (Fig. 6.8b). As can be seen in Fig. 6.8c-e, the membranes lost their glossy appearance and became duller with an increase in the amount of NaA zeolite, and the higher NaA zeolite content resulted in the rougher and duller surface.

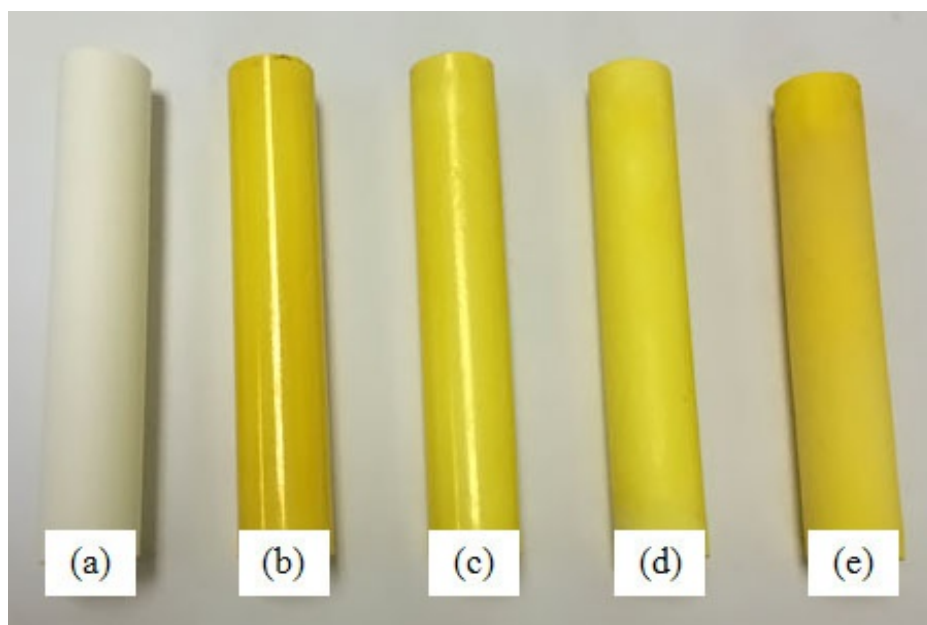


Figure 6.8 Physical appearances of (a) α - Al_2O_3 support; (b) PBZ membrane; (c) 5; (d) 15; and (e) 25 wt% NaA-PBZ MMM.

5 Effect of ethanol concentration in feed

The separation performances and stability of PBZ membrane and PBZ MMM containing 15 wt% of NaA were investigated using various ethanol concentration feeds. Experimentally, the pervaporation of ethanol/water mixture was done by permeating water and circulating the retentate back to the feed reservoir [25]. Thus, the amount of water in the feed decreased, allowing the ethanol concentration to increase overtime. To study whether these membranes are still stable in other ethanol concentrations besides the 50:50 ethanol:water ratio, a pervaporation test of the membrane in a whole range of ethanol concentration was thus designed, and the results are shown in Fig. 6.9a. The PBZ membrane exhibits a much lower permeation flux ($13.5\text{--}28.0 \text{ g m}^{-2} \text{ h}^{-1}$) than the 15 wt% NaA-PBZ MMM ($726.0\text{--}1,071.1 \text{ g m}^{-2} \text{ h}^{-1}$). The permeation flux slightly decreased when the feed ethanol concentration increased, owing to the reduction of the water partial pressure at the retentate side [26]. Moreover, both membranes show excellent stability since the separation factor values were still

maintained at higher than 10,000 at every feed ethanol concentrations (see Fig. 6.9b), due to the network structure of PBZ. Many other works reporting on the use of polymeric membranes noted that a damaged membrane resulted from an increase in ethanol concentration, causing a drastic reduction of the separation factor [10,27,28]. There was no observation of the membrane being damaged by solvent swelling in this work, confirming that these PBZ-based membranes provide an excellent stability in all ranges of ethanol/water pervaporation system. This is an important advantage for serving as the pervaporation membrane in any feed ethanol concentration.

6 Membrane swelling behavior

The swelling test of both membranes was conducted to confirm separation performance. Because these membranes were fully crosslinked, the degrees of swelling of all membranes obtained were less than 3 %, as seen in Fig. 6.10. The swelling degree increased with an increase in the ethanol concentration, revealing that the PBZ membrane has a higher affinity with the ethanol than with the water, indicating the hydrophobic behavior of the PBZ-based membranes [29]. It is worth noting that 100% ethanol produced a lower swelling degree than the ethanol:water mixture. As described by Xu et al., ethanol molecules could act as a small surfactant to interact with the PBZ surface and become more hydrophilic [30]. This changing property allows the water molecules in the ethanol-water mixture to be sorbed, resulting in a significant increase in the degree of swelling [31,32]. This phenomenon can probably relate to a mechanism in which the water molecules diffuse through the membrane matrix despite the fact that PBZ exhibits hydrophobic behavior. In addition, the swelling degree of MMM was slightly higher than the PBZ membrane due to the presence of hydrophilic NaA zeolite [24].

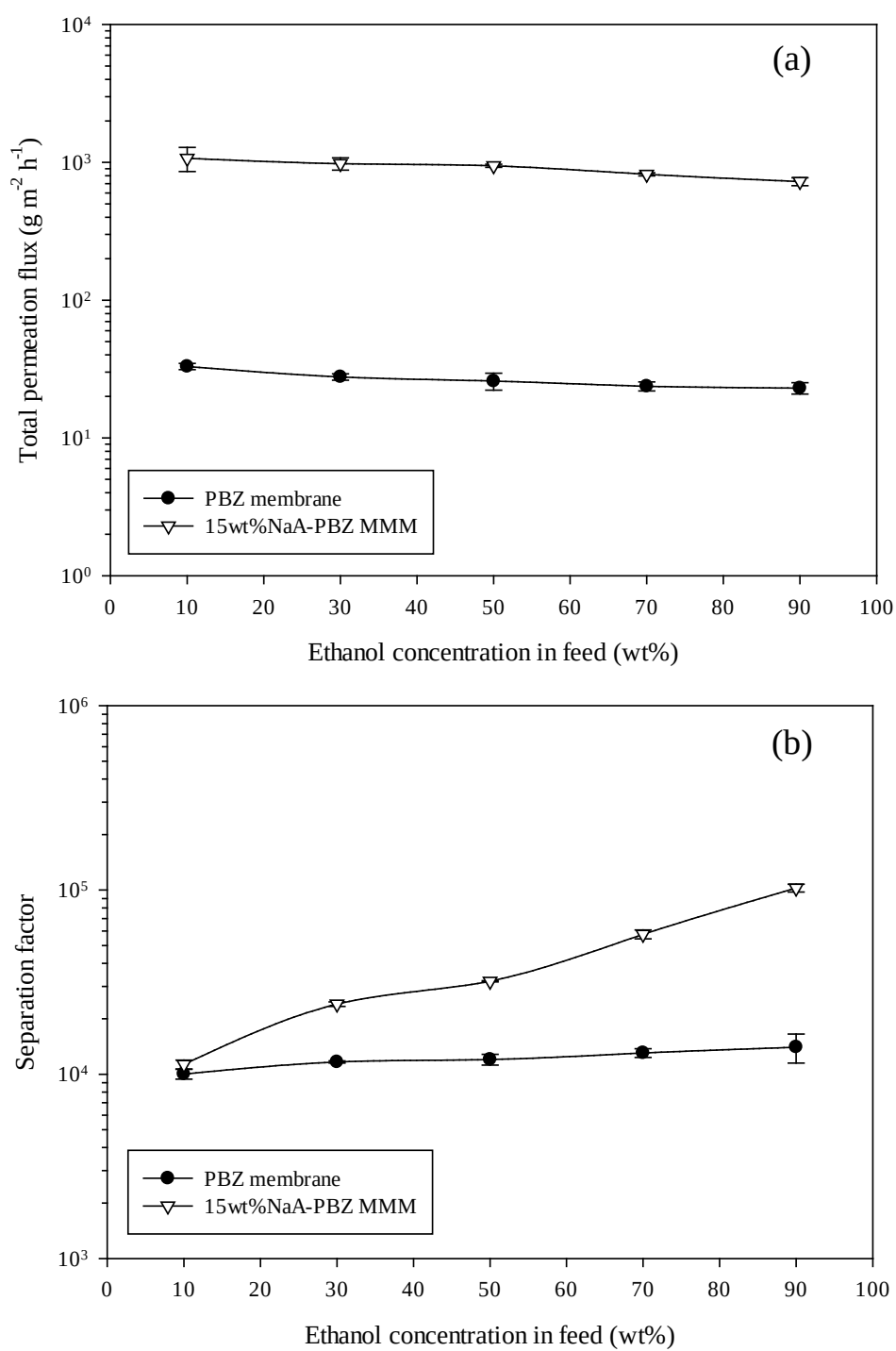


Figure 6.9 Effect of feed ethanol concentration on (a) total permeation flux and (b) separation factor at 70 °C

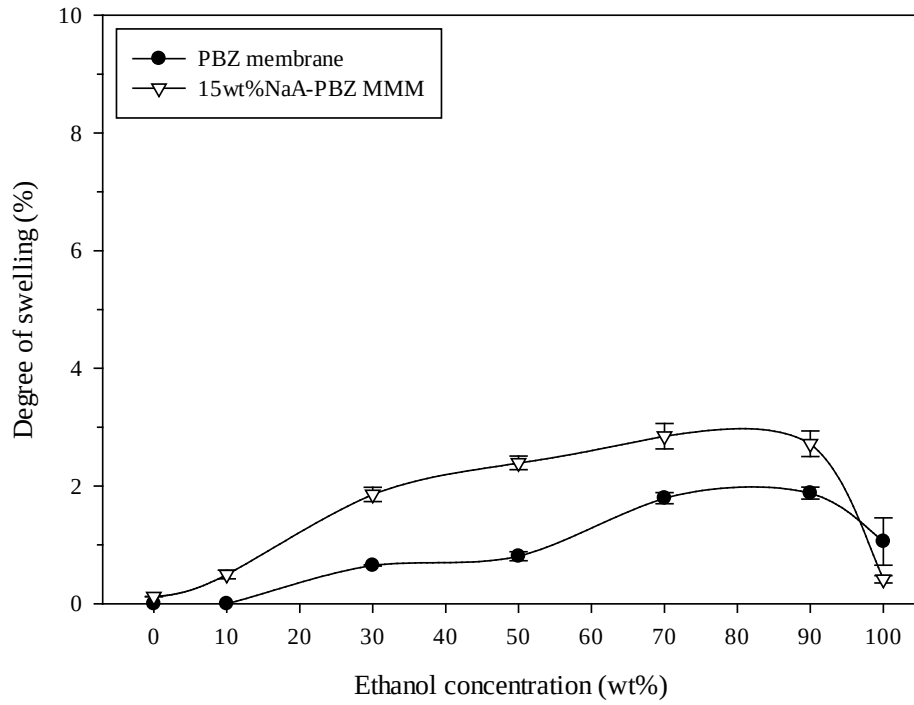


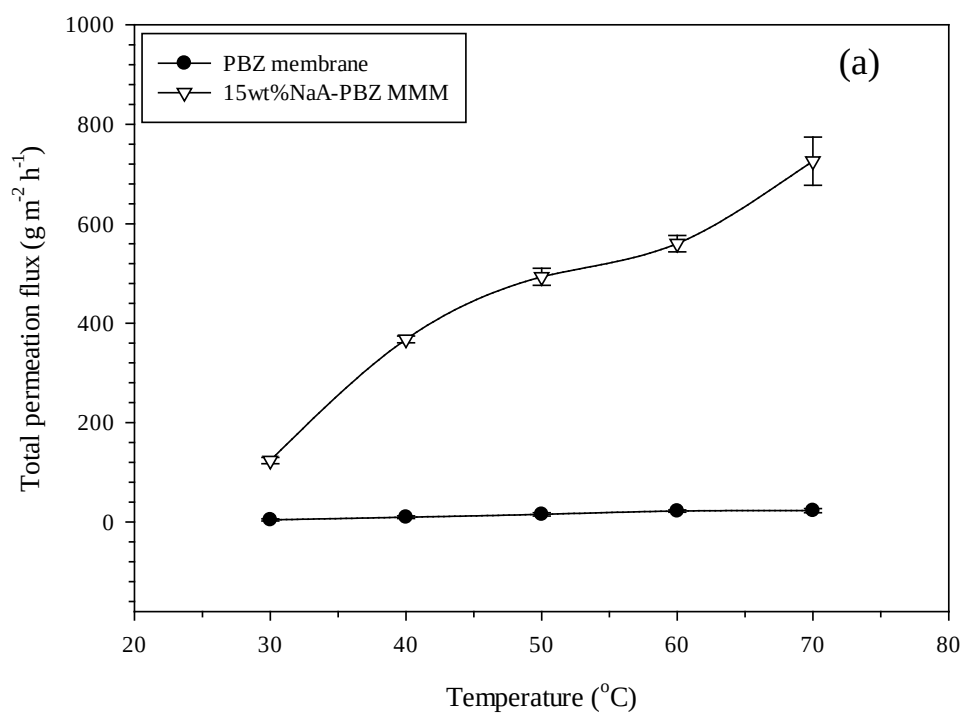
Figure 6.10 Swelling testing of membranes in various ethanol concentrations

7 Effect of temperature

As the separation temperature increased from 30° to 70 °C, the permeation fluxes of both PBZ membrane and NaA-PBZ MMM increased (Fig. 6.11a). It is well-known that the increase of temperature improves the polymer chain mobility as well as the kinetic energy of the diffusing molecules, resulting in a higher diffusing rate or permeation flux of both ethanol and water [33-35]. Moreover, the rising of temperature could alter the sorption behavior of both diffusing molecules that could lead to a higher permeation rate of ethanol molecule over the water molecule, resulting in the decreasing of the separation factor with increasing temperature (Fig. 6.11b) [24,36]. To further investigate the effect of temperature, the Arrhenius plot (Equation (4)) was used.

$$J = J_0 \exp\left(\frac{-E_a}{RT}\right) \quad (6.4)$$

where J is the total permeation flux, J_0 is the permeation rate constant, E_a is the apparent activation energy for permeation, R is the universal gas constant, and T is the temperature in Kelvin. The plot between $\ln(J)$ vs $1/T$, as given in Fig. 6.11c reveals that the apparent activation energies of the PBZ membrane and the 15 wt%NaA-PBZ MMM are 41.25 and 34.74 kJ mol⁻¹, respectively. The lower activation energy of the MMM indicates that an excessive chain movement of the PBZ is restrained by the presence of NaA zeolite in the polymer matrix, causing the permeation flux to be less sensitive with changes in temperature [33].



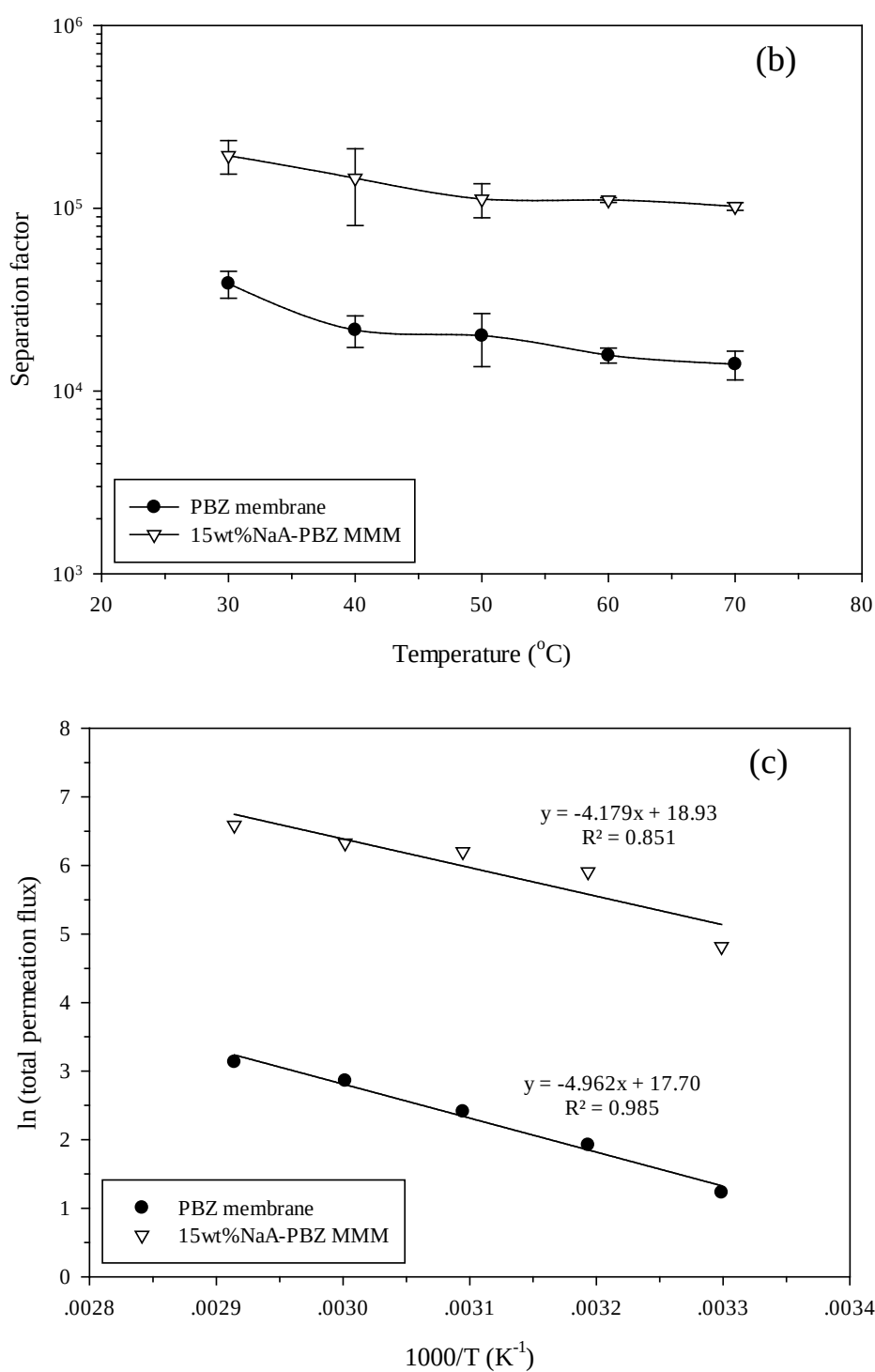


Figure 6.11 Effect of temperature on membrane separation performance (a) total permeation flux; (b) separation factor; and (c) Arrhenius plot

6.5 Conclusions

The PBZ membrane and NaA-PBZ MMM were successfully fabricated on the tubular α -alumina support for ethanol/water separation via pervaporation. Both PBZ and NaA-PBZ membranes exhibit excellent stability in all ethanol concentrations with the degree of swelling values of less than 3 %. The highest separation factor of the PBZ membrane was higher than 10,000 with the permeation flux of $13.5 - 28.0 \text{ g m}^{-2} \text{ h}^{-1}$ while that of the NaA-incorporated PBZ matrix increased to more than 100,000 with a permeation flux of $726.0 - 1,071.1 \text{ g m}^{-2} \text{ h}^{-1}$. In addition, the apparent activation energies of the PBZ membrane and the 15wt%NaA-PBZ MMM were 41.25 and 34.74 kJ gmol^{-1} , respectively.

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CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

PBZ membranes, NaA-PBZ double layered membranes, and NaA-PBZ mixed matrix membrane (NaA-PBZ MMM) were successfully prepared on a tubular α -Al₂O₃ support by using dip-coating technique. All of the prepared membranes showed an excellent stability in pervaporation in all feed ethanol concentrations with the degree of swelling less than 5%. The total permeation flux of three different PBZ membranes synthesized from BPA, formaldehyde, and different types of primary diamines; TEPA, DETA, and HDA, were in ranges of 2.3 – 20.2 g m⁻² h⁻¹, 12.3 – 19.5 g m⁻² h⁻¹, and 23 – 33 g m⁻² h⁻¹, respectively, depending on the feed ethanol concentration, with the separation factor more than 10,000 in all cases. The separation performance could be further improved by introducing NaA zeolite into the membrane system. For example, the total permeation flux of NaA-PBZ double layered membrane was increased up to 109 g m⁻² h⁻¹ while the separation factor was still more than 10,000. In case of NaA-PBZ MMM, both the total permeation flux and the separation factor were improved, depending on the amount of NaA zeolite loading. The optimum amount of 15 wt% NaA zeolite loading provided the membrane total permeation flux of 726 - 1,071 g m⁻² h⁻¹ with the increased separation factor of 100,000.

7.2 Recommendations

The PBZ membrane can be further developed by varying the following parameters; type of phenolic compound and primary amine to enhance a better separation performance, type of support to reduce production cost and improve the separation performance, and technique for preparing membrane, e.g. electro-spinning

technique, to increase the efficiency/precision of the preparation. The larger scale of pervaporation should also be conducted to estimate the potential of using PBZ membrane in an industrial-scale.

APPENDICES

A.1 PUBLICATIONS

1. P. Chuntanalerg, S. Kulprathippanja, T. Chaisuwan, P. Aungkavattana, K. Hemra, and S. Wongkasemjit, “Performance polybenzoxazine membrane and mixed matrix membrane for ethanol purification via pervaporation applications”, Journal of Chemical Technology and Biotechnology, In press
2. P. Chuntanalerg, R. Naraprawatphong, S. Kulprathippanja, P. Aungkavattana, K. Hemra, T. Chaisuwan, and S. Wongkasemjit, “Novel polymeric membrane materials for ethanol/water separation via pervaporation”, Materials Research Innovations, In press.
3. P. Chuntanalerg, T. Chaisuwan, and S. Wongkasemjit, “**Review on “Membranes for Ethanol-water Separation”**”, Journal of Silpakorn University, Accepted.

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Performance polybenzoxazine membrane and mixed matrix membrane for ethanol purification via pervaporation applications

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Abstract

BACKGROUND: Polybenzoxazine (PBZ) membranes have received increasing attention for serving as a high performance membrane for pervaporation processes owing to their good mechanical properties, high chemical resistance, high thermal stability, and low synthesis cost. This study aims to develop PBZ membrane and NaA-PBZ mixed matrix membrane (MMM) for purification of ethanol/water mixtures using a pervaporation process and to investigate the effects of preparation parameters on the membrane performance, including precursor concentrations, number of dippings, amount of NaA zeolite loading, temperature, and ethanol concentration.

RESULTS: It was found that PBZ membrane and NaA-PBZ MMM exhibited excellent stability in all feed ethanol concentrations tested, with a low degree of swelling. The highest separation factor of the pure PBZ membrane was more than 10 000 while the NaA-PBZ MMM was seven higher, up to and, in some cases, higher than 100 000 with the highest permeation flux of 10 71 g m⁻² h⁻¹ when using 25 wt% PBZ precursor with 15 wt% NaA zeolite loading. The permeation flux of MMM increased with increase in temperature or a decrease in the feed ethanol concentration. Swelling increased when the ethanol concentration was increased, revealing the hydrophobic behavior of NaA-PBZ MMM.

CONCLUSION: The membranes are capable of purifying ethanol over a wide feed ethanol concentration range with excellent performance and properties that promise great potential for use in bioethanol purifying applications.

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Keywords: polybenzoxazine; ethanol/water separation; mixed matrix membrane; pervaporation; NaA zeolite

INTRODUCTION

Currently, ethanol fuel is one of the most attractive alternative fuels to gasoline owing to its derivation from various biological renewable resources and its compatibility with internal combustion engines.^{1–3} However, the ethanol produced from these resources contains only a 10–12 wt% concentration, and thus distillation, a conventional process for ethanol purification and considered an energy-intensive technique, is employed.⁴ Moreover, the azeotrope of ethanol/water mixture at 95 wt% ethanol also limits the maximum concentration of ethanol that can be achieved.

Pervaporation, a well-known technique for the separation of an azeotropic and close-boiling point mixture, not only has great potential in producing ethanol fuel from fermented ethanol, but also is considerably more energy efficient than the distillation process.⁵ Since the economic feasibility of the pervaporation process is significantly dependent on production cost and membrane performance, a membrane with a high separation factor, a better permeation flux, and good stability has been studied and developed.^{5,6} A polymeric membrane is commonly selected owing to its high processability and low production cost. However, most pervaporation polymeric membranes have a tendency

to swell, drastically reducing the membrane stability and separation performance.^{7–9}

Polybenzoxazine (PBZ), a class of high-performance phenolic material, provides many interesting characteristics, including excellent mechanical properties, high thermal stability, tailorable chemical structure, and low synthesis cost. The potential of using PBZ as a separating membrane was studied by Pakkethathi *et al.*,¹⁰ who synthesized three different kinds of partially crosslinked PBZ membrane from bisphenol-A, formaldehyde, and three different types of multifunctional amines, viz. hexamethylenediamine (hda), tetraethylenepentamine (tepa), and tetraethylenetriamine (teta),

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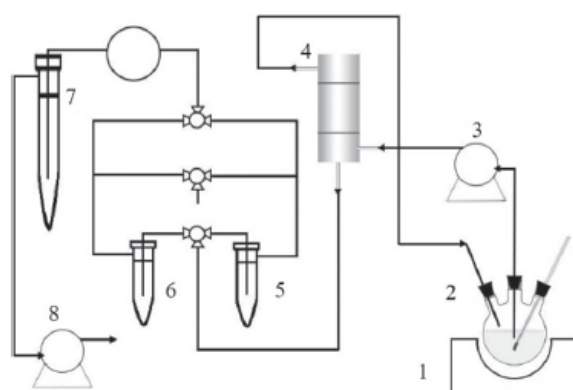


Figure 1. Schematic of pervaporation apparatus. (1) Heater; (2) feed reservoir; (3) peristaltic pump; (4) membrane module; (5), (6) and (7) condenser; and (8) vacuum pump.

and denoted as poly(BA-hda), poly(BA-tepa), and poly(BA-teta), respectively. They studied the membrane performance on a 10:90 ethanol:water separation via pervaporation process and found that only poly(BA-hda) provided the best separation performance in both permeation flux and separation factor. However, poly(BA-hda) lost its performance after a few days due to its swelling. One way to overcome these drawbacks is to crosslink the polymeric membrane to suppress the swelling behavior and to improve its durability.

One promising method for increasing stability and separation performance is to crosslink the polymer on a ceramic support while the permeation flux is still maintained if the polymer membrane is sufficiently thin.^{11–14} However, the diffusion of polymer into the support must be a primary concern in order to prepare a defect-free membrane. Many ceramic-supported polymeric membranes have been prepared using water to saturate the support and prevent polymer penetration into the support;¹⁵ however, water caused pin holes and voids when making contact with polymer systems.^{12,16}

Our research thus aimed to develop a thin film PBZ membrane and a NaA-PBZ mixed matrix membrane (NaA-PBZ MMM) on a tubular α -alumina support for the ethanol purification process. The effects of membrane preparation parameters and operating parameters on pervaporation performance were systematically investigated. Swelling behavior of the membranes was also tested to study separation behavior of the membranes.

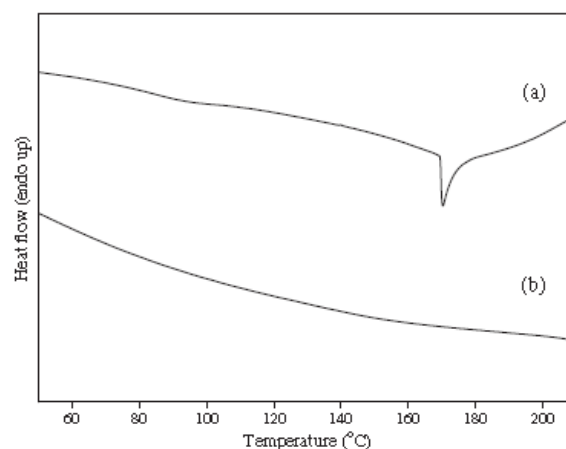


Figure 3. DSC thermograms of PBZ membrane. (a) Before and (b) after thermally crosslinked at 170 °C for 30 min.

EXPERIMENTAL

Materials

Formaldehyde (CH₂O, 37 wt% in water; Merk), bisphenol-A (BPA, 97% purity; Aldrich), and, hexamethylenediamine (HDA, 98% purity; Sigma-Aldrich) were used for PBZ precursor synthesis in 1,4-dioxane (analytical grade; RCI Labscan) as a solvent. Ethanol (absolute; RCI Labscan) mixed with deionized water was used as pervaporation feed. Sodium hydroxide (NaOH, 99% purity; RCI Labscan), aluminum hydroxide hydrate (Al(OH)₃ · xH₂O; Sigma), and fumed silica (SiO₂, AEROSIL® 380; supported by Evonik) were used for NaA zeolite synthesis. Tubular α -alumina support with inner and outer diameters of 9 and 11 mm, respectively, were purchased from MITEC.

Synthesis of PBZ precursor

The PBZ precursor was synthesized using the procedure described elsewhere.¹⁰ BPA (5.13 g) and HDA (2.61 g) were dissolved separately into 15 mL of 1,4-dioxane. Formaldehyde was then added into the BPA solution and stirred until a homogeneous mixture was obtained. The mixture was kept under 10 °C before adding HDA solution and then pretreated at 80 °C until a yellow viscous solution was obtained. The final mixture was diluted to 5–25 wt% PBZ concentrations for membrane preparation.

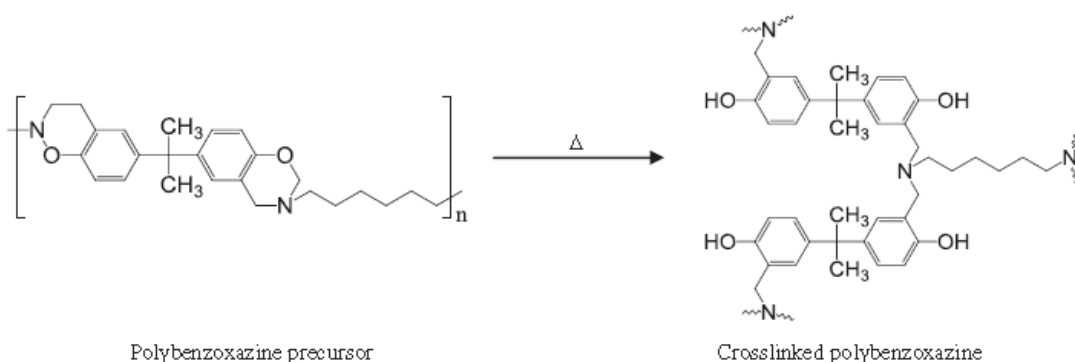


Figure 2. Thermal crosslinking of PBZ.

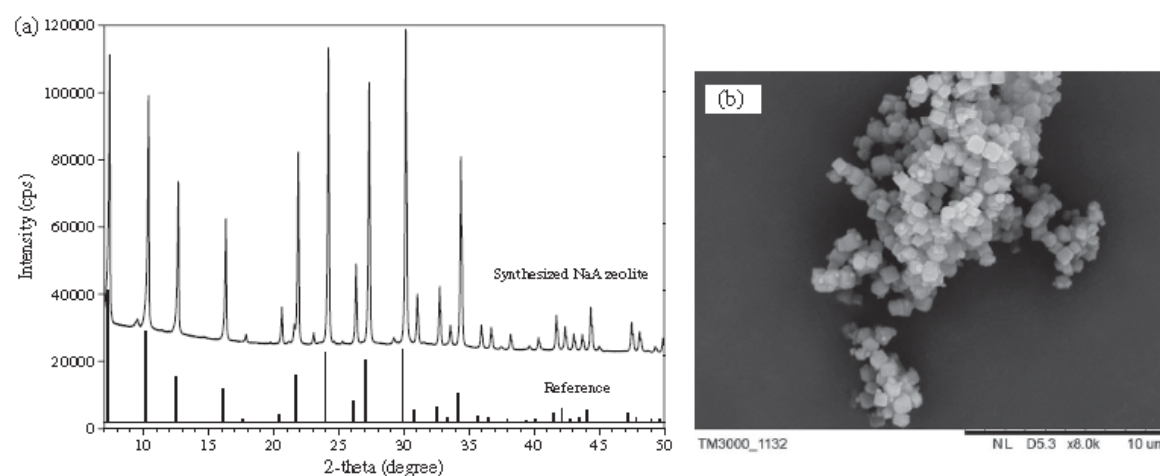


Figure 4. (a) XRD pattern and (b) SEM image of synthesized NaA zeolite particles.

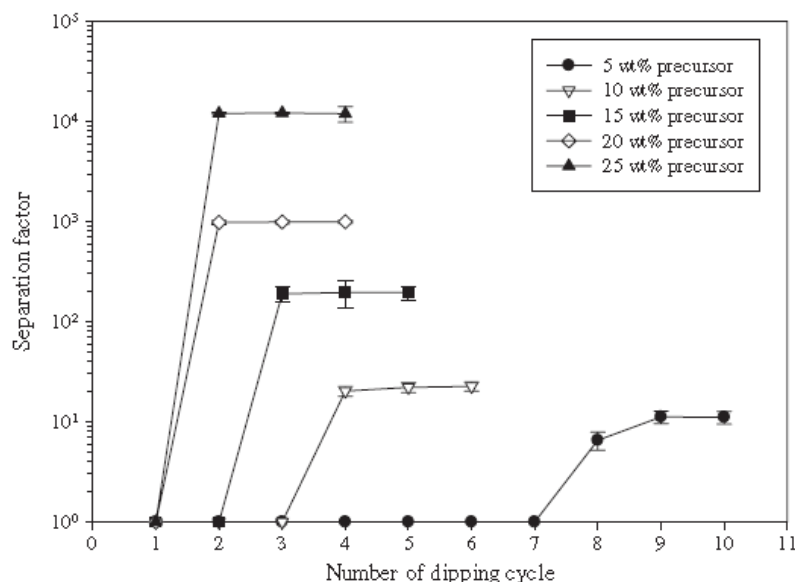


Figure 5. Effect of number of dipping cycle on membrane separation factor.

Synthesis of NaA zeolite

NaA zeolite used as a dispersed phase in this study was synthesized using $\text{Al}_2\text{O}_3:\text{SiO}_2:3\text{Na}_2\text{O}:410\text{H}_2\text{O}$ formula.^{17,18} NaOH was dissolved in deionized water, followed by adding aluminum hydroxide hydrate, and fumed silica, respectively. The mixture was stirred overnight before microwave heating treatment in a Milestone - ETHOS SEL microwave oven set at 60 °C for 10 h. The product obtained was washed with deionized water, dried, and calcined at 550 °C for 3 h.

Preparation of PBZ membrane

An alumina support tube was cleaned with deionized water using an ultrasonic bath to remove dirt and loose particles on its surface

before drying in an oven and being calcined in a furnace at 400 °C for 3 h to remove any organic impurities. The prepared PBZ solution was coated only on the outer surface of the tube, followed by drying in an oven set at 100 °C for 30 min. The dipping procedure was carried out by repeatedly dipping and drying in a cycle, and the number of dipping cycles was counted. The final membrane was obtained by crosslinking the PBZ-coated alumina tube in an oven.

Preparation of NaA-PBZ MMM

The method for preparing the PBZ membrane is also used in this case, except that NaA zeolite was first added to the PBZ precursor and dispersed by ultra-sonication before the dipping procedure. The optimum PBZ precursor concentration and the number of dipping cycles obtained from the PBZ membrane study were

Table 1. Membranes pervaporation performance and thickness

PBZ precursor concentration (wt%)	Number of dipping cycles required	Separation factor (α)	Total permeation flux ($\text{g m}^{-2} \text{h}^{-1}$)	Separation layer thickness (μm)
5	8	6	67.16	1.8 ± 0.18
10	4	20	45.59	3.2 ± 0.15
15	3	190	37.09	4.3 ± 0.22
20	2	980	25.68	10.2 ± 0.99
25	2	10 012	21.84	15.1 ± 0.83

applied for preparing the NaA-PBZ MMM. In this part, various amounts of NaA zeolite were studied, thus *xNaA-PBZ membrane* refers to the NaA-PBZ MMM containing an amount *x* (wt%) of NaA zeolite.

Characterization

A scanning electron microscope (SEM; Hitachi – TEM 3000) was used to identify the morphology of the prepared zeolite and the thickness of the prepared membranes. The structure of the prepared zeolite was determined by X-ray diffraction spectrometer (XRD; Rigaku – Smartlab) using $\text{CuK}\alpha$ as the X-ray source. Differential scanning calorimetry (DSC; Mettler Toledo – DSC-822e) was used to determine the crosslinking temperature of the PBZ membrane using a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 flow.

Pervaporation

A prepared membrane was installed in the module, as shown in Fig. 1. The pervaporation system was carried out at $30\text{--}70^\circ\text{C}$ with pressure of the permeate side maintained constantly at 10 mmHg using a vacuum pump (Edwards). A peristaltic pump (Masterflex) was used to feed the mixture of ethanol and water at a feeding rate of 900 mL min^{-1} . The quantities of ethanol and water from both retentate and permeate sides were determined using gas

chromatography (GC, Agilent 3890 N) equipped with TCD detector using He as a carrier gas.

The separation performance of the membranes was determined by the total permeation flux and the separation factor from the following equations;

Total permeation flux ($\text{J g m}^{-2} \text{h}^{-1}$) is defined as:

$$J = \frac{P}{A \times t} \quad (1)$$

where *P* is the weight of permeate (g), *A* is the effective membrane area (0.00149 m^2), and *t* is the pervaporation time (h).

Separation factor (α) is defined as:

$$\alpha = \frac{\left(\frac{W_{\text{H}_2\text{O}}^P}{W_{\text{EtOH}}^P} \right)}{\left(\frac{W_{\text{H}_2\text{O}}^R}{W_{\text{EtOH}}^R} \right)} \quad (2)$$

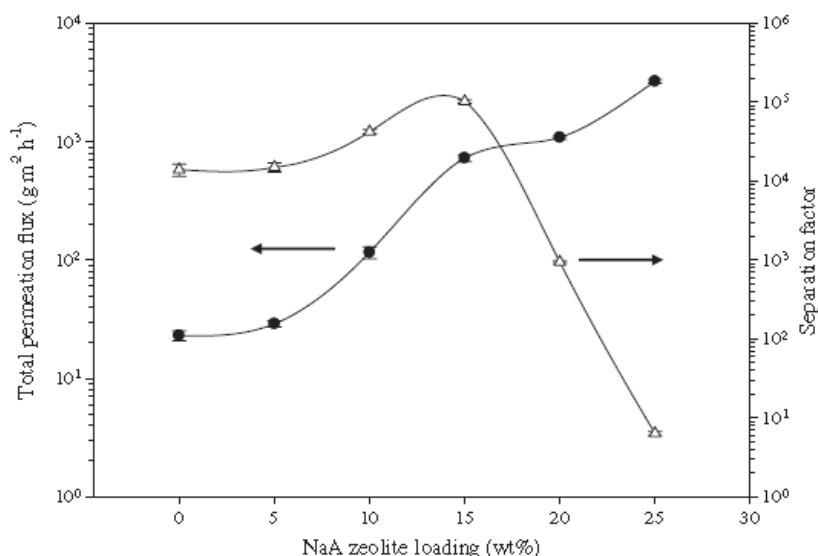
where $W_{\text{H}_2\text{O}}$ and W_{EtOH} are the weight fractions of water and ethanol from permeate side (superscript *P*) and retentate side (superscript *R*), respectively.

Swelling behavior of membrane

The test on swelling was conducted to investigate the separation mechanism of the membrane. A piece of thin membrane film was submerged under various solvents ranging from pure water, ethanol/water mixture, to absolute ethanol in a closed container. The system was kept at 70°C , similar to the actual pervaporation temperature, for 48 h. The degree of swelling (D_s) was calculated using the equation:

$$D_s (\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (3)$$

where W_d is the weight of dry membrane and W_s is the weight of the swollen membrane.

**Figure 6.** Membrane separation performance from various NaA zeolite loadings.

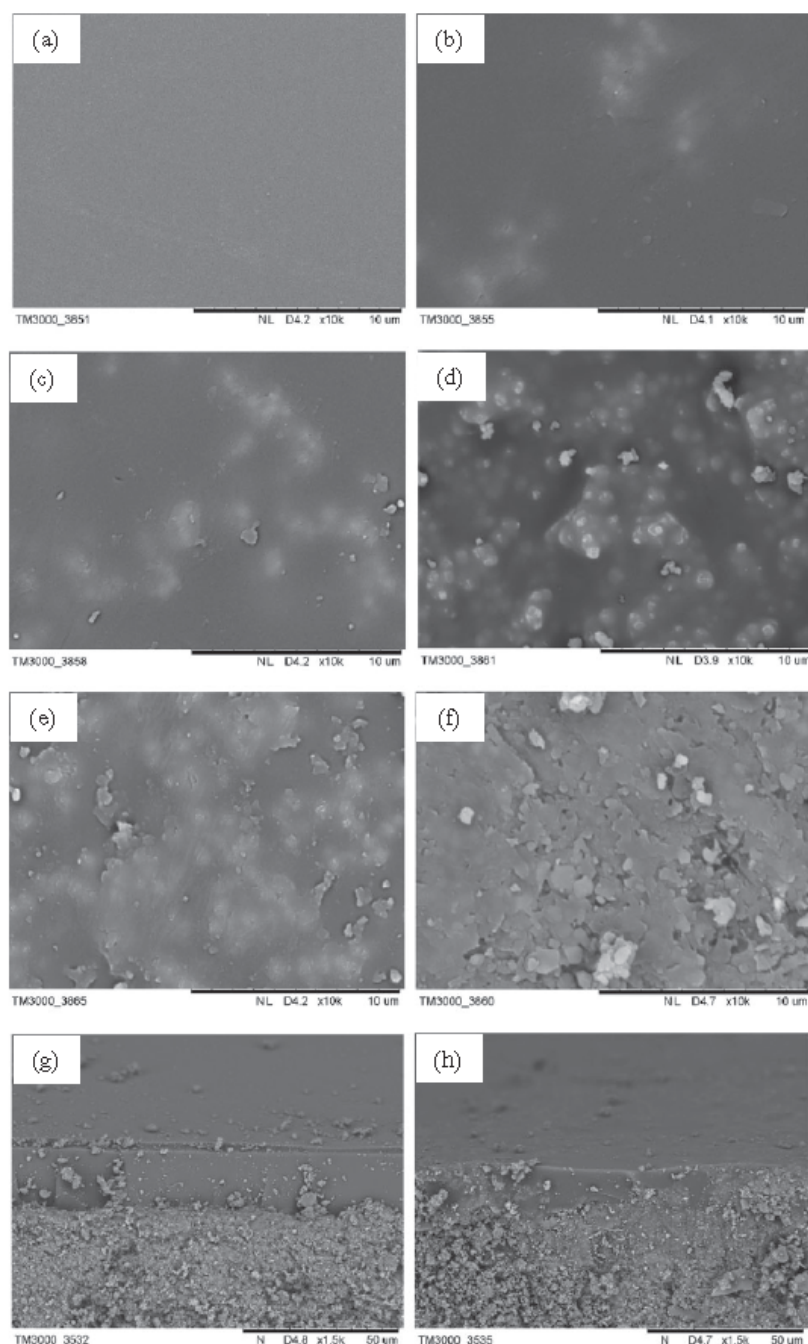


Figure 7. SEM surface images of (a) PBZ membrane; MMM with (b) 5; (c) 10; (d) 15; (e) 20; (f) 25 wt% NaA zeolite loadings; and cross-sectional images of (g) PBZ membrane and (h) 15 wt% NaA-PBZ MMM.

RESULTS AND DISCUSSION

Determination of membrane crosslinking condition

PBZ precursor was obtained after mixing BPA, HDA, and CH_3O together at low temperature. Heating the precursor causes ring-opening polymerization at the benzoxazine ring and creates

a network structure of PBZ, so-called crosslinked PBZ, as shown in Fig. 2. The network structure provides better mechanical properties, chemical stability, and swelling resistance.^{19–21} Therefore, the maximum degree of crosslinking must be focused to maximize the properties.

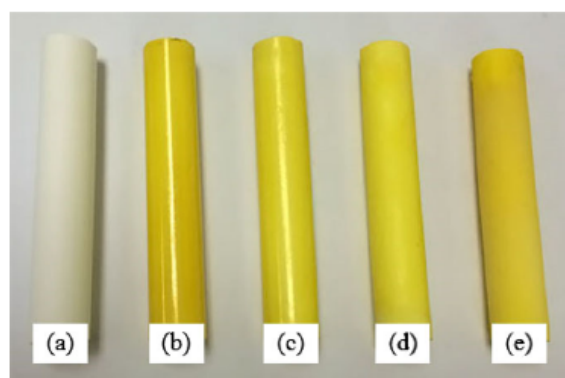


Figure 8. Physical appearances of (a) α - Al_2O_3 support; (b) PBZ membrane; (c) 5; (d) 15; and (e) 25 wt% NaA-PBZ MMM.

DSC technique was used to track the ring-opening polymerization of the precursor, which is identified by an exothermic peak.^{10,22} DSC thermograms of the PBZ precursor before and after heating are shown in Fig. 3. As can be seen from Fig. 3(a), the highest crosslinking rate is indicated by the maximum exothermic peak of the PBZ precursor at 170 °C. This temperature was thus selected as the crosslinking temperature for all fabricated membranes in this experiment. The thermogram of the PBZ precursor after heat treatment at 170 °C for 30 min (Fig. 3(b)) shows no peak, indicating that 170 °C was the maximum temperature to fully crosslink the PBZ precursor.

Characterization of NaA zeolite

The crystal structure of synthesized NaA zeolite particles was characterized using XRD technique matching with the reference data from PDF card number: 00-038-0241, as shown in Fig. 4(a). The peaks obtained were well-matched with the reference that indicated the cubic structure of NaA zeolite. To confirm the results, the SEM technique was used and the image is shown in Fig. 4(b). It revealed the cubic shape of the synthesized NaA zeolite with the size was in a range of 0.24–0.74 μm .

PBZ membrane

To obtain good separation performance, the fabricated membrane must have no defects and be sufficiently thin. Study of the precursor concentration and the number of dipping cycles was thus conducted, and results are shown in Fig. 5. The pervaporation testing was carried out using 50:50 water:ethanol mixture at 70 °C. It was found that the number of dipping cycles required to prepare a good membrane depends significantly on the precursor concentration. None of the membranes prepared using 5–25 wt% precursor can be achieved from only one dipping cycle. The first dipping cycle might be a pretreatment for the ceramic support surface before the dense thin film layers, i.e. separation layers, started to form during the second dipping step. However, except for the 5 wt% precursor, the additional dipping did not affect the membrane performance since nearly constant values were obtained beyond two dipping cycles at each precursor concentration (Fig. 5). The relationship between the required number of dipping cycles, separation performance, and membrane thickness is summarized in Table 1. The minimum number of dipping cycles required was found to be two when using the precursor concentrations of 20 and 25 wt%. It was noticed that a precursor concentration higher than 25 wt%, e.g. 30 wt%, resulted in a very viscous polymer solution, which hindered the dipping step. The membrane prepared from 30 wt% precursor was either impermeable or highly defective. Therefore, the highest performance membrane with a separation factor >10 000 can only be obtained when using a precursor concentration of 25 wt%. Moreover, the membrane thickness undoubtedly increased with an increase in the PBZ precursor concentration. As described previously, the separation performance also depends on the membrane thickness. The thickness values obtained thus reflect the permeation flux and the separation factor of each membrane. The thicker membrane resulted in a lower permeation flux, but also a higher separation factor.

NaA-PBZ mixed matrix membrane (NaA-PBZ MMM)

The key component of a membrane process is the membrane itself. The two most basic requirements for selecting a membrane are selectivity or separation factor and permeation rate. Compared with polymeric membranes, a significant improvement in separation properties with trivial loss in membrane flexibility is

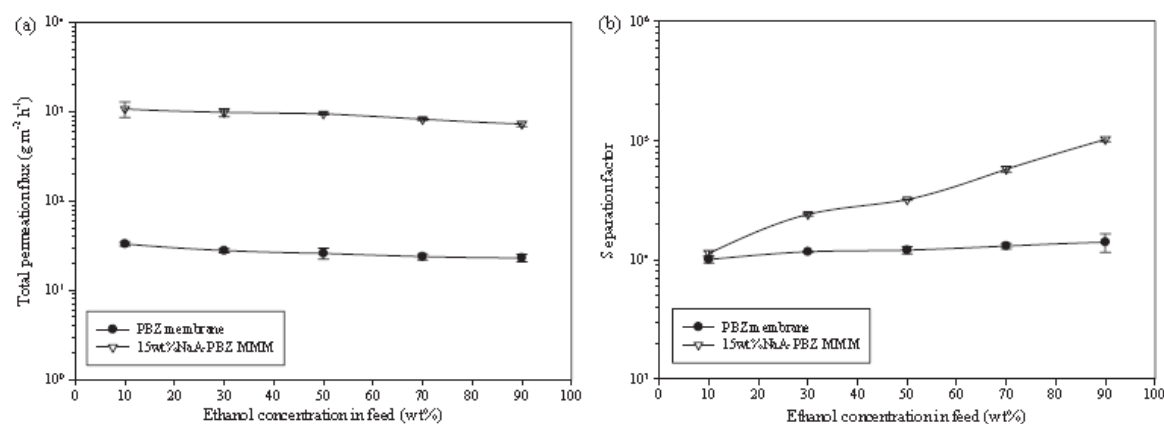


Figure 9. Effect of feed ethanol concentration on (a) total permeation flux and (b) separation factor at 70 °C.

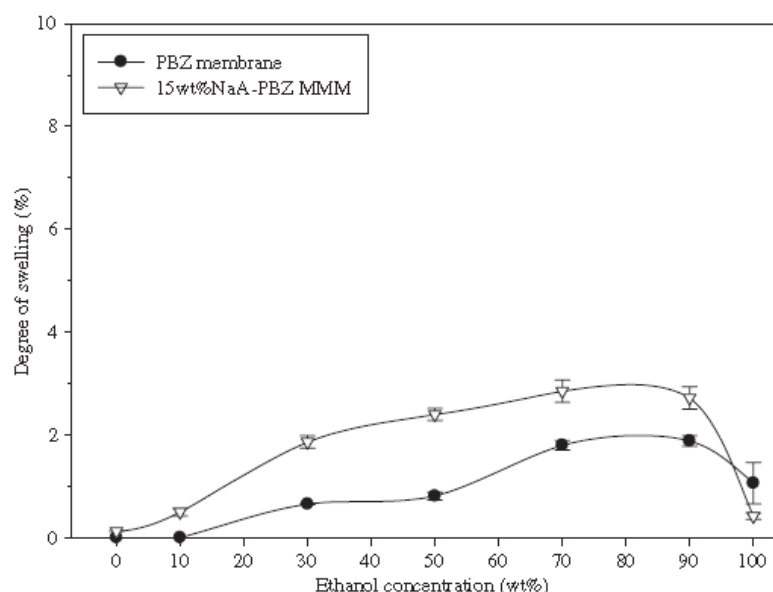


Figure 10. Swelling testing of membranes in various ethanol concentrations.

expected for the resultant MMMs due to the presence of inorganic fillers. In this study, NaA zeolite is the filler used in the PBZ matrix which was prepared by using a precursor concentration of 25 wt%. The pervaporation performance results of the PBZ membrane containing no NaA zeolite and NaA-PBZ MMM, containing various amounts of NaA zeolite (5–25 wt%), and using 90 wt% ethanol feed concentration are shown in Fig. 6. Due to the fully crosslinked PBZ making the material become very dense, the permeation flux of the pure PBZ membrane was low ($22.9 \text{ g m}^{-2} \text{ h}^{-1}$). However, the separation factor was impressively high, above 10 000. According to the mechanism proposed by Pakkethati,¹⁰ the diffusion of ethanol molecules in the membrane was reduced by the attraction between ethanol and hydrophobic PBZ chain. Thus, only water molecules can permeate throughout the membrane, resulting in very high membrane separation factor.

The addition of 5 wt% zeolite not only increased the flux, but also increased the separation factor. This is due to the molecular sieving effect of the NaA zeolite. The pore opening of NaA zeolite is about 4 Å which is large enough for water molecules (kinetic diameter of 2.65 Å) to diffuse through, but restricts the ethanol molecules (kinetic diameter of 4.46 Å).²³ Thus, the process enhances the membrane selectivity or the separation factor. Moreover, the hydrophilic property of the NaA zeolite also improves water transportation in the membrane, resulting in the increasing of total permeation flux, as well.²⁴ As the amount of zeolite was increased to 15 wt%, both the permeation flux and the separation factor remarkably increased to $1071 \text{ g m}^{-2} \text{ h}^{-1}$ and over 100 000, respectively. However, at loading beyond 15 wt% NaA, the separation factor dropped from the maximum value of more than 100 000 to 943 and 6 at 20 and 25 wt% NaA, respectively. This is due to the agglomeration of zeolite causing a defective membrane and promoting ethanol leaking, resulting in a decrease in the membrane separation factor.²⁴

This effect can be clearly identified in the SEM images shown in Fig. 7. The PBZ membrane surface is smooth and dense (Fig. 7(a))

while the PBZ membranes loaded with NaA zeolite show white particles dispersed underneath the PBZ smooth surface (Fig. 7(b) and 7(c)). The membrane surface started to become rough when loaded with 15 wt% of NaA zeolite (Fig. 7(d)). Voids and defects started to occur at 20 and 25 wt% NaA (Fig. 7(e) and 7(f)), leading to a greater chance for ethanol molecules to pass through the membrane, resulting in a drastic decrease in the separation factor, as shown in the results in Fig. 6. Thus, 15 wt% NaA-PBZ MMM, exhibiting the highest separation factor of more than 100 000, was selected as the optimum MMM for use in further experiments. In addition, examples of the cross-sectional images of the PBZ membrane and the MMM (Fig. 7(g) and 7(h), respectively) also revealed that the average membrane's thickness was in a range 19 to 23 µm.

The effect of NaA zeolite on the reduction of surface smoothness can also be determined through visual observation, as in Fig. 8, showing the appearance of the support and the supported membranes. The α -alumina support exhibits a white, dull appearance (Fig. 8(a)) while a yellow, smooth glossy surface was achieved when coated with pure, fully crosslinked PBZ (Fig. 8(b)). As can be seen in Fig. 8(c)–(e), the membranes lost their glossy appearance and became duller with increase in the amount of NaA zeolite, and the higher NaA zeolite content resulted in a rough and dull surface.

Effect of ethanol concentration in feed

The separation performances and stability of PBZ membrane and PBZ MMM containing 15 wt% of NaA were investigated using various ethanol concentration feeds. Experimentally, the pervaporation of ethanol/water mixture was done by permeating water and circulating the retentate back to the feed reservoir.²⁵ Thus, the amount of water in the feed decreased, allowing the ethanol concentration to increase over time. To study whether these membranes are stable in other ethanol concentrations besides the 50:50 ethanol/water ratio, a pervaporation test of the

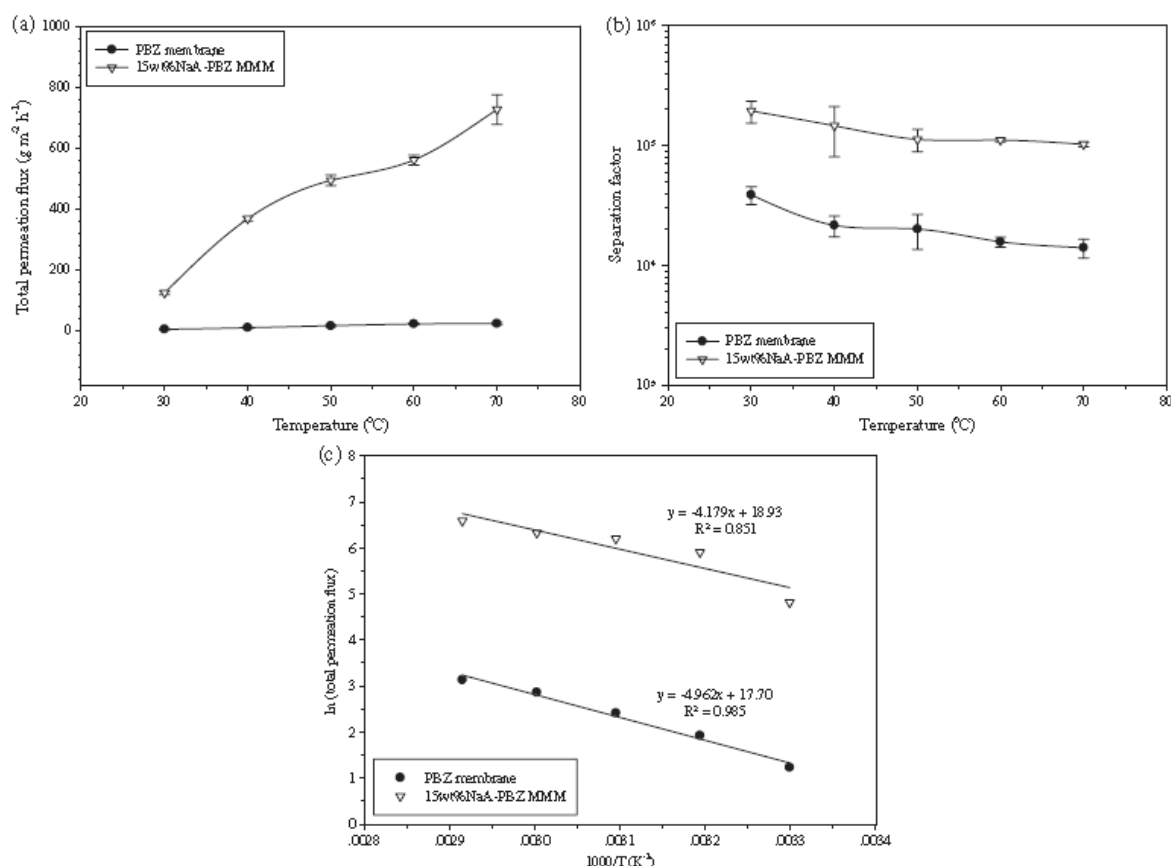


Figure 11. Effect of temperature on membrane separation performance (a) total permeation flux; (b) separation factor; and (c) Arrhenius plot.

membrane over a whole range of ethanol concentrations was designed, and the results are shown in Fig. 9(a). The PBZ membrane exhibits much lower permeation flux ($13.5\text{--}28.0 \text{ g m}^{-2} \text{ h}^{-1}$) than the 15wt% NaA-PBZ MMM ($726.0\text{--}1071.1 \text{ g m}^{-2} \text{ h}^{-1}$). The permeation flux slightly decreased when the feed ethanol concentration was increased, owing to the reduction in the water partial pressure at the retentate side.²⁶ Moreover, both membranes show excellent stability since the separation factor values were maintained at higher than 10 000 for every feed ethanol concentration (see Fig. 9(b)), due to the network structure of PBZ. Many other works reporting on the use of polymeric membranes noted that a damaged membrane resulting from an increase in ethanol concentration caused a drastic reduction of the separation factor.^{10,27,28} There was no observation of the membrane being damaged by solvent swelling in this work, confirming that these PBZ-based membranes provide excellent stability over all ranges of ethanol/water pervaporation system. This is an important advantage when serving as the pervaporation membrane in any feed ethanol concentration.

Membrane swelling behavior

A swelling test of both membranes was conducted to confirm separation performance. Because these membranes were fully crosslinked, the degrees of swelling of all membranes obtained were less than 3%, as seen in Fig. 10. The swelling degree increased

with increase in the ethanol concentration, revealing that the PBZ membrane has a higher affinity for ethanol than for water, indicating the hydrophobic behavior of the PBZ-based membranes.²⁹ It is worth noting that 100% ethanol produced a lower swelling degree than the ethanol/water mixture. As described by Xu *et al.*, ethanol molecules could act as a small surfactant to interact with the PBZ surface and become more hydrophilic.³⁰ This changing property allows the water molecules in the ethanol–water mixture to be sorbed, resulting in a significant increase in the degree of swelling.^{31,32} This phenomenon can probably relate to a mechanism in which the water molecules diffuse through the membrane matrix despite the fact that PBZ exhibits hydrophobic behavior. In addition, the degree of swelling of MMM was slightly higher than the PBZ membrane due to the presence of hydrophilic NaA zeolite.²⁴

Effect of temperature

As the separation temperature was increased from 30 $^{\circ}\text{C}$ to 70 $^{\circ}\text{C}$, the permeation fluxes of both PBZ membrane and NaA-PBZ MMM increased (Fig. 11(a)). It is well known that the increase of temperature improves the polymer chain mobility as well as the kinetic energy of the diffusing molecules, resulting in a higher diffusing rate or permeation flux of both ethanol and water.^{33–35} Moreover, the rising of the temperature could alter the sorption behavior of both diffusing molecules that could lead to a higher permeation

rate of the ethanol molecule over the water molecule, resulting in a decrease of the separation factor with increasing temperature (Fig. 11(b)).^{24,36} To further investigate the effect of temperature, the Arrhenius plot was used:

$$J = J_0 \exp \left(\frac{-E_a}{RT} \right) \quad (4)$$

where J is the total permeation flux, J_0 is the permeation rate constant, E_a is the apparent activation energy for permeation, R is the universal gas constant, and T is the temperature in Kelvin. The plot between $\ln(J)$ vs $1/T$, as given in Fig. 11(c) reveals that the apparent activation energies of the PBZ membrane and the 15wt%NaA-PBZ MMM are 41.25 and 34.74 kJ mol⁻¹, respectively. The lower activation energy of the MMM indicates that an excessive chain movement of the PBZ is restrained by the presence of NaA zeolite in the polymer matrix, causing the permeation flux to be less sensitive to changes in temperature.³³

CONCLUSIONS

The PBZ membrane and NaA-PBZ MMM were successfully fabricated on tubular α -alumina support for ethanol/water separation via pervaporation. Both PBZ and NaA-PBZ membranes exhibit excellent stability in all ethanol concentrations with degree of swelling values of less than 3%. The highest separation factor of the PBZ membrane was greater than 10 000 with permeation flux of 13.5–28.0 g m⁻² h⁻¹ while that of the NaA-incorporated PBZ matrix increased to more than 100 000 with a permeation flux of 726.0–1071.1 g m⁻² h⁻¹. In addition, the apparent activation energies of the PBZ membrane and the 15 wt% NaA-PBZ MMM were 41.25 and 34.74 kJ mol⁻¹, respectively.

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Novel polymeric membrane materials for ethanol/water separation via pervaporation

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In this research, novel polybenzoxazine (PBZ) membranes, synthesized from bisphenol-A, formaldehyde and diamines, were coated on a tubular alumina support by dip-coating technique for ethanol purification application via pervaporation. The effects of dipping time and precursor concentration on the membrane preparation and the separation performance showed that both PBZ membranes were remarkably stable, resistant to swelling, and provided an impressively high separation factor of higher than 10,000 for all ethanol concentration ranges, characteristics implying that they could be a good candidate for high purity ethanol production.

Keywords: Polybenzoxazine membrane, Swelling behavior, Separation performance

Introduction

An increase in energy use has spurred greater interest in producing ethanol fuel for vehicle use. The ethanol fuel, however, must be highly pure to prevent damage to vehicles. It is well known that in obtaining highly pure ethanol, membrane technology can be much more energy efficient than conventional technology. Thus, a membrane with high mechanical strength and chemical resistance is required.^{1,2} Polybenzoxazine (PBZ), a thermosetting phenolic resin, is a good candidate for serving this purpose because it has a high performance in both mechanical and chemical properties owing to its thermally activated structure, allowing the ring polymerization to occur and form strong network structures.^{3–5} Pakkethathi *et al.*⁶ studied three different partly cross-linked PBZ membranes for separating 10:90 ethanol:water mixture via pervaporation, and found that only one membrane revealed a good performance in both permeation flux and selectivity. However, all membranes have low mechanical strength and chemical resistance since they cannot tolerate both vacuum force and higher ethanol concentration. In this research, fully cross-linked PBZ membranes were studied to overcome these problems. To prevent brittleness from fully cross-linking PBZ as well as to improve membrane strength, a tubular alumina support was employed.⁷ The effect of PBZ type on swelling behavior and separation performance was also investigated.

Experimental

Tubular alumina supported membrane preparation

Two different partly cross-linked PBZ precursors were first synthesized using two different diamines, namely, tetraethylenepentamine (tepa, 85% purity, Aldrich) and diethylenetriamine (deta, 99% purity, Aldrich), as described elsewhere.^{4,6} Meanwhile, the α -alumina tube (effective length—43 mm, purchased from National Metal and Materials Technology Center (MTEC), Thailand) was cleaned with deionized water in an ultrasonicator bath before calcining at 400°C for 3 h to remove organic dirt.

The PBZ precursors synthesized from tepa or deta were denoted as poly(BA-tepa) and poly(BA-deta), respectively. Using dip-coating technique, PBZ precursors were first diluted by 1,4-dioxane (analytical grade, Labscan) to prepare 10–30 wt-% of poly(BA-tepa) and poly(BA-deta) solutions. The calcined alumina support (one end closed with Teflon cap) was dipped into the solution before drying at 100°C in oven, followed by polymerization at 200 or 180°C, for poly(BA-tepa) or poly(BA-deta), respectively. Both dipping and drying steps were carried out as a cycle, the so called dipping cycle, and were repeated until a functional membrane (or a membrane giving a good separation performance) was obtained.

Membrane characterization

Surface morphology and thickness of membranes were characterized by scanning electron microscope (SEM, JEOL JSM-540LV). Gas chromatography (GC, Agilent 6890N) equipped with TCD detector was used to determine the quality of ethanol in both permeate and retentate while testing performance.

To study the swelling behavior, three different solvents (pure ethanol (absolute EtOH, Labscan), water,

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and 50 : 50 (w/w) ethanol/water), were used. Into each solvent, 0.1 g PBZ thin film was immersed, and the system was maintained at 70°C similar to the actual performance study. The degree of swelling (D_s) of the membrane sample was defined as⁶

$$D_s = \frac{w_t - w_0}{w_0} \times 100 \quad (1)$$

where w_0 is the initial weight of the membrane sample and w_t is the weight of the membrane swollen.

Performance study

The performance of PBZ membranes was carried out in batch pervaporation with a feed flowrate of 900 mL/min using a peristaltic pump (Masterflex). The interior pressure was maintained constantly at 10 mmHg using a vacuum pump (Edwards). The ethanol concentration and temperature in the feed were varied to study the pervaporation performance of each PBZ membrane. The amount of permeate was measured to determine the total permeation flux and the ethanol concentrations in both permeate and retentate were determined for the separation factor, as follows:^{7,8}

Total permeation flux (J) ($\text{g m}^{-2} \text{h}$) is defined as

$$J = \frac{W}{A \cdot t} \quad (2)$$

where W is the weight of permeate, A is the membrane effective surface area, and t is the pervaporation time.

Separation factor (α) is defined as

$$\alpha_{\text{H}_2\text{O}/\text{EtOH}} = \frac{\left[\frac{X_{\text{H}_2\text{O}}}{X_{\text{EtOH}}} \right]_{\text{permeate}}}{\left[\frac{X_{\text{H}_2\text{O}}}{X_{\text{EtOH}}} \right]_{\text{retentate}}} \quad (3)$$

where $X_{\text{H}_2\text{O}}$ and X_{EtOH} are the weight fractions of water and ethanol in permeate and retentate, respectively.

Results and discussion

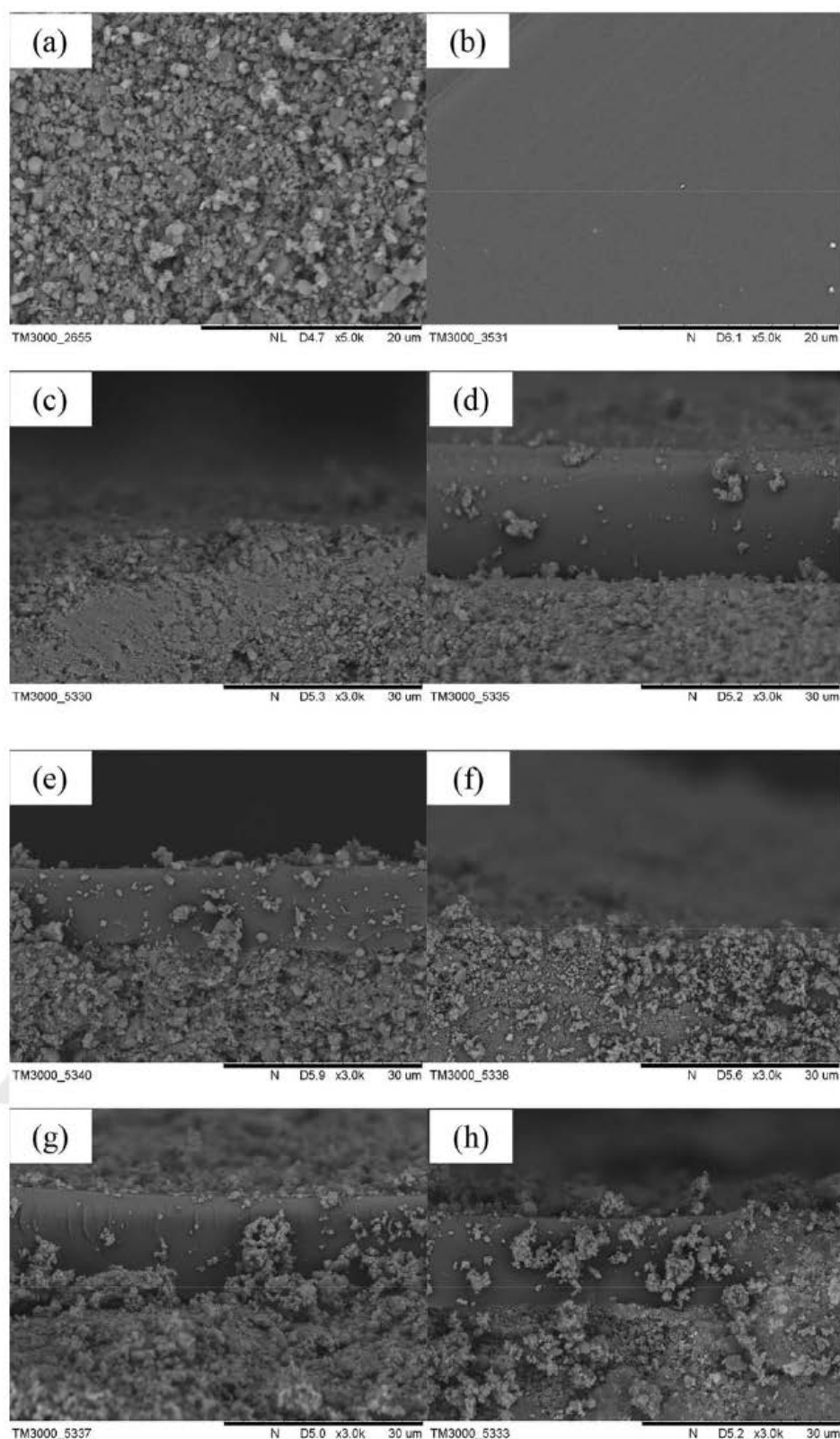
Membrane fabrication

The images of the prepared membranes are shown in Fig. 1. The surface image of α -alumina support shows that the particle size varied from 0.5 to 3 μm (Fig. 1a). After finishing the dipping process, the surface is completely covered with a smooth and dense polymer layer, as shown in Fig. 1b. Because the major separation mechanism occurs at this polymer layer,⁹ it is important to prepare the membrane with a minimum of defect. The cross-sectional images of poly(BA-*tepa*) and poly(BA-*deta*) are shown in Fig. 1c–h. The thickness of the prepared polymer layer was analyzed and summarized in Table 1. As can be seen in Fig. 1c and f, no dense poly(BA-*tepa*) and poly(BA-*deta*) membrane layers prepared from 10 and 20 wt-% precursors, respectively were observed on the support surface even when they were continuously dipped up to 10 times (Table 1), indicating that those concentrations were too low for preparing the membranes. However, instead of coating on the surface, the polymers penetrated into the support, probably owing to a very low solution viscosity. The dense polymer layer was observed when the precursor concentration was up to 20 and 30 wt-% for poly(BA-*tepa*) and poly(BA-*deta*), respectively. It is worth noting that only 20 wt-% poly(BA-*tepa*) was needed to obtain a

dense layer while poly(BA-*deta*) needed 30 wt-% concentration. *Teпа* contains more amine groups, resulting in more intermolecular H-bonding and making poly(BA-*teпа*) membrane fabrication easier to achieve.¹⁰ This result can be confirmed by the thicker poly(BA-*teпа*) membrane layer. In addition, when comparing membranes produced at the same precursor concentration (i.e. 30 wt-%, see Fig. 1e and g), poly(BA-*teпа*) also requires fewer dipping cycles to obtain a dense membrane. Not only fewer dipping cycles were needed to produce a membrane, but also the resultant thinner membrane layer improved the membrane performance, resulting in a thinner polymer layer and consequently providing a higher permeation flux.^{6,9} Conclusively, a defect-free polymer layer cannot be obtained if the precursor concentration is too high or too low. The optimal precursor concentrations for preparing poly(BA-*deta*) and poly(BA-*teпа*) membranes were at 30–40 and 20–30 wt-%, respectively.

Membrane performance

To study the membrane performance, pervaporation is generally utilized and in this study a batch system containing a mixture of water–ethanol was operated. Thus, retentate was recycled back to feed while water was permeated through the membrane. As expected, the feed ethanol concentration increased with time. A pervaporation experiment using a feed ethanol concentration ranging from 10 to 90 wt-% EtOH was conducted to study the performance and stability of the membranes. Poly(BA-*teпа*) and poly(BA-*deta*) membranes prepared from 30 to 40 wt-% precursor concentrations, respectively, were chosen since the lowest number of dipping cycles in preparation was needed, taking the shortest time in fabrication. Moreover, the thinnest membrane layer was obtained, maximizing the permeation flux. From Fig. 2, the highest total permeation flux of both poly(BA-*teпа*) and poly(BA-*deta*) are observed at 10 wt-% EtOH feed with a value of 20.25 $\text{g m}^{-2} \text{h}$ (Fig. 2a) and 19.45 $\text{g m}^{-2} \text{h}$ (Fig. 2b), respectively, with a separation factor higher than 10,000, indicating that the permeate contained mostly water. As the ethanol concentration gets higher; the water partial pressure in the feed should be lower, causing a lower permeation flux.¹¹ Although the separation factor of the membranes are not different, the poly(BA-*teпа*) membrane shows a greater reduction in the total permeation flux than the poly(BA-*deta*) membrane at higher feed ethanol concentrations. To clarify this result, a swelling behavior test was conducted in pure water, pure ethanol, and 50 : 50 water:ethanol solvents, and the results are shown in Fig. 3a–c, respectively. Neither membrane was swollen by water molecules after more than 10 days, but both were swollen by ethanol molecules, with the maximum swelling degree of 3.1 and 2.1 for poly(BA-*teпа*) and poly(BA-*deta*), respectively (Fig. 3b). Although these swelling degree results are considerably small, they could indicate that the membranes are more hydrophobic. Fu *et al.*¹² suggested that the sorption of ethanol in hydrophobic membranes restricts the molecular transport in the polymer layer, which would be the major reason in decreasing of permeation flux besides the lowering of water partial pressure. Thus, the drastic decrease of the total permeation flux of poly(BA-*teпа*) at higher ethanol



1 SEM surface Images of *a* uncoated α -alumina support; *b* α -alumina supported PBZ membrane; cross-sectional Images of poly(BA-tepa) at *c* 10 wt-%; *d* 20 wt-%; *e* 30 wt-% and poly(BA-deta) at *f* 20 wt-%; *g* 30 wt-%; *h* 40 wt-%, respectively

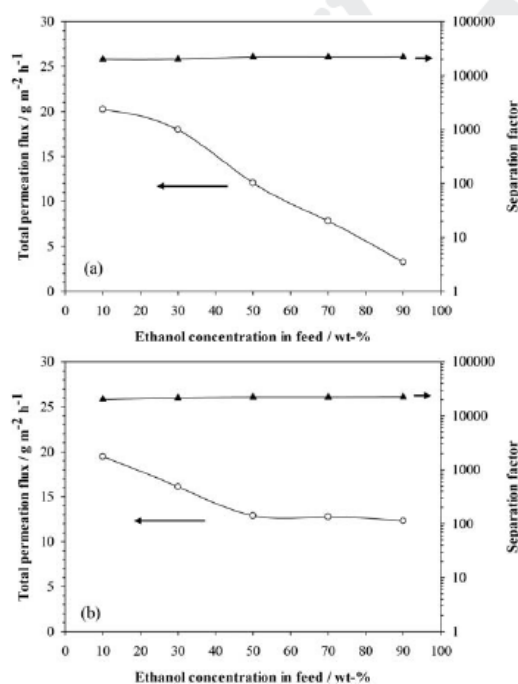
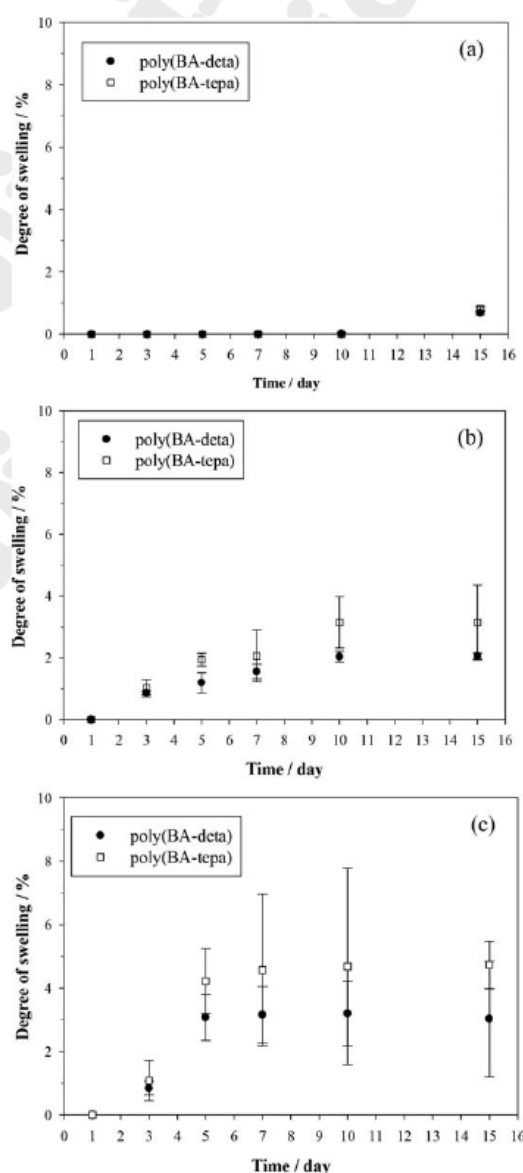
Table 1 Effect of PBZ concentration on number of dipping cycle requirement and membrane separation performance

Polymer	Precursor concentration/wt-%	Number of dipping cycle requirement	Averaged membrane layer thickness/ μm^*
Poly(BA- <i>tepa</i>)	10	10†	...
	20	5	19.8
	30	2	11.9
Poly(BA- <i>deta</i>)	10	10†	...
	20	10†	...
	30	4	15.4
	40	2	13.0

* : measured from SEM.

† : all membranes prepared up to 10 times of dipping cycles are leaked and no separation performance was observed.

concentration (Fig. 2a) may result from the higher molecular restriction by ethanol molecules adsorbed in the membrane, as confirmed by the larger amount of the swollen membrane in ethanol (Fig. 3b). The swelling behavior testing also revealed the multiple sorption of water and ethanol molecules in a mixture of ethanol and water (Fig. 3c). The water molecules could adsorb in the membrane via H-bonding with ethanol, resulting in a higher degree of swelling than in pure ethanol conditions.¹³ However, those swelling results are again very small, thus still resulting in a separation factor higher than 10,000 with no sign of being damaged since no drastic drop in the separation factor was observed in all ethanol concentrations.^{14,15} The results could suggest the excellent stability of PBZ membranes in any ethanol/water mixture, leading to a great potential for the use of these membranes in the ethanol purification process, especially in a highly pure ethanol concentration for renewable energy.

**2** Effect of feed ethanol concentration on membrane separation performance of a poly(BA-*tepa*) and b poly(BA-*deta*)**3** Swelling behavior of fully cross-linked PBZ thin film in a pure water; b absolute ethanol and c 50 : 50 water/ethanol mixture

Conclusions

Poly(BA-deta) and poly(BA-tepa) membranes on tubular α -alumina support were successfully fabricated. The PBZ precursor concentration was a major factor in controlling the membrane performance. Poly(BA-tepa) required less precursor concentration to obtain a functional membrane than poly(BA-deta). However, both membranes provide good stability and separation performance at all ethanol concentrations, indicating a potential material for high purity ethanol production.

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Review on “Membranes for Ethanol-water Separation”

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Abstract

The use of bioethanol fuel produced directly from the renewable biomass should be one of the truly sustainable energy developments. However, the amount of ethanol concentration in bioethanol obtained from fermentation is quite low; an energy-effective separation method is required for concentrating ethanol up to the fuel level. The less energy-intensive technique of pervaporation is a promising method in producing high-purity ethanol, but the overall economic feasibility is dependent upon the membrane. Thus, in this review, various membranes are reported, discussed, and compared as to their advantages, disadvantages, and separation performance via the pervaporation process. It is found that different membranes provide different performances and advantages in ethanol separation. Other parameters governing the separation performance, such as temperature, ethanol concentration, membrane production method, and production cost, are also included.

Keywords: Pervaporation, Membrane, Ethanol, Purification, Separation performance

INTRODUCTION

Due to the depletion of fossil fuel reserves and an increase in global demand, the development of sustainable energy alternatives for replacing fossil fuel has attracted great attention for many years, and ethanol fuel, being a good candidate, has been extensively studied. One of the reasons for ethanol's ascendancy is that it can be produced from a variety of resources, such as sugar cane, corn, grasses, etc., using fermentation. However, the current fermentation technique provides a very low ethanol concentration of less than 15 wt% (Mohanty et al., 2009; Lee et al., 2013). This concentration certainly cannot be used in any engine technology; thus, in using bioethanol as the vehicle fuel, the conventional process of azeotropic distillation is used for separating the ethanol-water mixture to obtain a high purity of ethanol of at least 99.5 wt%. The azeotropic distillation, however, is an energy-intensive technique, increasing the cost of the produced fuel (Van Hoof et al., 2004; Kunnakorn et al., 2013). Other techniques, such as pressure swing absorption, liquid-

liquid extraction, and crystallization, are not only costly and energy intensive, but also limited in terms of practical production (Kim et al., 2002). Membrane separation technique using pervaporation is thus an attractive process to be considered.

PERVAPORATION PROCESS

Pervaporation, a separation of liquid mixture using a selective membrane especially for the azeotropic and close-boiling point mixtures, is well known to be a less energy-intensive operation than the common azeotropic distillation process, leading to a more energy-efficient way to produce a high purity of ethanol for fossil fuel replacement (O'Brien et al., 2000). A liquid mixture is fed to contact with the membrane at the upstream side while the downstream side is being held under vacuum. The undesired component is able to permeate through the membrane preferentially in the form of vapor by means of the low pressure before flowing out. The desired component is concentrated by recycling the retentate to the feed reservoir, as shown in Fig. 1. The separation performance of the membrane is determined by two major factors, permeation flux and separation factor, which relate to both the productivity and quality of the separation, as given in eq. 1 and 2, respectively.

Insert Figure 1

The permeation flux (J , $\text{kg m}^{-2} \text{h}^{-1}$) is defined as:

$$J = \frac{W}{A \cdot t} \quad (1)$$

where W is the weight of permeate (kg), A is the effective membrane area (m^2), and t is the pervaporation time (h).

The separation factor (α) is defined as:

$$\alpha = \frac{\left(\frac{w_{H_2O}}{w_{EtOH}} \right)_{Per}}{\left(\frac{w_{H_2O}}{w_{EtOH}} \right)_{Ret}} \quad (2)$$

where w_{H_2O} and w_{EtOH} are the weight fractions of water and ethanol from the permeate side (denoted as Per) and the retentate side (denoted as Ret), respectively.

MEMBRANE DEVELOPMENT

Currently, the major focus of membrane development is to improve membrane performance in both high separation factor and permeation flux, thereby enhancing the economic feasibility of ethanol production (Di Luccio et al., 2002). A variety of materials have been studied in development of the membrane. In this report, the membranes for only ethanol-water mixture are reviewed and categorized into three main classes, viz., polymeric membranes, inorganic membranes, and mixed-matrix membranes. In polymeric membranes, the separating layer is made from organic polymers, while inorganic membranes are made from ceramics or zeolites. Mixed-matrix membranes are composed of both ceramic and polymer, working together for the separation (Kittur et al., 2005).

POLYMERIC MEMBRANES

The polymeric membrane is the most common membrane in the membrane separation and can be fabricated by various simple techniques, such as casting, extruding, and coating. These techniques facilitate ethanol's economic feasibility in terms of membrane product and cost (Chowdhury et al., 2001; Widjojo and Chung, 2009). The polymeric membrane can be used as a self-supporting membrane or supported membrane. Generally, the support for a polymeric membrane is made of porous ceramics or stronger polymer to improve the membrane strength for a better separation performance (Fu et al., 2014). The self-supporting membrane is normally cast as a thin polymer film which generally provides low mechanical properties, low separation performance, and high swelling. These drawbacks limit its application for use in the ethanol purification area (Zhao et al., 2013). Thus, many researchers have focused on improving the membrane stability as well as its separation performance by increasing crosslinking degree, blending with other polymers, and co-polymerizing with other monomers (Zhang et al., 2009). Due to the high polarity of the ethanol-water mixture, the membrane to be used in the ethanol-water separation must be hydrophilic polymers, such as poly(vinyl alcohol) (PVA), chitosan, and cellulose. However, hydrophobic membranes have also gained more attention for ethanol-water separation due to their better mechanical properties, higher chemical resistance, and higher thermal stability (Ghofar and Kokugan, 2004; Smuleac et al., 2010). Examples of hydrophobic membranes are polydimethylsiloxane (PDMS), polyimides, and a new class of phenolic resins, so-called polybenzoxazine (PBZ).

Self-supporting polymeric membranes

Praptowidodo (2005) studied the influence of two different hydrophilic groups, itaconic acid and N-3-trimethyl-ammonio-propyl-acrylamide-chloride, in PVA co-polymer membranes, and compared them with the pure PVA membrane. The pervaporation result of 90:10 ethanol:water mixture showed that the separation factor of the PVA-itaconic acid copolymer membrane was the

highest, as a result of having the highest hydrophilicity, while the second copolymer containing ammonium group provided a lower separation factor, but a higher one than the pure PVA due to lower hydrophilicity. However, the permeation fluxes of both copolymer membranes were decreased due to their higher rigidity, causing brittleness. The results were in good agreement with the study of the crosslinking effect using glutaraldehyde. With an increase in crosslinking time, the separation factor increased, but the permeation flux decreased.

A PVA copolymer containing a hydrophilic group was also studied by Zhang et al. (2009). They prepared a PVA membrane grafted with quaternary ammonium group called quaternized PVA membrane using trimethyl ammonium chloride with the degree of quaternization (DQ) ranging from 2.024 to 4.035. They found that increasing the DQ value in the membrane increased the hydrophilicity and improved water selectivity, but also increased the swelling. Thus, they minimized the swelling by crosslinking the membrane using glutaraldehyde even at 85 wt%EtOH, resulting in a higher selectivity. However, the permeation flux was reduced. Since a good pervaporation membrane requires high permeation flux and selectivity, these membranes must be optimized between degree of quaternization and degree of crosslinking.

Gimenes et al. (2007) prepared a blend between sericin, extracted from the silkworm cocoons, and PVA for ethanol pervaporation membrane. The dimethylolurea (DMU) was used as a crosslinking agent which was expected to crosslink only at hydroxyl groups and leave the amino groups of sericin to interact with water during the pervaporation. They found that the increase in hydrophilicity by introducing PVA into sericin caused the membrane to swell more, resulting in a higher permeation flux and lower separation factor.

Pandey et al. (2005) prepared a bacterial cellulose membrane for separation of glycerol, ethylene glycol, ethanol, formalin, and acetone from water. They claimed that bacterial cellulose was able to serve as the pervaporation membrane in an ethanol/water system, providing an excellent permeation flux of $1.43 \text{ kg m}^{-2} \text{ h}^{-1}$ at 75°C . However, the separation factor obtained was very low, only 1.3. They explained that the membrane was not modified or crosslinked, causing the membrane to swell and resulting in such a low separation factor.

Dubey et al. (2005) worked on improving chitosan membrane by preparing chitosan/bacterial cellulose and chitosan/PVA membranes. Based on their previous work (Dubey et al., 2002), bacterial cellulose showed high mechanical strength, high chemical resistance, and good water flux. The bacterial cellulose was selected to blend with chitosan. The results showed that although the chitosan/bacterial cellulose membrane possessed a higher mechanical strength than the chitosan/PVA membrane, the membrane exhibited an identical strength to the pure chitosan

membrane, meaning that adding bacterial cellulose did nothing to improve the chitosan membrane strength. Moreover, the separation performance of the chitosan/PVA membrane revealed unsatisfactory results, showing a further reduction of permeation flux. The chitosan/bacterial cellulose also showed a moderate separation performance, but both the permeation flux and the mechanical strength were still less than those obtained from the pure bacterial cellulose membrane.

Lai et al. (2012) prepared PDMS membrane using UV/ozone treatment. Naturally, the PDMS membrane exhibits the hydrophobic property, but its surface structure could be changed by the UV/ozone treatment. Thus, the treatment was expected to change the surface hydrophobicity to a hydrophilic form, which would be more suitable for the ethanol/water pervaporation. They found that the UV/ozone treatment indeed affected the membrane surface. The working distance, relating to the UV intensity, and the pretreatment time were optimized to maximize the hydrophilicity of the membrane. However, the pervaporation results demonstrated a trade-off between the permeation flux and the separation factor after the treatment. As hydrophilicity increased, the separation factor also dramatically increased since the structure was changed to more silica-like structure, which was more restrictive to larger molecules like ethanol. However, it was also denser, reducing the total permeation flux.

Pakkethati et al. (2011) prepared PBZ membranes for ethanol/water pervaporation using a simple film-casting technique. Due to the extraordinary properties of PBZ, the PBZ was expected to exhibit higher mechanical strength and thermal stability. In their work, three different PBZs were synthesized from the bisphenol-A (BPA), formaldehyde, and three different amines, viz., hexamethylenediamine (HDA), tetraethylenepentamine (TEPA), and tetraethylenetriamine (TETA). They found that all PBZ membranes showed a high thermal stability up to 240 °C, which is much higher than the operating temperature in the pervaporation system. The pervaporation results revealed that the fabricated PBZ membrane synthesized from HDA exhibited the highest stability with a service time longer than 120 h, a permeation flux of 1.52 kg m⁻² h⁻¹, and separation factor of more than 10,000 at 70 °C, indicating outstanding separation performance for the ethanol/water separation with no need of additional membrane modification. They explained that the chain flexibility of the long aliphatic chain in the HDA structure played a significant role.

Le and Chung (2014) demonstrated a copolyimide membrane prepared from poly(1,5-naphthalene/3,5-benzoic acid-2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropanedimide) (6FDA-NDA/DABA) blending with its sulfonated polymer. The blend of sulfonated polymer with its pure form was expected to control the membrane performance and reduce the cost since the sulfonated polyimide provides a hydrophilicity of the membrane which increases the permeation flux, but reduces the membrane strength. According to Le and Chung, it is difficult to control the properties

of the prepared membrane, resulting in poor repeatability. In their study, the preparation procedure was done by spinning process to make the hollow fiber membrane. The pervaporation result showed that the permeation flux increased when adding sulfonated polyimide, but the separation factor was lower due to the looser polymer structure, as confirmed by the increase in swelling of the polyimide blend membranes. Thus, they further studied to improve the separation factor by coating the membrane surface with PDMS layer and thermal treatment. This modification improved the membrane for the separation factor only, since the permeation flux was still reduced.

Recently, Chen et al. (2014) studied the PDMS membrane pervaporation of bioethanol produced from corn stover via fermentation process using a mixture of glucan, cellulose, and β -glucosidase enzymes. The impurities produced during the fermentation process were expected to somehow affect the pervaporation. They found that the major components were acetic acid and furan derivatives. The pervaporation with the addition of impurity was carried out individually. The effect of acetic acid was explained by the interaction between acid and PDMS, blocking the water molecules ability to diffuse through, thus reducing permeation flux. The effect of the furan derivatives was observed by using ijR value, indicating the interaction between PDMS and chemicals based on the solubility parameters. The higher ijR value obtained, the more interruption caused by the chemicals.

The separation performance data of all self-supporting membranes discussed above are summarized in Table 1. As can be seen, this membrane class is mostly produced from PVA, owing to its highly hydrophilic property. The PVA membranes provide a good separation performance with the permeation flux and the separation factor in the ranges of $0.03\text{--}0.3 \text{ kg m}^{-2} \text{ h}^{-1}$ and $10\text{--}300$, respectively. However, the hydrophobic PBZ membrane has also attracted a great attention in ethanol production application because it can provide superior separation performance with the permeation flux up to $3 \text{ kg m}^{-2} \text{ h}^{-1}$ and the separation factor of over 10,000. Thus, the PBZ membrane could have a greater potential in a practical process.

Insert Table 1

Supported polymeric membranes

The limitation of self-supporting polymeric membranes, aka unsupported membranes, in some aspects, such as poor mechanical properties, low separation performance, etc., have led to the development of the supported polymeric membranes to overcome those drawbacks (Kim et al., 2000; Wei et al., 2011). Porous ceramic materials or strong porous polymers are generally used to support the polymeric membrane. Because the molecular transport occurs in both the membrane (or

separating) and the support layers, mechanical properties and separation performance are thus improved (Yoshida and Cohen, 2003).

Kim et al. (2000) prepared a thin poly(amic methyl ester) membrane on the commercial porous polysulfone support via interfacial polymerization of 2,5-bis(methoxycarbonyl terephthaloyl chloride) (BMTC) with various diamines, viz., ethylene diamine (EDA), hexamethylene diamine (HDA), and m-phenylene diamine (m-PDA), directly on the support surface. They found that poly(amic methyl ester) supported polysulfone improved the separation factor when compared to the performance of the support itself. However, the permeation flux decreased due to the increase in the transport resistance. The HDA-BMTC and EDA-BMTC membranes were found to provide superior pervaporation performance for 90:10 ethanol:water because the separating layer of these membranes was very thin while the PDA-BMTC membrane was poor in film-forming ability. Moreover, the HDA-BMTC membrane was further tested for its stability and demonstrated an excellent stability up to six days after the operation.

Yanagishita et al. (2001) studied the pervaporation performance of polyimide synthesized from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) using poly(amic acid) salt (PAA salt), and coated on commercial asymmetric polyimide (PI-2080) support. The result showed that the performance of the supported membrane significantly better than the self-supported one because the separating layer thickness was greatly reduced.

Li et al. (2006) worked on chitosan (CS)-PVA blends prepared on polyacrylonitrile (PAN) support for separation of ethanol, similar to the work by Jiratananon et al. (2002), who prepared chitosan-hydroxycellulose (CS-HEC) blends on cellulose acetate (CA) support. The separation performance of the chitosan was expectedly improved by blending with a highly hydrophilic polymer, such as PVA or HEC, to increase the membrane hydrophilicity. Li et al. found that the separation factor of the CS-PVA/PAN membrane increased to maximum at 40 wt% of PVA concentration before slightly decreasing, probably due to the phase inversion of the CS-PVA matrix. However, when comparing the performances between the pure CS, CS-PVA/PAN, and PVA/PAN membranes. The PVA/PAN membrane provided fair permeation flux and an excellent separation factor while the CS membrane was superior in the permeation flux, but fairly low in the separation factor. The CS-PVA/PAN membrane, however, provided a permeation flux as low as the PVA/PAN membrane, and separation factor as low as the CS membrane.

Huang et al. (2008) studied poly(thiol ester amide) prepared on the modified polyacrylonitrile (m-PAN) support. The interfacial polymerization technique was used in preparing poly(thiol ester amide) thin film by reacting cystamine (2-aminoethanethiol) with trimesoyl chloride (TMC) or

succinyl chloride (SCC) on the support. They found that the poly(thiol ester amide) membrane synthesized from TMC performed better separation in terms of selectivity than the membrane synthesized from SCC because of the aromatic ring and the network structure of TMC, providing less swelling. They also measured the free volume of the membrane using Doppler-broadened linewidth and shape (S) parameters. The results confirmed the presence of the network structure in the TMC membrane and that the active layer thickness was only 100 nm, much thinner than the typical self-supported polymeric membranes.

Zhu et al. (2010) prepared PVA-chitosan membrane on a tubular asymmetric $\text{ZrO}_2\text{-Al}_2\text{O}_3$ support, and studied the effect of the support pore size on the performance of t-butanol/water pervaporation. It was found that the support pore size of 0.2 μm was the optimum. A too-narrow pore size of 0.05 μm provided very low permeation flux due to the high molecular transport resistance, while a too-large pore size of 0.5 μm provided very low separation factor and permeation flux because the support was not compact enough, easily causing defects. Moreover, filling of polymer into the support pores also caused a huge permeation resistance. For the separating layer, chitosan concentration was found to reduce the compactness of the PVA structure, providing more permeation flux and a slightly lower separation factor. These results were contradictory to the study of Dubey et al. (2005) who found that the structure was more compact when blending PVA with chitosan, causing further reduction of permeation flux in ethanol/water pervaporation. The membranes were further tested for various organic-water mixtures; ethanol, t-butanol, methyl acetate, and ethyl acetate, and the results showed that the pervaporation of the ethanol/water system revealed the highest activation energy.

The tubular asymmetric $\text{ZrO}_2\text{-Al}_2\text{O}_3$ was also studied to support PDMS membrane in the work of Wei et al. (2011). The tubular PDMS/ $\text{ZrO}_2\text{-Al}_2\text{O}_3$ membrane was tested and compared with PDMS membrane supported by blended cellulose acetate (BCA) or PDMS/BCA membrane. The PDMS/ $\text{ZrO}_2\text{-Al}_2\text{O}_3$ membrane was prepared by dip-coating technique while PDMS/BCA membrane was prepared by casting technique. Reduction of polymer penetration into the support and a more uniform coating when increasing molecular weight of PDMS were found to be the major reason for the increase of separation factor of the PDM/ $\text{ZrO}_2\text{-Al}_2\text{O}_3$. The membrane thickness was found to be governed by the polymer concentration and the dipping time. The pervaporation performance result of the PDMS/ $\text{ZrO}_2\text{-Al}_2\text{O}_3$ was not only superior, but also the long-term pervaporation results showed that the PDMS/ $\text{ZrO}_2\text{-Al}_2\text{O}_3$ was quite stable up to 30 days with no sign of delamination while the PDMS/BCA was delaminated after 11 days of the operation.

The potential of using fully crosslinked polybenzoxazine (PBZ) membrane for ethanol/water pervaporation was studied by Chuntanalerg and coworkers (in press, b). Two different PBZs

synthesized from bisphenol-A, formaldehyde, and tetraethylenepentamine (tepa) and diethylenetriamine (deta), denoted as poly(BA-tepa) and poly(BA-deta), respectively, were coated on tubular alumina support in order to prevent brittleness and to improve membrane strength. As both poly(BA-tepa) and poly(BA-deta) membrane were fully crosslinked, the swelling property was minimized, allowing them to better tolerate in a wide range of the feed ethanol concentration, from 10 to 90 wt%, with the separation factor values of higher than 10,000. However, the reduction of the permeation was observed at high ethanol concentration, due to the restriction of molecular transport caused by sorbed ethanol. From the study, it was found that the permeation flux of poly(BA-tepa) membrane was reduced greater than that of poly(BA-deta) due to the higher amount of ethanol sorption in poly(BA-tepa).

The separation performance data of all supported polymeric membranes are summarized in Table 2. PVA was widely used as the separating layer along with chitosan. In this case, there is more than one layer involved in the separating mechanism, membrane and support layers. The major improvement of the pervaporation performance should depend on the membrane selectivity.

Insert Table 2

INORGANIC MEMBRANES

Unlike the polymeric membranes, the inorganic membranes for ethanol/water separation are dominated by a single type of zeolite membrane called NaA zeolite (is referred to as zeolite A or 4A zeolite) membrane. The NaA zeolite, a sodium aluminosilicate with Linde Type A (LTA) framework, has a well-defined pore opening of about 4 Å, perfectly lying in between the molecular sizes of ethanol (kinetic diameter of 5.2 Å) and water (kinetic diameter of 2.6 Å) (Shah et al., 2000). It thus provides a molecular sieving ability in separating those two molecules, leading to a high performance membrane with an exceptional permeation flux and separation factor.

Kondo et al. (1997) prepared NaA zeolite membrane on various supports having different $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios. The supports were produced by mixing $\alpha\text{-Al}_2\text{O}_3$, mullite, and cristobalite together. They found that the membrane selectivity increased when increasing the Al_2O_3 content up to 70 % before becoming constant. However, the most cost-effective support was at 65% Al_2O_3 content, although the price of a support tube with I.D., O.D., and length of 9, 12, and 800 mm, respectively, were 1,300 JPY or about 11.18 USD.

Ikegami et al. (1999) studied the pervaporation of ethanol/water using silicalite membrane. The effects of sugars and yeast cells presented in bioethanol on pervaporation performance were

investigated. The reduction of permeation flux was found when any of the impurities are presented in the mixture, due to the restriction of molecular diffusion by those impermeable molecules. This finding was opposite to that of Chen et al. (2014) who found that the presence of yeast cells provided a positive effect to the permeation flux for their polymeric membrane. This report was a good example of using inorganic membranes in bioethanol pervaporation in comparison with polymeric membranes.

Ma et al. (2009) synthesized microporous silica membrane for ethanol/water pervaporation. The total sample of 15 replicates was used in their pervaporation testing. They found that the separation factors and the permeation fluxes obtained were in the ranges of 10 to 500 and 0.3 to $0.8 \text{ kg m}^{-2} \text{ h}^{-1}$, respectively. The best performance membrane, based on the optimization between the separation factor and the permeation flux, was selected for the stability test. The results showed that the membrane was stable up to 1,600 min of the operation. As time progressed, a decrease the permeation flux and an increase in the separation factor were observed. These results are similar to the results obtained from the other porous inorganic membranes, which is related to the decrease of water amount in feed.

Kuanchertchoo et al. (2006) synthesized NaA zeolite membrane on alumina support via seeding and microwave heating techniques using nano-size NaA zeolite seed synthesized from silatrane and alumatrane precursors. The advantages of using atrane precursors in the synthesis of uniformly nano-sized zeolites have been proven and reported in Wongkasemjit's laboratory (Sathupunya et al., 2002; Phiriyawirut et al., 2003). The presence of NaA zeolite seed helps NaA zeolite to uniformly and continuously grow on the alumina support surface. Moreover, Kuanchertchoo et al. (2007) studied the effect of seed concentration, seeding time, reaction time and temperature on the membrane preparation. The optimization of NaA zeolite membrane was justified based on the pervaporation of ethanol/water results. They found that using 3 g of NaA zeolite seed per 1 liter of water is the optimal condition for synthesizing the membrane; amount of seed caused the membrane to become too thick, while a low amount of seed was not enough for zeolite membrane to form a defect-free continuous layer. In this study, the optimal condition for preparing NaA zeolite membrane was to use 3g/l of NaA zeolite seed with 2 min of seeding time and 15 min microwave heating time at 363 K.

Kunnakorn et al. (2011a, 2011b) compared NaA zeolite membranes synthesized from microwave and autoclave techniques. The time-dependent parameters, separation factor, and permeation flux with respect to time were studied and selected to describe the membrane stability. They found that a high purity of ethanol, at least 99.5%, for fuel specification, can be obtained from both membranes using microwave and autoclave techniques. These membranes also provided good

performance and stability in ethanol/water pervaporation for a long-term period with multiple runs, although the membrane prepared from microwave gave slightly higher permeation flux. However, judging from the preparation procedure, the autoclave technique requires significantly longer synthesis time (600 min) than the microwave heating (30 min). They also conducted a techno-economic investigation, comparing energy usage data between the conventional azeotropic distillation and the hybrid process combining distillation and membrane pervaporation systems (Kunnakorn et al., 2013). A chemical process simulation program (PRO II by Provision version 8.0) was used in the study. The simulation was based on the practical distillation process and pervaporation data obtained from the NaA zeolite membrane in their laboratory research. The results showed that the hybrid system provided the lowest energy usage in producing 99.5% ethanol. The highest amount of energy consumption was found in the azeotropic distillation column, which requires almost 20 times more energy than that utilized in the pervaporation unit.

The data of separation performance of all inorganic membranes discussed above are summarized in Table 3. As can be seen, NaA zeolite membranes exhibit the best pervaporation performance, with a permeation flux range of 1.5–2.8 kg m⁻² h⁻¹ and a separation factor of more than 10,000.

Insert Table 3

MIXED-MATRIX MEMBRANE

Basically, a mixed-matrix membrane (MMM), a mixture of an inorganic additive, such as zeolites, and a polymer matrix, is prepared to improve the overall separation performance, and also to overcome the trade-off barrier between permeation flux and separation factor in polymeric membranes (Robeson, 2008; Vane et al., 2008). Generally, zeolites provide exceptional separation performance, but exhibit poor ability in fabrication to achieve a homogeneous membrane.

Sun et al. (2008) prepared a MMM by incorporating H-ZSM-5, an aluminosilicate with MFI type framework with pore opening of 5.4 Å, into chitosan. H-ZSM-5 exhibits high acid strength which was expected to increase the hydrophilicity of the membrane as well as to improve the selectivity by its size-selective effect. The results showed that the H-ZSM-5/chitosan MMM improved the permeation flux. The maximum separation performance was observed when 8 wt% H-ZSM-5 was mixed with chitosan. Although addition of H-ZSM-5 into chitosan did improve the permeation flux when compared to the pure chitosan membrane, the separation factor was reduced, probably due to the larger pore size of H-ZSM-5 than the kinetic diameters of both ethanol and water molecules. They also demonstrated that an increase of the Si/Al in the H-ZSM-5 improved the permeation flux

and separation factor, owing to the increase in the Si-OH-Al framework which improved the adhesion between chitosan and zeolite.

Amnuaypanich et al. (2009) incorporated zeolite 4A into natural rubber/PVA semi-interpenetrating polymer network (NR/PVA semi-IPN). The PVA was expected to improve the hydrophilicity of the hydrophobic NR matrix, while zeolite 4A, having molecular-sieving ability, was expected to improve the permeation flux and separation factor of this MMM. The increase of PVA (which in turn increases –OH group in the NR matrix caused the membrane to absorb more water due to stronger bonding to the water molecules, leading to more swelling. However, the swelling decreased with an increase in the zeolite 4A loading because the zeolite particles restricted the polymer chains movement in the matrix, reducing the total free volume of the polymer matrix. They also found that 30 wt% of zeolite 4A loading resulted in the optimal separation factor and permeation flux.

Lue et al. (2011) loaded a commercial zeolite (trade name: TZP-9023 with a Si/Al ratio of 666) into PDMS membrane. They found that the zeolite consisted of two different pore sizes of 5.93 Å (99.7%) and 29.1 Å (0.3%) with the BET surface area of 243 m²/g. They prepared membranes using two different techniques, adding zeolite into PDMS before and after crosslinking. The pervaporation performance showed a significant improvement in post-addition membrane, while exhibiting only a slightly increase in pre-addition membrane when compared to the dense PDMS membrane. They demonstrated that the non-uniform distribution of zeolite, created by the post-addition of zeolite into the polymer matrix, enhanced the pervaporation performance while the uniform distribution of zeolite caused the chain rigidity which reduced the permeation flux.

Zhan et al. (2012) prepared PDMS/ZSM-5 (Si/Al ratio = 300) MMM loaded etched with HF acid. The etching was expected to improve the adhesion between zeolite and hydrophobic PDMS surface by reducing the hydrophilicity of the ZSM-5 at its surface. The effects of the acid concentration and zeolite loading on the membrane preparation were determined to obtain the optimal condition for a better water-ethanol separation performance. They found that the etching created the pin-holes in micrometer-scale on the zeolite surface, which later filled with PDMS, and enhanced the adhesion between PDMS and zeolite surfaces. The result was confirmed by increasing the HF acid concentration; the membrane separation factor increased while the permeation flux decreased since there was more polymer filling into the zeolite pores, decreasing the polymer chain movement, thus reducing the permeation rate. However, loading 30 wt% ZSM-5 zeolite into PDMS matrix was found to improve both permeation and separation factor. Moreover, they also suggested that this MMM was able to perform the ethanol pervaporation in all ranges of ethanol concentration of 5-90 wt%, which is suitable for bioethanol purification, but the best selectivity was achieved when the ethanol concentration was below 10 wt%.

Flynn et al. (2013) studied a MMM prepared from PVA and mesoporous silica sphere, and found that up to 10 wt% loading of mesoporous silica in PVA matrix increased the permeation flux and the selectivity before causing the drastically decreasing to below the value of those using the pure PVA membrane due to the agglomeration of the silica. The increase of permeation flux with an increase in the silica loading was explained by the increase in the membrane hydrophilicity and free volume while the increase in selectivity was claimed from the conditioning and relaxation effects.

Polybenzoxazine (PBZ) and NaA zeolite were used to prepare MMM (Chuntanaler et al., in press, a). The effects of PBZ concentration, amount of NaA zeolite loading, feed ethanol concentration, and operating temperature on the pervaporation performance were studied and discussed in this work. It was found that the incorporation of NaA zeolite into PBZ matrix, up to 15wt%NaA zeolite loading, improved both permeation flux and separation factor due to an increase in the water transportation and the molecular sieving effect provided by NaA zeolite, respectively. However, when increasing the %loading more than 15wt%, the defect was resulted, causing a drastically decrease of separation factor. The membrane stability evaluated in a wide range of ethanol concentration (10 to 90wt%) was found that the degree of swelling was low, giving a high separation factor of more than 10,000 at the 10wt% ethanol feed and went up to higher than 100,000 at the 90wt% ethanol feed, implying that this MMM was very stable and applicable in the pervaporation of these feed mixtures.

All separation performance data described above for MMMs are summarized in Table 4. The permeation flux and the separation factor of the membranes could be simultaneously improved when adding zeolites into the polymer matrix due to its size-selective ability, which creates a promising way to achieve a higher performance.

Insert Table 4

CONCLUSIONS

Different kinds of membrane provide different characteristics. The self-supported polymeric membranes may provide an economic attraction in membrane production, but not in performance, due to their poor mechanical properties, low chemical resistance, and swelling. The supported membranes improve mechanical strength and separation performance. The inorganic membranes provide an outstanding separation performance, but are extremely difficult in processability, leading to a higher price in industrial usage. The mixed-matrix membranes thus provide an

attractive alternative that are able to overcome all barriers while achieving both permeation flux and separation factor.

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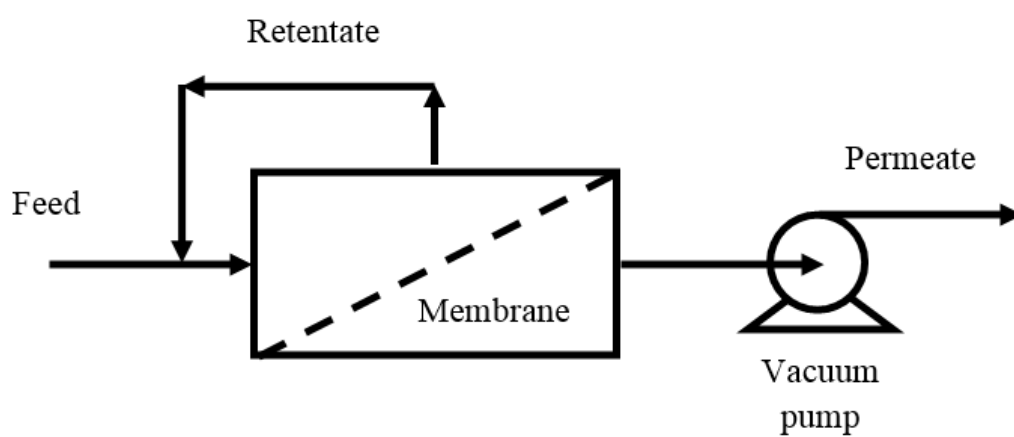


Figure 1: The schematic diagram of pervaporation process

Table 1: Separation performance of self-supported polymeric membranes

Membrane	Modification	Crosslinking agent / condition	Feed ethanol concentration (wt%)	Temperature (°C)	Permeation flux (kg/m ² ·h)	Separation factor	Reference
PVA	-	glutaraldehyde	96	40	0.279	107	Praptowidodo, 2005
PVA	Copolymerized with itaconic acid	glutaraldehyde	96	40	0.123	216	Praptowidodo, 2005
PVA	Copolymerized with ammonium group	glutaraldehyde	96	40	0.119	228	Praptowidodo, 2005
PVA	Quaternized with trimethyl ammonium chloride, DQ = 3.260	-	85	50	0.042	40.2	Zhang <i>et al.</i> , 2009
PVA	Quaternized with trimethyl ammonium chloride, DQ = 3.336	-	85	50	0.048	52.8	Zhang <i>et al.</i> , 2009
PVA	Quaternized with trimethyl ammonium chloride, DQ = 4.035	-	85	50	0.052	58.3	Zhang <i>et al.</i> , 2009
PVA	Quaternized with trimethyl ammonium chloride, DQ = 3.260	glutaraldehyde	85	50	0.033	58.3	Zhang <i>et al.</i> , 2009
PVA	-	dimethylolurea	10	60	≈0.110	≈100	Gimenes <i>et al.</i> , 2007

Sericin	-	dimethylolurea	10	60	≈ 0.070	≈ 90	Gimenes <i>et al.</i> , 2007
Sericin	Blended with PVA	dimethylolurea	10	60	≈ 0.095	≈ 125	Gimenes <i>et al.</i> , 2007
Sericin	Blended with PVA	Thermally crosslinking	10	60	≈ 0.070	≈ 92	Gimenes <i>et al.</i> , 2007
Bacterial cellulose	-	-	54	75	1.43	1.3	Pandey <i>et al.</i> , 2005
Bacterial cellulose	Treated with alkaline	-	70	70	0.112	287	Dubey <i>et al.</i> , 2002
PVA	-	-	95	24	0.190	10.1	Dubey <i>et al.</i> , 2005
Bacterial cellulose	-	-	95	24	0.754	1.6	Dubey <i>et al.</i> , 2005
Chitosan	-	-	95	24	0.120	2.4	Dubey <i>et al.</i> , 2005
Chitosan	Composited with bacterial cellulose	-	95	24	0.214	9.2	Dubey <i>et al.</i> , 2005
Chitosan	Blended with with PVA (1:3)	-	95	24	0.077	19.3	Dubey <i>et al.</i> , 2005
Chitosan	Blended with with PVA (1:1)	-	95	24	0.028	22.0	Dubey <i>et al.</i> , 2005
Chitosan	Blended with with PVA (3:1)	-	95	24	0.029	2.8	Dubey <i>et al.</i> , 2005

PDMS	-	-	90	40	0.360	11	Lai <i>et al.</i> , 2012
PDMS	Treated with UV/O ₃	-	90	40	0.220	130	Lai <i>et al.</i> , 2012
PBZ (from hda)	-	Thermally crosslinking	10	70	1.52	>10,000	Pakkethati <i>et al.</i> , 2011
6FDA-NDA/DABA	-	-	85	60	1.2	110	Le <i>et al.</i> , 2014
6FDA-NDA/DABA	Blended with 3% its sulfonated polymer	-	85	60	3.2	55	Le <i>et al.</i> , 2014
6FDA-NDA/DABA	Blended with 3% its sulfonated polymer and coated with PDMS	-	85	60	2.7	104	Le <i>et al.</i> , 2014
6FDA-NDA/DABA	Blended with 3% its sulfonated polymer and thermal treatment	-	85	60	2.6	130	Le <i>et al.</i> , 2014
PDMS	-	Thermally crosslinking	5	40	1.124	5.5	Chen <i>et al.</i> , 2014

Table 2: Separation performance of supported polymeric membranes

Membrane	Support	Feed ethanol concentration (wt%)	Temperature (°C)	Permeation flux (kg/m ² ·h)	Separation factor	Reference
Polyimide (BMTC-HDA)	Asymmetric polysulfone	90	40	1.7	240	Kim <i>et al.</i> , 2000
Polyimide (PMDA-ODA)	Asymmetric polyimide (PI-2080)	94	30	0.2	800	Yanagishita <i>et al.</i> , 2001
HEC/chitosan	Cellulose acetate	90	60	0.424	5469	Jiraratananon <i>et al.</i> , 2002
PVA	PAN	80	60	≈0.90	≈148	Li <i>et al.</i> , 2006
PVA/chitosan	PAN	80	60	≈1.50	≈40	Li <i>et al.</i> , 2006
Poly(thiol ester amide) (AETH-TMC)	Modified-PAN	90	25	1.60	1130	Huang <i>et al.</i> , 2008
PVA/chitosan	Asymmetric ZrO ₂ /Al ₂ O ₃	8	70	≈0.18	≈1300	Zhu <i>et al.</i> , 2010
PDMS	Blend cellulose acetate	5	40	≈0.62	≈7.8	Wei <i>et al.</i> , 2011
PDMS	Asymmetric ZrO ₂ /Al ₂ O ₃	5	40	1.6	8.9	Wei <i>et al.</i> , 2011

Table 3: Separation performance of inorganic membranes

Membrane	Feed ethanol concentration (wt%)	Temperature (°C)	Permeation flux (kg/m ² h)	Separation factor	Reference
NaA zeolite	95	95	2.35	>5,000	Kondo <i>et al.</i> , 1997
Silicalite	4	30	0.26	23	Ikegami <i>et al.</i> , 1999
Microporous silica	94	70	0.3-0.8	10-500	Ma et al., 2009
NaA zeolite	95	70	1.6	1760.5	Kuanchertchoo <i>et al.</i> , 2007
NaA zeolite (with intermediate layer)	95	70	1.7	6532.7	Kuanchertchoo <i>et al.</i> , 2007
NaA zeolite (via microwave synthesis)	87.7	70	0.5-1.0	>10,000	Kunnakorn <i>et al.</i> , 2011a
NaA zeolite (via autoclave synthesis)	87.7	70	0.4-0.5	>10,000	Kunnakorn <i>et al.</i> , 2011a
NaA zeolite	90	70	2.82	>10,000	Kunnakorn <i>et al.</i> , 2011b
NaA zeolite	90	70	2.12	>10,000	Kunnakorn <i>et al.</i> , 2013

Table 4: Separation performance of mixed matrix membranes

Polymer matrix	Inorganic additive	Feed ethanol concentration (wt%)	Temperature (°C)	Permeation flux (kg/m ² ·h)	Separation factor	Reference
Chitosan	-	10	80	0.054	158.02	Sun <i>et al.</i> , 2008
Chitosan	H-ZSM-5 (8 wt%, Si/Al = 25)	10	80	≈0.119	≈178	Sun <i>et al.</i> , 2008
Chitosan	H-ZSM-5 (8 wt%, Si/Al = 38)	10	80	≈0.119	≈165	Sun <i>et al.</i> , 2008
Chitosan	H-ZSM-5 (8 wt%, Si/Al = 50)	10	80	0.231	152.82	Sun <i>et al.</i> , 2008
NR/PVA	-	8.06	80	1.56	766	Amnuaypanich <i>et al.</i> , 2009
NR/PVA	Zeolite 4A (10 wt%)	8.06	80	2.28	940	Amnuaypanich <i>et al.</i> , 2009
NR/PVA	Zeolite 4A (20 wt%)	8.06	80	2.83	1506	Amnuaypanich <i>et al.</i> , 2009
PDMS	-	10	25	0.002	9.21	Lue <i>et al.</i> , 2011
PDMS	TZP-9023 (30 wt%)	10	25	0.016	12.5	Lue <i>et al.</i> , 2011
PDMS	ZSM-5 (30 wt%, etched with HF acid)	10	50	≈0.200	≈11	Zhang <i>et al.</i> , 2012
PDMS	ZSM-5 (30 wt%, etched with	90	50	≈2.15	≈1.5	Zhang <i>et al.</i> ,

	HF acid)					2012
PVA	Mesoporous silica (10 wt%, sphere shape)	90	60	0.855	42	Flynn <i>et al.</i> , 2013

A.2 PRESENTATIONS

1. Chuntanalerg, P., Saelim, N., Kulprathipanja, S., Chaisuwan, T., and Wongkasemjit, S. (2013, May 12nd-16th) Performance of fully-cured polybenzoxazine membranes for water-ethanol separation via pervaporation. Poster presentation at 2nd International Conference on Materials for Energy EnMat II, Karlsruhe, Germany.
2. Chuntanalerg, P., Saelim, N., Kulprathipanja, S., Chaisuwan, T., and Wongkasemjit, S. (2013, November 25th) Crosslinked polybenzoxazine/ceramic composite membranes – The separation performance in water-ethanol pervaporation. Poster presentation at JSPS Core-to-Core Program Future Vision of Green Mobility and Advanced Technologies for Realizing the Vision -New Science and Technology for Materials, Polymer and Energy-, Hanoi, Vietnam.
3. Chuntanalerg, P., Saelim, N., Kulprathipanja, S., Chaisuwan, T., Aungkavattana, P., Hemra, K., and Wongkasemjit, S. (2014, April 22nd) Mechanistic study of polybenzoxazine membranes formation on tubular α -Al₂O₃ support. Oral presentation at The 5th research symposium on Petrochemical and materials technology and The 20th PPC Symposium on Petroleum, Petrochemicals and Polymers, Bangkok, Thailand.
4. Chuntanalerg, P., Saelim, N., Kulprathipanja, S., Chaisuwan, T., Aungkavattana, P., Hemra, K., and Wongkasemjit, S. (2015, May 6th-9th) Performance of NaA/Polybenzoxazine Mixed Matrix Membrane in Pervaporation Separation of Ethanol/water Mixtures. Oral presentation at The 3rd International Workshop on Solution Plasma and Molecular Technologies & The 2nd International Mini-Workshop on Solution Plasma and Molecular Technologies (SPM-3 & Mini SPM-2), Bangkok, Thailand.

6. Chuntanalert, P., Kulprathipanja, S., Chaisuwan, T., and Wongkasemjit, S. (2015, August 31th-September 2nd) Use of PBZ for ethanol-water separation application. Oral presentation at The 10th International Symposium in Science and Technology 2015, Bangkok, Thailand.

The separation performance in water-ethanol pervaporation

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Due to the depletion of fossil fuel and increasing of global warming concerns, the alternative energy has been attracted the interest of many researchers in the recent year. Bioethanol, one of well-known alternative energy, is commonly used as fossil fuel substitute. Deriving from fermentation of renewable resources, the process to produce bioethanol requires low energy which is applicable in fuel production. However, the major problem of fuel bioethanol production is the separation process which consumes much higher energy to recover ethanol from the fermented mixture. Instead of using conventional energy-intensive separation process, such as extractive distillation or azeotropic distillation, the pervaporation process provides more energy efficient way to produce fuel ethanol. To increase the efficiency of pervaporation, the development of higher membrane separation performance with low production cost is the main focus. Polybenzoxazine (PBZ) has an excellent candidate due to the ability to tailor its molecular structure leading to the proper design of the membrane separation ability while the membrane production cost is low. Moreover, the membrane stability and separation performance can be remarkably improved by using as the fully cross-linked PBZ membrane. In this study, the separation performance of various fully cross-linked PBZ membrane supported on alumina tube for water-ethanol pervaporation was investigated. The membranes were prepared by dip-coating tubular alumina support. The separation performance of each membrane was determined by separation factor and permeation flux. The resulting membranes show the superior separation factor (more than 10,000) with a good membrane stability.

Mechanistic study of polybenzoxazine membranes formation on tubular $\alpha\text{-Al}_2\text{O}_3$ support

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Tubular $\alpha\text{-Al}_2\text{O}_3$ -supported polybenzoxazine (PBZ) membranes were prepared by dip-coating technique for ethanol-water separation via pervaporation. The effect of PBZ concentration on the number of dipping cycle required and on separation performance was studied. Based on the obtained results, a possible mechanism of the membrane formation was investigated and proposed. It was found that two membrane preparation steps were involved, viz. transition layer accumulation and separation layer formation. The membrane prepared by using 25 wt% PBZ needed the shortest preparation time and provided the highest separation factor. Moreover, the membrane had excellent stability in every ethanol feed concentration with a separation factor higher than 10,000. The study of a long-term pervaporation in 90:10 ethanol:water feed was also carried out and the results showed excellent durability during 11 days of operation with 99.45 wt% of ethanol.

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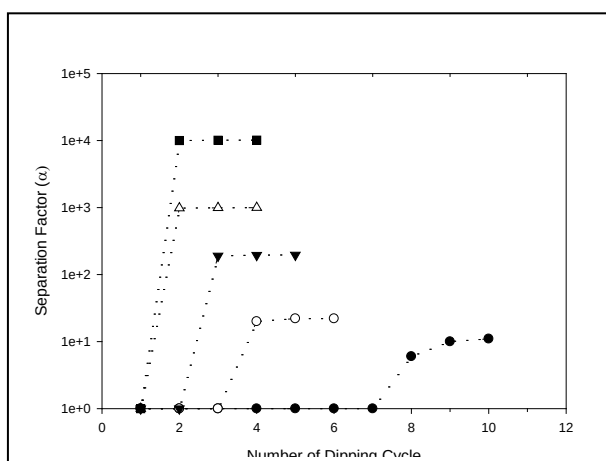


Figure 6 Effect of number of dipping cycle on membranes separation factor.

Performance of fully-cured polybenzoxazine membranes for water-ethanol separation via pervaporation

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Partially-cured polybenzoxazine membranes have a great potential for separation of low ethanol concentration in water via pervaporation. The process provides a good performance in term of the separation factor, over 10,000, but the membrane can be damaged at high ethanol concentration. In this study, fully-cured polybenzoxazine membrane was applied for a higher ethanol concentration to study whether it provided superior ethanol resistance. It was found that the synthesized membrane is a promising one to be used in a wide range of the ethanol concentration in pervaporation process, especially when the fully-cured polybenzoxazine membranes were prepared on tubular alumina support by dip-coating technique. The thickness of the membranes was characterized by FE-SEM and the membrane performance was tested by pervaporation in various ethanol-water solutions (10, 30, 50, and 90% ethanol) at 70 °C. The averaged thickness of membranes was less than 15 μm and the separation factors were over 10,000 for all membranes.

Use of polybenzoxazine for ethanol-water separation application

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Bioethanol has attracted great attention for many years as one of the promising sustainable energy alternatives and a good candidate for replacing gasoline usage. However, to use bioethanol in a vehicle and not to harm the engine, a highly concentrated ethanol of at least 99.5% is a major requirement. Thus, a separation process has played an important role. One of the well-known techniques for separation of ethanol-water is pervaporation. This technique is not only has a great potential in producing ethanol fuel from bioethanol, but also considerably more energy efficient than the conventional distillation process. The overall separation performance of the pervaporation process is significantly dependent of properties of the membrane used, thus, the development of the membrane to exhibit a higher separation factor, a better permeation flux, and stability was focused in this talk.

Polybenzoxazine (PBZ) is a class of high-performance phenolic resins, providing many unique characteristics, such as, high mechanical properties, high chemical stability, high thermal stability, tailorable structure, etc. We thus selected PBZ as a candidate for using as the separating membrane. Various PBZ membrane preparation techniques were investigated to achieve a better separation performance in ethanol-water separation. The obtained results will be discussed in detail.

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6. สาขาวิชาการที่มีความชำนาญพิเศษ

การสังเคราะห์ การตรวจสอบโครงสร้าง และการประยุกต์สารอินทรีย์ สารโลหะอินทรีย์ และพอลิเมอร์

7. ประสบการณ์ที่เกี่ยวข้องกับการบริหารงานวิจัยทั้งภายในและภายนอกประเทศ โดยระบุสถานภาพในการทำการวิจัยว่าเป็นผู้อำนวยการแผนงานวิจัย หัวหน้าโครงการวิจัย หรือผู้ร่วมวิจัยในแต่ละข้อเสนอการวิจัย เป็นต้น

7.1 หัวหน้าโครงการวิจัย :

- 7.1.1 ชื่อโครงการ: นวัตกรรมการผลิตเอทานอลบริสุทธิ์ด้วยกระบวนการแยกด้วยแผ่นเยื่อบางพอลิเบนซอกซาซีน

แหล่งทุน: งบประมาณแผ่นดิน

1,600,000 บาท

- ระยะเวลาดำเนินการ: 1 ตุลาคม 2556–30 กันยายน 2558
- 7.1.2 ชื่อโครงการ: การประยุกต์สารไซลาเทรน
แหล่งทุน: กองทุนรัชดาภิเษกสมโภช จุฬาลงกรณ์มหาวิทยาลัย 1,000,000 บาท
ระยะเวลาดำเนินการ: 1 สิงหาคม 2556–31 กรกฎาคม 2557
- 7.1.3 ชื่อโครงการ: Two- stage Microwave/Chemical Pretreatment Process of *Napier Grass* for Ethanol Production
แหล่งทุน: Asahi Glass Foundation 219,000 บาท
ระยะเวลาดำเนินการ: 1 กรกฎาคม 2555–30 มิถุนายน 2556
- 7.1.4 ชื่อโครงการ: Synthesis and Applications of MCM-48
แหล่งทุน: CU-TRF 2,000,000 บาท
ระยะเวลาดำเนินการ: 31 พฤษภาคม 2553–30 พฤษภาคม 2556
- 7.1.5 ชื่อโครงการ: การสังเคราะห์สารบิวทิลแอลกอฮอล์จากกากข้าวโพด (วัสดุเหลือใช้ทางการเกษตร) และการประยุกต์เพื่อผลิตก๊าซไฮโดรเจน/ดีไฮโดรเจน
แหล่งทุน: งบประมาณแผ่นดิน 2,600,000 บาท
ระยะเวลาดำเนินการ: 1 ตุลาคม 2554–30 กันยายน 2556
- 7.1.6 ชื่อโครงการ: การสังเคราะห์ Mo-SBA15 และ Ti-SBA-15 โดยผ่านกระบวนการโซล-เจล และใช้ไซลาเทรนเป็นสารตั้งต้น และศึกษาความว่องไวของสารในชั้นต้น
แหล่งทุน: กองทุนรัชดาภิเษกสมโภช จุฬาลงกรณ์มหาวิทยาลัย 440,000 บาท
ระยะเวลาดำเนินการ: 7 เมษายน 2553–6 เมษายน 2554
- 7.1.7 ชื่อโครงการ: นวัตกรรมการผลิตเอทานอลบริสุทธิ์ด้วยกระบวนการแยกด้วยแผ่นเยื่อบางชนิดไฮเดียม-เอ
แหล่งทุน: สำนักงานคณะกรรมการวิจัยแห่งชาติ 960,000 บาท
ระยะเวลาดำเนินการ: 8 มีนาคม 2553–6 พฤษภาคม 2554
- 7.1.8 ชื่อโครงการ: Development of Carbon Aerogel via Functionalized Polybenzoxazine for Catalyst Support Applications
แหล่งทุน: ศูนย์นาโนเทคโนโลยี 737,000 บาท
ระยะเวลาดำเนินการ: 23 กันยายน 2551–22 กันยายน 2553

7.2 ผลงานวิจัย (5 ปีย้อนหลัง)

- 7.3.1 การตีพิมพ์ในวารสารนานาชาติ
1. P. Chuntanalerg, S. Kulprathippanja, T. Chaisuwan, P. Aungkavattana, K. Hemra, and S. Wongkasemjit, "Performance polybenzoxazine membrane and mixed matrix membrane for ethanol purification via

- pervaporation applications”, *Journal of Chemical Technology and Biotechnology*, In press
2. P. Chuntanalerg, R. Naraprawatphong, S. Kulprathippanja, P. Aungkavattana, K. Hemra, T. Chaisuwan, and S. Wongkasemjit, “Novel polymeric membrane materials for ethanol/water separation via pervaporation”, *Materials Research Innovations*, In press.
 3. Hussaya Maneesuwan, Supakorn Tantisriyanurak, Thanyalak Chaisuwan, Sujitra Wongkasemjit, “Impressive phenol hydroxylation activity using Fe-Ti-TUD-1 synthesized from silatrane via sol-gel process”, *J. of Appl. Cat. A*, In press.
 4. Uthen Thubsuang, Darunee Sukanan, Somboon Sahasithiwat, Sujitra Wongkasemjit, Thanyalak Chaisuwan, “Highly sensitive room temperature organic vapor sensor based on polybenzoxazine-derived carbon aerogel thin film composite”, *Materials Science and Engineering: B*, 2015, 200, 67-77.
 5. Uthen Thubsuang, Sujitra Wongkasemjit, Thanyalak Chaisuwan, “Advanced and economical ambient drying method for controlled mesopore polybenzoxazine-based carbon xerogels: Effects of non-ionic and cationic surfactant on porous structure”, *Journal of Colloid and Interface Science*, 459, 20656, pp. 241-249
 6. Alison Banka, Tidarat Komolwanich, and Sujitra Wongkasemjit, A review on “Potential Thai grasses for Bioethanol Production”, *Cellulose*, 22 (2015), 9-29.
 7. Thitirat Inprasit, Sujitra Wongkasemjit, Stephen J. Skinner, Mónica Burriel, Pimpa Limthongkul, “Effect of Sr substituted $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ($x = 0, 0.2, 0.4, 0.6, \text{ and } 0.8$) on oxygen stoichiometry and oxygen transport properties”, *RSC Advances*, 5 (2015), 2486.
 8. Akarin Boonsombuti, Apanee Luengnaruemitchai, Sujitra Wongkasemjit, “Effect of Phosphoric Acid Pretreatment of Corncobs on the Fermentability of *Clostridium beijerinckii* TISTR 1461 for

- Biobutanol Production”, *Preparative Biochemistry & Biotechnology*, 45 (2015):173–191
9. Rapeephat Vichuwat, Akarin Boonsombuti, Apanee Luengnaruemitchai, Sujitra Wongkasemjit, “Enhanced butanol production by immobilized *Clostridium beijerinckii* TISTR 1461 using zeolite 13X as a carrier”, *Bioresource Technology*, 172 (2014) 76–82.
 10. Uthen Thubsuang, Hatsuo Ishida, Sujitra Wongkasemjit, and Thanyalak Chaisuwan, “IMPROVEMENT IN THE PORE STRUCTURE OF POLYBENZOXAZINE-BASED CARBON XEROGELS THROUGH A SILICA TEMPLATING METHOD”, *J. of Porous Mater.*, (2014) 21:401–411.
 11. Akarin Boonsombuti, Kittinan Komolpis, Apanee Luengnaruemitchai, Sujitra Wongkasemjit, “Enhancement of ABE fermentation through regulation of ammonium acetate and D-xylose uptake from acid-pretreated corncobs”, *Annual Microbiology*, (2014) 64:431–439.
 12. Chonnikarn Deeprasertkul, Rujirat Longloilert, Thanyalak Chaisuwan, Sujitra Wongkasemjit, “Impressive low reduction temperature of synthesized mesoporous ceria via nanocasting”, *Materials Letters*, 130(2014) 218–222.
 13. Sirirat Prasertwasu, Darin Khumsupan, Tidarat Komolwanich, Thanyalak Chaisuwan, Apanee Luengnaruemitchai, Sujitra Wongkasemjit*, “Efficient process for ethanol production from Thai Mission Grass (*Pennisetum polystachyon*)”, *Bioresource Technology*, 163 (2014) 152–159.
 14. Hussaya Maneesuwan, Thanyalak Chaisuwan, Sujitra Wongkasemjit, “Synthesis of Fe-Ti-MCM-48 from silatrane precursor via sol-gel process and its hydrothermal stability”, *Materials Chemistry and Physics*, 146 (2014) 374-379.
 15. Uthen Thubsuang, Hatsuo Ishida, Sujitra Wongkasemjit, and Thanyalak Chaisuwan, “Self-formation of 3D interconnected macroporous carbon xerogels derived from polybenzoxazine by selective solvent during the sol-gel process”, *Journal of Materials Science*, (2014) 49:4946–4961.

16. Tidarat Komolwanich, Patomwat Tatijarern, Sirirat Prasertwasu, Darin Khumsupan, Thanyalak Chaisuwan, Apanee Luengnaruemitchai, Sujitra Wongkasemjit*, "Comparative potentiality of Kans grass (*Saccharum spontaneum*) and Giant reed (*Arundo donax*) as a lignocellulosic feedstock for release of monomeric sugars by microwave/chemical pretreatment", *Cellulose*, (2014) 21:1327-1340.
17. Bussarin Ksapabutr, Tanapol Chalermkiti, Sujitra Wongkasemjit Manop Panapoy, "Controllable deposition of gadolinium doped ceria electrolyte films by magnetic-field-assisted electrostatic spray deposition", *Thin Solid Films*, 546 (2013), 423-430
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21. Ruethaithip Wisedsri, Thanyalak Chaisuwan, Sujitra Wongkasemjit*, "A simple route to bismuth titanate from bismuth glycolate precursor via sol-gel process", *Materials Research Innovations*, (2013) 17, 43-8.
22. Hussaya Maneesuwan, Rujirat Longloilert, Thanyalak Chaisuwan, Sujitra Wongkasemjit, "Synthesis and characterization of Fe-Ce-MCM-48 from silatrane precursor via sol-gel process", *Materials Letters*, 94 (2013) 65-68.

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36. Busaraporn Samran, Timothy J. White, and Sujitra Wongkasemjit, "A novel room temperature synthesis of mesoporous SBA-15 from silatrane", *Journal of Porous Materials*, 18 (2011) 167-175.
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 42. T. Inprasit, P. Limthongkul, and S. Wongkasemjit*, “Property Study of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$, “Sol-gel and Solid State Synthesis and Property Study of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ ($x \leq 0.8$)”, *Journal of The Electrochemical Society*, 157 (2010), Issue 11, B1726-B1730.
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7.3.3 การตีพิมพ์ในวารสารภายในประเทศ

1. ฌีรณัฐ ควรเชิดชู เอกชัย จารุपालี และสุจิตรา วงศ์เกษมจิตต์ “การสังเคราะห์ซีโอไลต์ชนิดโซเดียมเอโดยใช้ดินดำสุราษฎร์เป็นแหล่งของซิลิกาและอลูมินา และการเติบโตของผลึกแบบทุติยภูมิ” วารสารวิจัยรามคำแหง (วิทยาศาสตร์และเทคโนโลยี) ปีที่ 16 ฉบับที่ 2 กรกฎาคม-ธันวาคม 2556
2. รองศาสตราจารย์ ดร. สุจิตรา วงศ์เกษมจิตต์ และ นายเดโช ชุนนกร “เอทานอล : พลังงานทดแทนในวิถีพอเพียง” หนังสือชุด เศรษฐกิจพอเพียง ลำดับที่ ๒

จุฬาลงกรณ์มหาวิทยาลัย จัดพิมพ์เนื่องในโอกาสที่พระบาทสมเด็จพระเจ้าอยู่หัว
ทรงเจริญพระชนม์พรรษา ๘๔ พรรษา

7.3.4 การเสนอผลงานวิจัยในที่ประชุมวิชาการนานาชาติ

1. Thanyalak Chaisuwan¹, Sujitra Wongkasemjit² and Nicharat Manmuanpom. Hierarchichal N-Rich Nanoporous Carbon Derived from Polybenzoxazine Via Sol-Gel Process and Its Application As the CO₂ Adsorbent. AIChE-2015 Annual Meeting
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3. P. Chuntanalerg, S. Kulprathippanja, P. Aungkavattana, K. Hemra, T. Chaisuwan, and S. Wongkasemjit*(2015, May 6-8) Performance of NaA/Polybenzoxazine Mixed Matrix Membrane in Pervaporation Separation of Ethanol/water Mixtures. SPM-3 &Mini SPM-2, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand
4. Ninlerd, A.; Ksapabutr, B.; Wongkasemjit, S.; and Chaisuwan T. (2014, November 22-25) Nanoporous Carbon for the Applications in Supercapacitor and Batteries. Poster presented at the 2014 Energy Materials Nanotechnology (EMN) Fall Meeting, Orlando, FL, USA.
5. Thawepornpuriphong, T.; Ksapabutr, B.; Wongkasemjit, S.; and Chaisuwan T. (2014, November 22-25) Study of morphologically-designed polybenzoxazine as electrode material for supercapacitor by using soft-templating method. Poster presentation at the 2014 Energy Materials Nanotechnology (EMN) Fall Meeting, Orlando, FL, USA.
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8. Maneesuwan, H.; Chaisuwan, T.; and Wongkasemjit, S. (2014, August 10-14) Synthesis and characterization of bimetallic MCM-48 nanostructure from silatrane via sol-gel process. Paper presented at The 248th ACS National Meeting & Exposition Conference 2014, San Francisco, USA.
9. Ratchadaporn Kaewmuang, Thanyalak Chaisuwan, Sujitra Wongkasemjit, “High selectivity of benzoquinone using Ti-Fe-SBA-15 catalyst synthesized from Silatrane”, International Conference on Surfaces, Coatings and Nanostructured Materials, May 19-22, 2014, Houston, Texas, USA
10. Watcharin Khatdet, Sujitra Wongkasemjit, Thanyalak Chaisuwan, “Modification of Polybenzoxazine-Derived Nanoporous Carbon by Heat Treatment ”, the 2014 MRS Spring Meeting, April 21-25 2014, San Francisco, California, USA.
11. Khemrada Chaiwichian, Sujitra Wongkasemjit, Thanyalak Chaisuwan, “Green Porous Hybrid Composite and Its Application as a Carbon Dioxide Adsorbent ”, the 2014 MRS Spring Meeting, April 21-25 2014, San Francisco, California, USA.
12. Nattikarn Moonpho, Sujitra Wongkasemjit, Thanyalak Chaisuwan, “Preparation of Polybenzoxazine Based Mesoporous Carbon by Soft-Templating Method for Application in Supercapacitor”, the 2014 MRS Spring Meeting, April 21-25 2014, San Francisco, California, USA.
13. Sedthakij Udom, Sujitra Wongkasemjit, Thanyalak Chaisuwan, “Morphological and Electrochemical Studies of a Hybrid Composite of Iron Oxide/Carbon Xerogel Nanocomposites for Supercapacitors”,

the 2014 MRS Spring Meeting, April 21-25 2014, San Francisco, California, USA.

14. Darin Khumsupan, Tidarat Komolwanich, Sirirat Prasertwasu Thanyalak Chaisuwan, Apanee Luengnaruemitchai, and Sujitra Wongkasemjit, "Efficient method to ethanol production from Mission grass", JSPS Core-to-Core Program on Future Vision of Green Mobility and Advanced Technologies for Realizing the Vision, Bangkok, Thailand, December 2, 2013.
15. Chonlada Choedchun, Panupong Chuntanaler, Nion SaeLim, Thanyalak Chaisuwan, and S. Wongkasemjit, "High purity of ethanol using polybenzoxazine membranes on α -Al₂O₃ support via pervaporation technique", JSPS Core-to-Core Program on Future Vision of Green Mobility and Advanced Technologies for Realizing the Vision, Bangkok, Thailand, December 2, 2013.
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Vision of Green Mobility and Advanced Technologies for Realizing the Vision, Hanoi, Vietnam, November 25, 2013.

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21. Settakit Udom, Thanyalak Chaisuwan, and Sujitra Wongkasemjit, "Electrodes for supercapacitors from hybrid composites of Fe_2O_3 and porous carbon", the 2nd International Symposium on Polybenzoxazine, the 246th ACS National Meeting, Indianapolis, Indiana, September 8-12, 2013.
22. Sujitra Wongkasemjit*, and Rujirat Longloilert, "Mesoporous materials from a novel silica source", International Conference on Porous Powder Materials (PPM-2013), Izmir, Turkey, September 3-6, 2013.
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26. Thanyalak Chaisuwan, Uthen Thubsuang, and Sujitra Wongkasemjit, "Effects of Non- and Cat-ionic Surfactants on Textural Properties of Polybenzoxazine-based Carbon Xerogel", the 2013 MRS Spring Meeting, on April 1-5, 2013, San Francisco, California, USA.
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36. Kriangkrai Chaikul, Thanyalak Chaisuwan, David A. Schiraldi, and Sujitra Wongkasemjit (2013, March 3-7) Aerogel from Egg Shell for Artificial Bone, Third International Conference on Multifunctional, Hybrid and Nanomaterials, The Hilton Sorrento Palace Hotel in Sorrento, Italy
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39. Tatijarern, P., Prasertwasu, S., Komolwanich., T., Luengnaruemitchai, A., Chaisuwan, T., Wongkasemjit, S., (2012, November 29-30) Evaluation of monomeric sugar yield from various grasses grown in Thailand as biofuel feedstocks by two stage microwave/chemical pretreatment process. Oral presented at the 24th Annual Meeting of Thai Society for Biotechnology and International Conference (TSB 2012), Ubon Ratchathani, Thailand.
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Chaisuwan*, “Polybenzoxazine-based porous carbon: Pore structure
design and its application”, The 4th *International Conference "Smart
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Convention Center, Bangkok, Thailand, April 24, 2012.
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24-29, 2012

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 62. Wisedsri, R., Chaisuwan, T., Wongkasemjit, S. (20-24 March, 2011) “A simple route to bismuth titanate from bismuth glycolate precursor via sol-gel process”, POLYCHAR 19 – World Forum on Advanced Materials, Kathmandu, Nepal
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“Effects of Pretreatment Conditions on Sugar Production of Sugarcane baggasse”, the International Conference on Chemical and Biomolecular Engineering (ChemBiotech’09-10), National University of Singapore, Singapore.

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67. Luangsukrerk, S.; Wongkasemjit, S.; and Chaisuwan, T. (2010, March 21-25) Removal of Trace Contaminants from Wastewater by Using Polybenzoxazine-based Aerogel: an Approach via Polymeric Ligand Exchange. Paper Presented at the 239th ACS National Meeting & Exposition, San Francisco, USA.
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69. Ngamlertassamee, P.; Kunnakorn, D.; Chaisuwan, T.; and Wongkasemjit, S. (2010, March 21-25) Synthesis of NaA zeolite membrane on polybenzoxazine support using autoclave technique and its performance. Paper presented at the 239th ACS National Meeting & Exposition Conference 2010, San Francisco, USA.
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ผู้ร่วมโครงการวิจัย

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6. สาขาวิชาการที่มีความชำนาญพิเศษ (แตกต่างจากวุฒิการศึกษา) ระบุสาขาวิชาการ
Polymer Composites, Hybrid Organic-Inorganic Composites,
Nanocomposites, Functionalization of Polymers
7. ประสบการณ์ที่เกี่ยวข้องกับการบริหารงานวิจัยทั้งภายในและภายนอกประเทศ โดย
ระบุสถานภาพในการทำการวิจัยว่าเป็นผู้อำนวยการแผนงานวิจัย หัวหน้าโครงการวิจัย หรือผู้
ร่วมวิจัยในแต่ละข้อเสนอการวิจัย เป็นต้น

7.1 หัวหน้าโครงการวิจัย

- 7.1.1 ชื่อโครงการ: การสังเคราะห์วัสดุคาร์บอนรูพรุนในระดับนาโนเมตรที่มีธาตุ N
บนพื้นผิวเพื่อเพิ่มประสิทธิภาพในการดูดซับก๊าซคาร์บอนไดออกไซด์
แหล่งทุน: กองทุนรัชดาภิเษกสมโภช จุฬาลงกรณ์มหาวิทยาลัย
ระยะเวลาดำเนินการ: 1 มิถุนายน 2557–31 พฤษภาคม 2558
- 7.1.2 ชื่อโครงการ: การพัฒนาตัวเก็บประจุไฟฟ้าแบบยัดหยุ่นได้จากวัสดุคอมพอสิต
ของคาร์บอนรูพรุนระดับนาโนเมตรและกราฟีน
แหล่งทุน: สำนักงานคณะกรรมการวิจัยแห่งชาติ
ระยะเวลาดำเนินการ: ปีงบประมาณ 2559-2560

7.2 ผลงานวิจัย (5 ปีย้อนหลัง)

7.2.1 บทความวิชาการตีพิมพ์ในวารสารนานาชาติ

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7.2.2 การเสนอผลงานวิจัยในที่ประชุมวิชาการนานาชาติ

1. Thanyalak Chaisuwan¹, Sujitra Wongkasemjit² and Nicharat Manmuanpom. Hierarchical N-Rich Nanoporous Carbon Derived from Polybenzoxazine Via Sol-Gel Process and Its Application As the CO₂ Adsorbent. AIChE-2015 Annual Meeting
2. Sujitra Wongkasemjit, Hussaya Maneesuwan (2015, May 6-8) Synthesis and application of bimetallic mesoporous silica. SPM-3 & Mini SPM-2, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand
3. P. Chuntanalerg, S. Kulprathipanja, P. Aungkavattana, K. Hemra, T. Chaisuwan, and S. Wongkasemjit* (2015, May 6-8) Performance of NaA/Polybenzoxazine Mixed Matrix Membrane in Pervaporation Separation of Ethanol/water Mixtures. SPM-3 & Mini SPM-2, The

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4. Ninlerd, A.; Ksapabutr, B.; Wongkasemjit, S.; and Chaisuwan T. (2014, November 22-25) Nanoporous Carbon for the Applications in Supercapacitor and Batteries. Poster presented at the 2014 Energy Materials Nanotechnology (EMN) Fall Meeting, Orlando, FL, USA.
5. Thawepornpuriphong, T.; Ksapabutr, B.; Wongkasemjit, S.; and Chaisuwan T. (2014, November 22-25) Study of morphologically-designed polybenzoxazine as electrode material for supercapacitor by using soft-templating method. Poster presentation at the 2014 Energy Materials Nanotechnology (EMN) Fall Meeting, Orlando, FL, USA.
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