Research Article

Received: 5 March 2015 Revised: 10 April 2015 Accepted article published: 15 April 2015 Published online in Wiley Online Library:

(wileyonlinelibrary.com) DOI 10.1002/jctb.4704

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 even higher, up to and, in some cases, higher than 100 000 with the highest permeation flux of 1071 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.

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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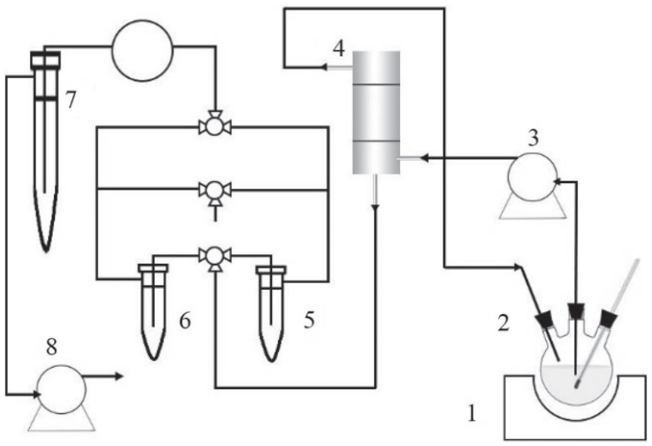


Figure 1. Schematic of pervaporation apparatus. (1) Heater; (2) feed reservoir; (3) peristaltic pump; (4) membrane module; (5), (6) and (7) condenser; and (8) vacuum pump.

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.

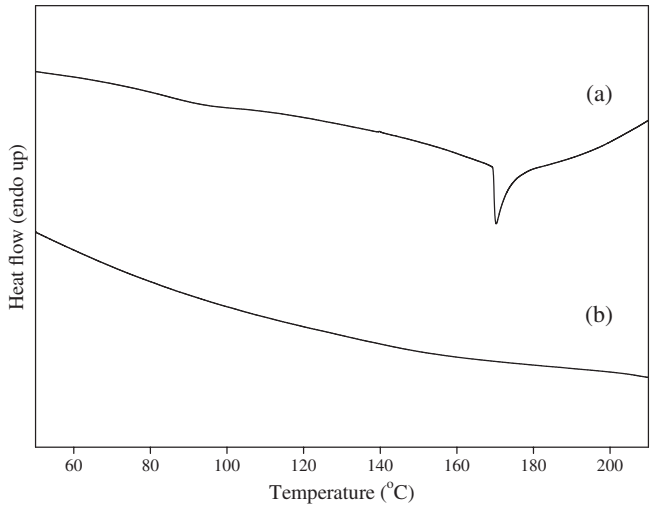


Figure 3. DSC thermograms of PBZ membrane. (a) Before and (b) after thermally crosslinked at 170 °C for 30 min.

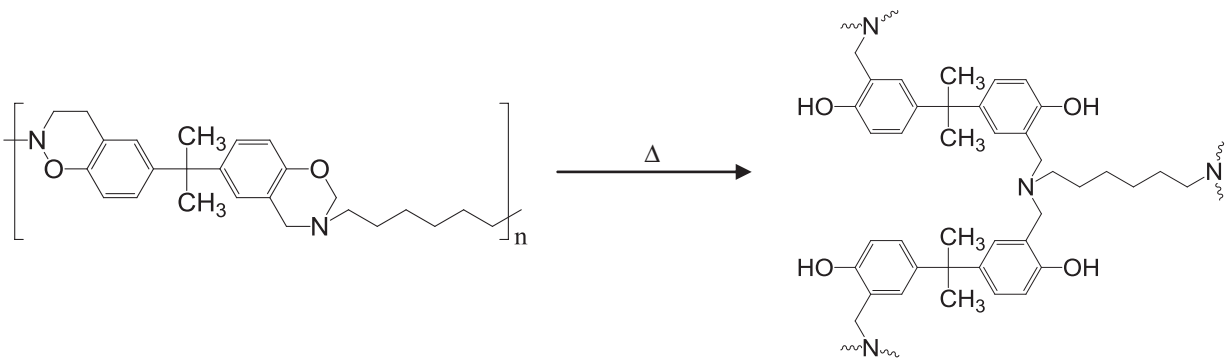
EXPERIMENTAL

Materials

Formaldehyde (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 ($Al(OH)_3 \cdot xH_2O$; 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.

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.



Polybenzoxazine precursor Crosslinked polybenzoxazine

Figure 2. Thermal crosslinking of PBZ.

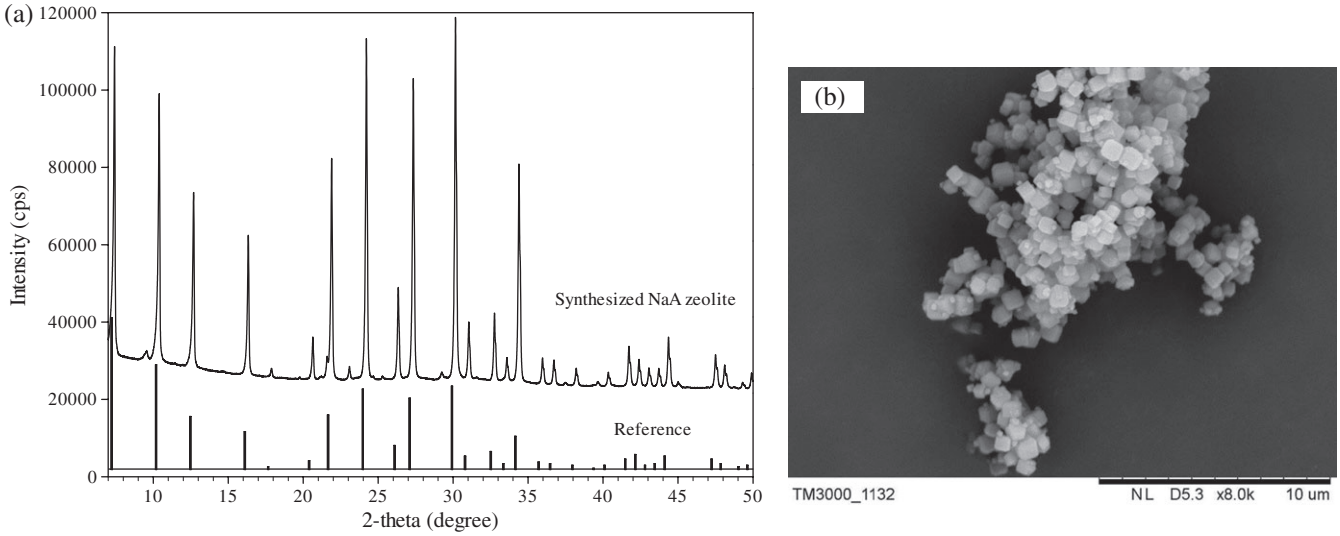


Figure 4. (a) XRD pattern and (b) SEM image of synthesized NaA zeolite particles.

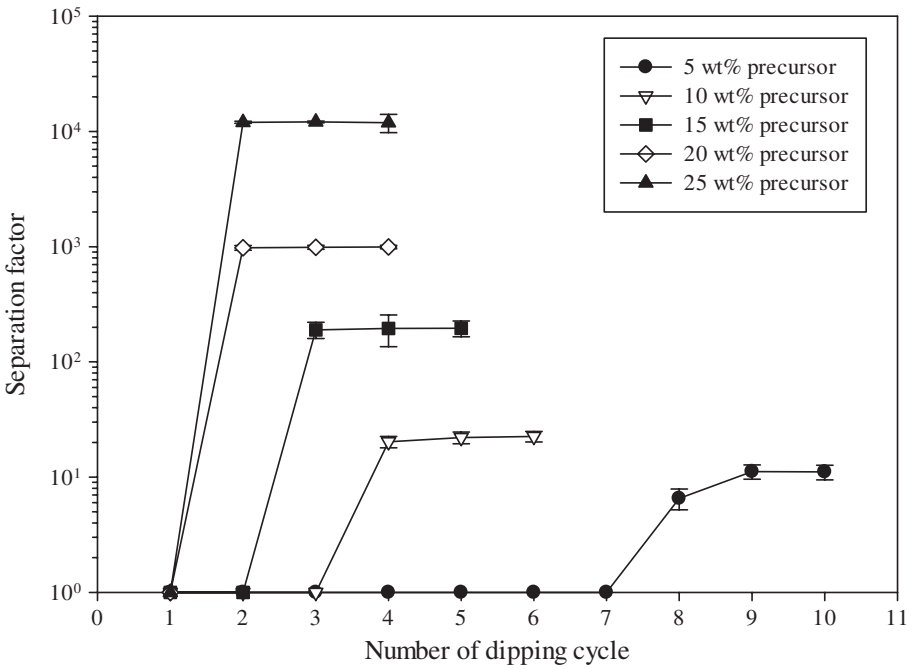


Figure 5. Effect of number of dipping cycle on membrane separation factor.

Synthesis of NaA zeolite

NaA zeolite used as a dispersed phase in this study was synthesized using Al_2O_3:SiO_2:3Na_2O:410H_2O 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 (g m^{-2} 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 × (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 CuKα 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 N_2 flow.

Pervaporation

A prepared membrane was installed in the module, as shown in Fig. 1. The pervaporation system was carried out at 30–70 °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 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 (J, g m^{-2} h^{-1}) is defined as:

$$J = \frac{P}{A * t} \tag{1}$$

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:

$$\alpha = \frac{\left(\frac{w^P_{H2O}}{w^P_{EtOH}}\right)}{\left(\frac{w^R_{H2O}}{w^R_{EtOH}}\right)} \tag{2}$$

where W_{H2O} 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:

$$D_S\ (\%) = \frac{W_s - W_d}{W_d} x\ 100 \tag{3}$$

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

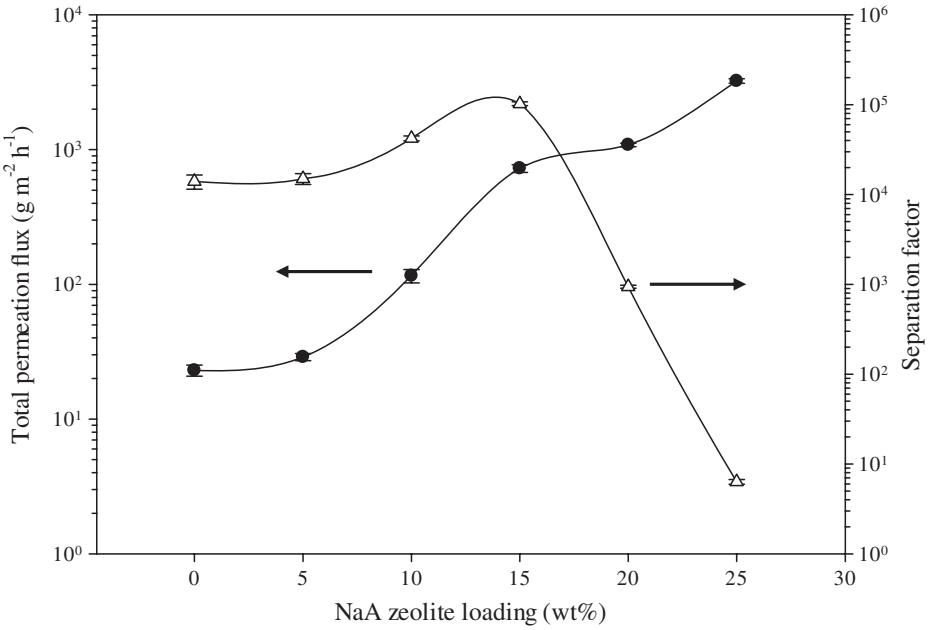


Figure 6. Membrane separation performance from various NaA zeolite loadings.

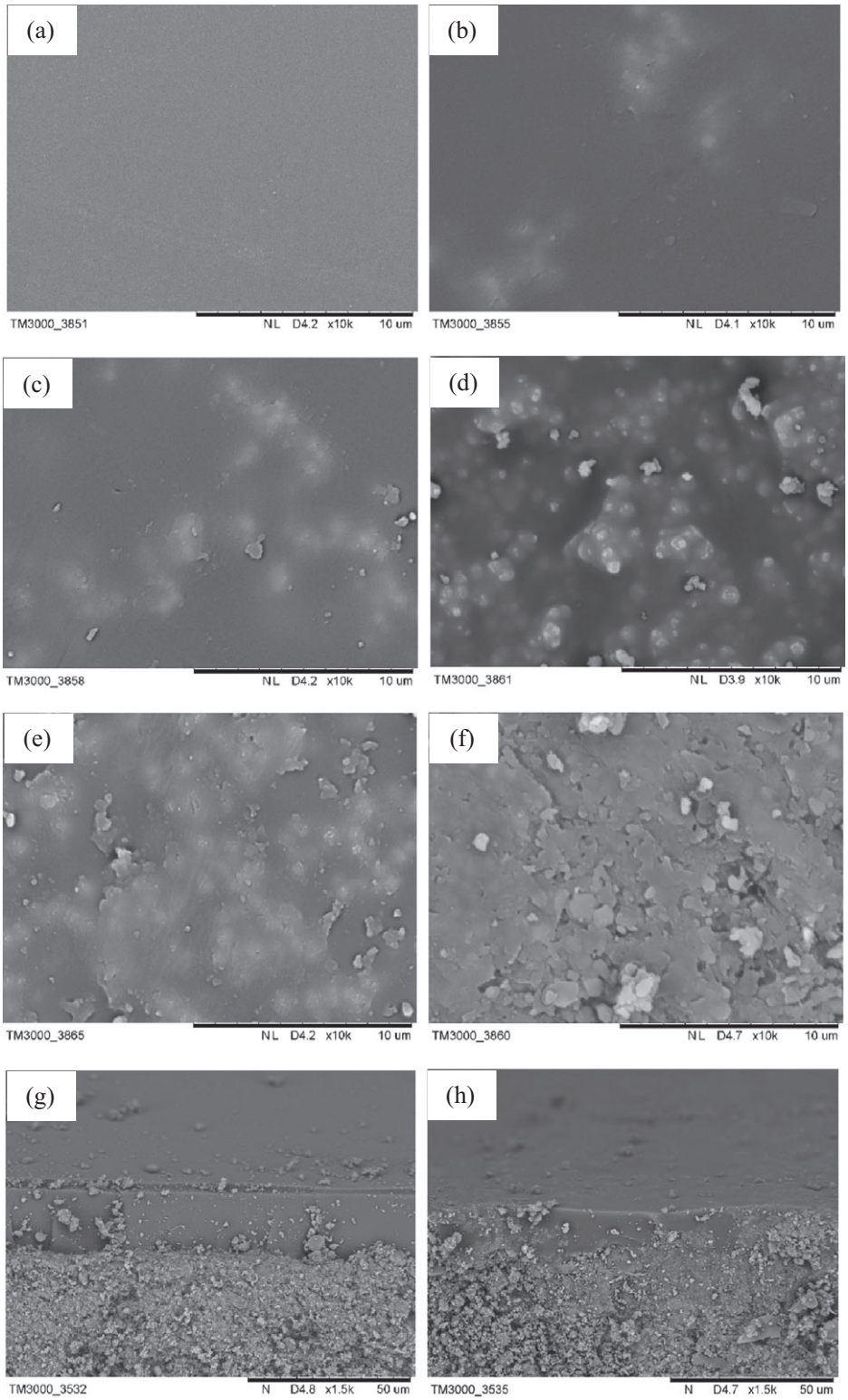


Figure 7. SEM surface images of (a) PBZ membrane; MMM with (b) 5; (c) 10; (d) 15; (e) 20; (f) 25 wt% NaA zeolite loadings; and cross-sectional images of (g) PBZ membrane and (h) 15 wt%NaA-PBZ MMM.

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.

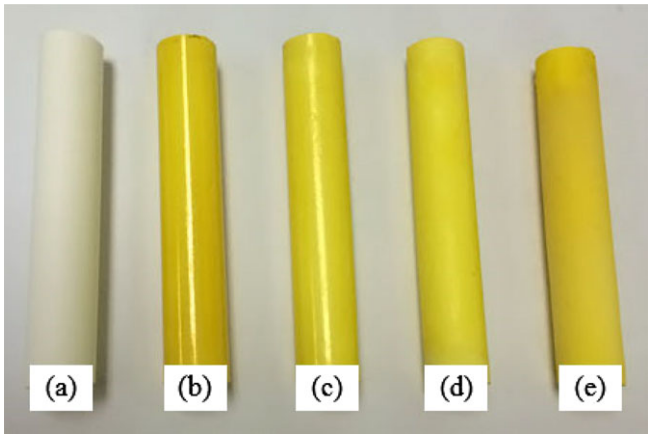


Figure 8. Physical appearances of (a) α-Al_2O_3 support; (b) PBZ membrane; (c) 5; (d) 15; and (e) 25 wt% NaA-PBZ MMM.

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

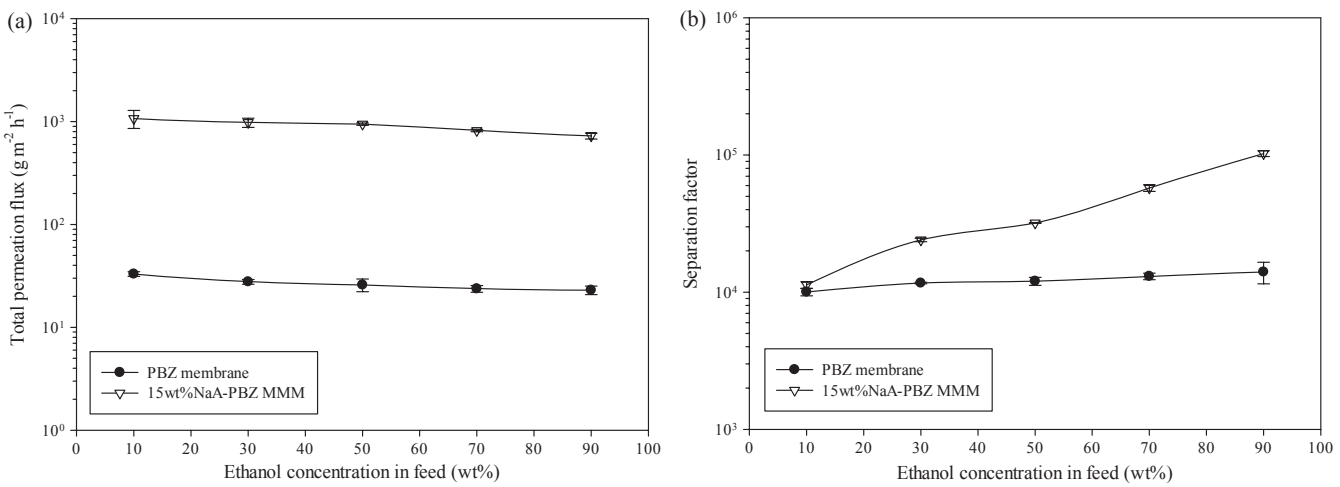


Figure 9. Effect of feed ethanol concentration on (a) total permeation flux and (b) separation factor at 70 °C.

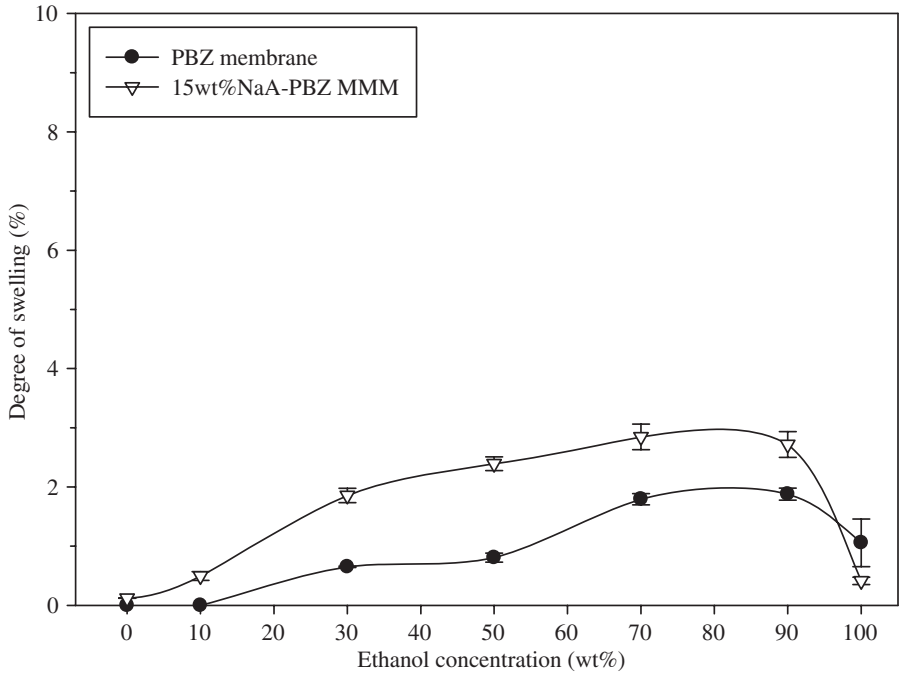


Figure 10. Swelling testing of membranes in various ethanol concentrations.

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 g m^{-2} 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 g m^{-2} 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, 15wt%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

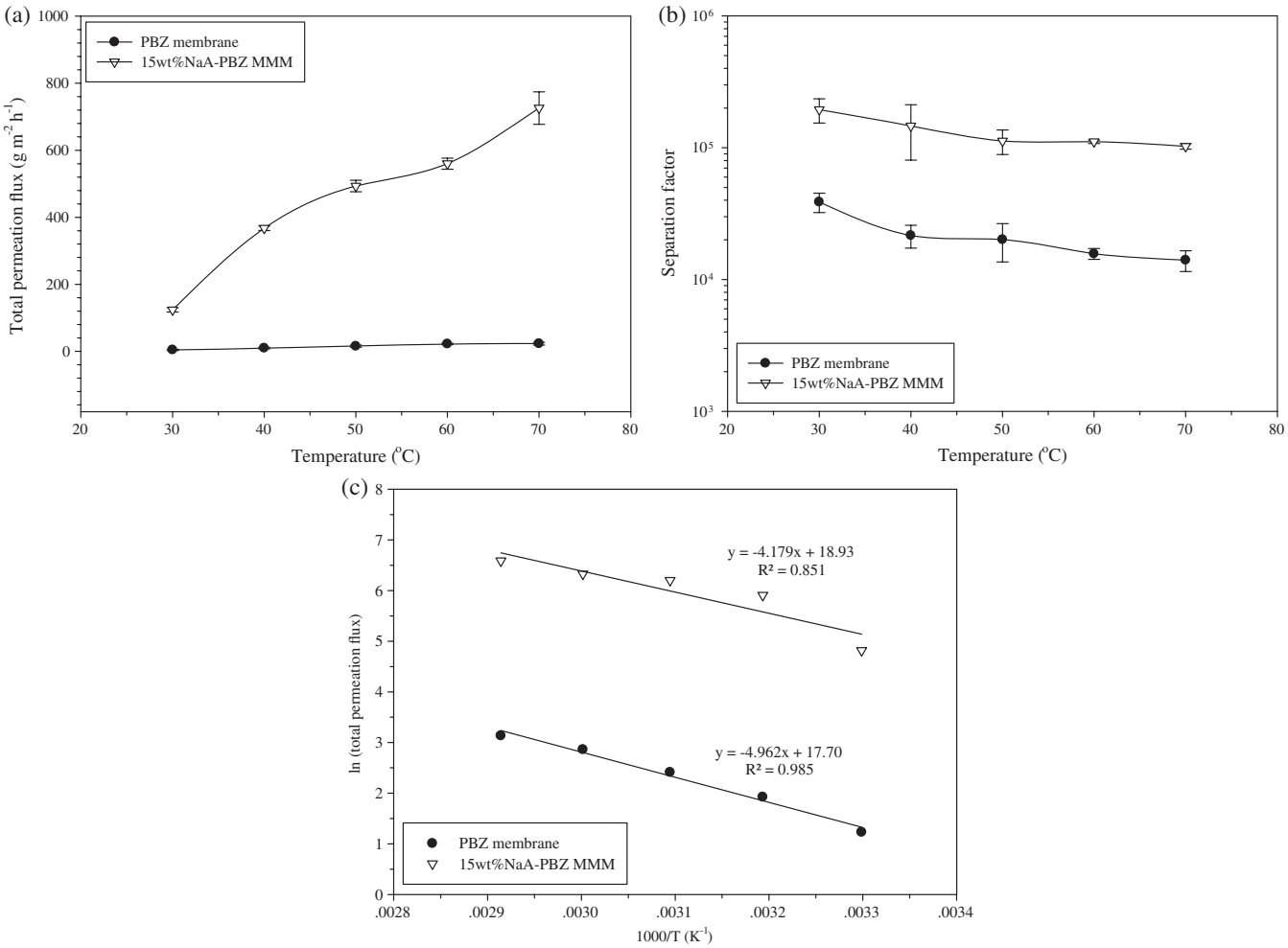


Figure 11. Effect of temperature on membrane separation performance (a) total permeation flux; (b) separation factor; and (c) Arrhenius plot.

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 (13.5–28.0 g m^{-2} h^{-1}) than the 15 wt% NaA-PBZ MMM (726.0–1071.1 g m^{-2} 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 °C to 70 °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 gmol^{-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 gmol^{-1}, respectively.

ACKNOWLEDGEMENTS

This research has been supported financially by the Thailand Research Fund (TRF) - The Royal Golden Jubilee PhD Program, the Ratchadapisake Sompote Endowment Fund, and the Excellent Center for Petrochemicals and Materials Technology, Chulalongkorn University. The authors would also like to thank Mr John M. Jackson for proof-reading this paper.

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